The Geometry of Electronically -Excited States: Vibronic Intensity Distributions and Bond Length Changes.

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THE GEOMETRY OF ELECTRONICALLY-EXCITED STATES:
VIBRONIC INTENSITY DISTRIBUTIONS AND BOND LENGTH CHANGES

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
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in partial fulfillment of the
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in
The Department of Chemistry

by
Dorothy Marie Wood
B.S., University of Florida, USA, 1993
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TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................ ii

LIST OF TABLES ........................................................................................................ v

LIST OF FIGURES ....................................................................................................... vi

ABSTRACT ..................................................................................................................... xii

1. THE FOUNDATION ............................................................................................... 1
   1.1 Geometry of Electronically-Excited States .............................................. 2
   1.2 Diffraction Techniques .......................................................................... 3
   1.3 Rotational Spectroscopic Methods ....................................................... 3
   1.4 The Quantitative Discussion of Vibronic Spectra ................................ 8
   1.5 The Model .................................................................................................. 11
   1.6 The Separation of Molecular Motions ................................................ 11
   1.7 Intramolecular Motions ....................................................................... 13
   1.8 Potential Energy Curves ..................................................................... 15
   1.9 Vibrational Motions and Spectra ......................................................... 17
   1.10 The Vibronic Intensity Distributions ................................................. 20
   1.11 Franck's Ideas .................................................................................. 24
   1.12 Geometry and Force Constant Changes ....................................... 26
   1.13 Quantum Mechanical Models of Intensity Distribution .................. 28
   1.14 Requirements of a Model .................................................................. 29
   1.15 The Diatomic Model Specification .................................................. 32
   1.16 Franck-Condon Integrals, FCI's ..................................................... 35
   1.17 Observed and Calculated Transition Probabilities ......................... 40
   1.18 Emission and Absorption of Radiation ............................................. 44

2. THE THEORETICAL EQUATIONS ...................................................................... 46
   2.1 Franck-Condon Integral, FCI .............................................................. 46
   2.2 The Ratio Equation ............................................................................. 48

3. THE THEORETICAL SPECTRA: PRELIMINARIES ........................................ 54
   3.1 Objectives ............................................................................................. 62
   3.2 The Model ............................................................................................ 64
   3.3 Approximations ..................................................................................... 67
   3.4 The Franck-Condon Window/Region, FCW/FCR ............................. 68
   3.5 Synopsis ................................................................................................ 68

4. THE THEORETICAL SPECTRA: LIMITATIONS AND ACCURACY .......... 70
   4.1 Objectives .............................................................................................. 70
   4.2 The Franck-Condon Window (FCW) .................................................. 71
   4.3 The Linear Approximation ................................................................. 73
      4.3.1 Analytical Details of the Linear Approximation .......................... 75

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
4.3.1 Analytical Details of the Linear Approximation .......................... 75
4.3.2 Results of the Linear Approximation ......................................... 81
4.4 The Quadratic Approximation .............................................................. 81
4.5 Conclusions .......................................................................................... 83

5. THE THEORETICAL PATTERNS ................................................................. 91
5.1 Emission versus Absorption ................................................................. 91
5.2 Patterns ................................................................................................ 94
5.3 Intensity Alternation ........................................................................... 108
5.4 Conclusions ........................................................................................ 109

6. THE EXPERIMENTAL SPECTRA: RESULTS ............................................. 111
6.1 Objectives ........................................................................................... 113
6.2 The Data Set ...................................................................................... 120
6.3 Conclusions ........................................................................................ 128

7. RESULTS OF THIS WORK ............................................................................ 131
REFERENCES AND BIBLIOGRAPHY ................................................................. 134
APPENDIX I THE GENERAL FRANCK-CONDON INTEGRAL (FCI) .................. 137
APPENDIX II A SPECIFIC CASE OF AN EXACT FRANCK-CONDON INTEGRAL ................................................................. 140
APPENDIX III FRANCK-CONDON INTEGRAL RESULTS ................................. 142
APPENDIX IV EXACT SOLUTIONS FOR TWO FRANCK-CONDON INTEGRALS ......................................................................................... 144
APPENDIX V COMPARATIVE FRANCK-CONDON INTEGRALS .......................... 154
VITA ...................................................................................................................... 156
LIST OF TABLES

Table 3.1 The Franck-Condon regions, FCR's, of the examples discussed in Chapter 3 and shown in Figures 3.3, 3.4 and 3.5. .................................................. 69

Table 3.2 The Franck-Condon windows, FCW's, of the examples discussed in Chapter 3 and shown in Figures 3.3, 3.4 and 3.5. .................................................. 69

Table 4.1 Analysis of the Franck-Condon Window (FCW). ........................................... 72

Table 4.2 A comparison of the exact values of $\Delta$ and $\Delta R_\text{g}$ with the corresponding values extracted from the FCIM's by the linear and quadratic approximations. ........................................................................................................... 76

Table 4.3 The exact set of intensity ratios, $\frac{I_{v'}}{I_{v'-1}}$, Exact, calculated from Equation 2.5 using the exact parameters

\[ \Delta_E = 0.2000 \]
\[ \Delta R_{g,E} = 0.2000 \times 10^{-10} \text{ m} \]

for $v' = 0, 1, 2, 3, 4, 5, 6, 7$ and $8$ are compared with those obtained using the value $\Delta R_{g,L}$, obtained by Equation 2.19 for the linear least-squares analysis. .......................................................................................................................... 79

Table 4.4 The quadratic (Q) approximation, Equation 2.17, applied to the case $\Delta_E = 0.2$ and $\Delta R_{g,E} = 0.2 \times 10^{-10} \text{ m}$. ................................................................. 84

Table 4.5 The quadratic approximation for the case $\Delta = 0.4$ and $\Delta R_g = 0.2 \times 10^{-10} \text{ m}$. .................................................................................................................. 86

Table 4.6 The case $\Delta = 0.6$ and $\Delta R_g = 0.2 \times 10^{-10} \text{ m}$. Note the alternation of intensity ratios in the last four rows of this table. ..................................................... 89

Table 6.1 Diatomic Parameters [19,23,24] and $\Delta R_\text{g}$ Results. ................................................. 114

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### LIST OF FIGURES

**Figure 1.1** The energy separations for individual types of energy states are
- **electronic** levels, many eV
- **vibrational** levels, tenths of an eV
- **rotational** levels, hundredths of an eV ................................ 5

**Figure 1.2** The spectrum of the $O_2$ Schumann-Runge region [12]. The $\nu^\prime = 8^\prime, 7^\prime, 6^\prime, 5^\prime, 4^\prime$ vibrational electronic transitions are accompanied by rotational transitions. The electronic excitation, from ground to excited state, is $A^3 \Sigma_u^+ \leftarrow X^3 \Sigma_g^-$. ........................................................................................................... 6

**Figure 1.3** The vibronic spectrum of the permanganate ion [13]. The individual vibronic bands are detectable in both the solution (- - - -) and the crystal (——); the rovibronic components of the spectrum are unresolved 10

**Figure 1.4** The fitting together of the solutions of Equation 1.10 for various values of $R$ generate the manifold of potential energy curves. Only three of these are shown. ............................................................................................................... 16

**Figure 1.5** The vibrational levels obtained when the Schrödinger equation, $\hat{H}_e \chi(R) = E \chi(R)$ where the Hamiltonian, $\hat{H}_e = \hat{T} + s_x(R)$, for nuclear motion is solved. The harmonic potential is indicated by the dotted lines, see Figure 1.6. The solid line is a Morse potential. The edge of the continuum, drawn as a series of connected diagonals, denotes the dissociation energy of the molecule. ................................................................................................................ 19

**Figure 1.6** Parabolic Model

\[
k_x = \frac{d^2 s_x(R)}{dR^2} \bigg|_{R=R_x}
\]

\[
\nu_x = \frac{1}{2} \pi \sqrt{\frac{k_x}{\mu}}
\]

\[
\mu = \frac{m_1 m_2}{m_1 + m_2}
\]

\[
h = \text{Planck's constant}
\]

The harmonic approximation to the potential curve where $k_x$ is the force constant, $\nu_x$ is the fundamental vibrational frequency. The relations between the curvature of the harmonic potential, the vibrational force constant, and the fundamental vibrational frequency are also shown. ................................................................. 21

**Figure 1.7** The schematic of potential energy curves, low-energy manifold of vibrational states, and a typical pattern observed experimentally in the expected distribution of probabilities. ............................................................................................................. 22
Figure 1.8 The schematic of vibronic excitations. Three sets of harmonic potential energy curves in various relationships. .......................................................... 27

Figure 1.9 A schematic of the optimization procedure, one used with Equation 2.10 to assay the degree of fit of the linear and quadratic approximations, and the "best fit" procedure to the experimental results. .................. 31

Figure 1.10 The parameters υ₀, υ₀, υ₀ and ΔR₀ are schematized. .................. 33

Figure 1.11 An illustration of vertical transition probability. The impact of the Franck-Condon Principle is depicted by the vertical column that traverses the vibrational functions, Χ₀ and Χ. ................................................................. 37

Figure 1.12 The Franck-Condon factors (unnormalized) are plotted as a function of the quantum number v'. The regular change of the probability distribution pattern with the value of v' is quite apparent. ................................................................. 38

Figure 1.13 The dependence of the probability distribution (unnormalized) on the value of the ratio, v², is shown. In this case, the γ parameter is held constant at γ = 2. .................................................................................................................. 39

Figure 1.14 The schematic of a vibronic band with (lower) and without (upper) accompanying rotational excitations. ............................................................... 42

Figure 2.1 The photoelectron spectrum of the hydrogen diatomic molecule for the transition [16]:

\[ \text{H}_2 : \Sigma^1_g (v'' = 0) \rightarrow \text{H}_2 : \Sigma^3_u (v' = 0, 1, 2, ...) \]

This spectrum is shown here only for illustrative purposes. It's analysis will be discussed in Chapter 6. The transitions 0' - 0", 1' - 0", 2' - 0", ..., 9' - 0" occur proceeding form left to right, with the most intense, according to Lee & Rabalais [16], being the 2' - 0" transition. The small numbers at the base of each transition are the relative intensities. ............................................... 49

Figure 3.1 The Franck-Condon Integral Maps, FCIM’s, FCI versus ΔR₀, where -∞ < ΔR₀ < ∞, for Δ = 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 and for the FCI’s denoted on the right side of Figure 3.1 (f). The ellipses demark the Franck-Condon region, FCR. The FCR encloses all the values ΔR₀, ΔR₀, ΔR₀, and ΔR₀ Best Fit. ................................................................. 55

Figure 3.2 A close-up of the regions marked by ellipses in Fig. 3.1(b, d & f). As indicated in the caption for Figure 3.1, these are the Franck-Condon regions. The FCR encloses all ΔR₀ that are relevant to the discussion. ............................. 56

Figure 3.3 The Franck-Condon region (FCR) in Figure 3.2(a) on which are marked all values of ΔR₀ that are relevant to the discussion. ............................. 57
Figure 3.4 The Franck-Condon region (FCR) in Figure 3.2(b) on which are marked all values of $\Delta R_e$ that are relevant to the discussion. ........................................ 58

Figure 3.5 The Franck-Condon region (FCR) in Figure 3.2(c) on which are marked all values of $\Delta R_e$ that are relevant to the discussion. ........................................ 59

Figure 3.6 Theoretical vibronic spectra (unnormalized) extracted from Figure 3.1 for the cited values of $\Delta R_e$. ................................................................. 60

Figure 4.1 Analysis of the Franck-Condon Window (FCW). ........................................ 74

Figure 4.2 Graphs of $\Delta R_{e_L}$ and $\Delta R_{e_Q}$ versus $\Delta R_{e_E}$. The cases represented are listed in Table 4.2. The values of $\Delta R_{e_L}$ represented by a blue square, and $\Delta R_{e_Q}$ represented by a red circle, are plotted along the vertical axis. The red line lies at 45° to the x-axis. ..................................... 77

Figure 4.3 The plot of the $\Delta_L$ versus $\Delta_E$. The cases represented are given in Table 4.2. The center blue line lies at 45° angle to the $\Delta$ axis. ......................... 78

Figure 4.4 The LLS plot of $\frac{\nu^{o^2}}{L_{(v'-1, o')}}, \text{Exact}$ versus $\frac{\nu}{\nu}$ for the case listed in Table 4.3. ................................................................. 80

Figure 4.5 (a) The bar-plot of $\frac{\nu^{o^2}}{L_{(v'-1, o')}}, \text{Exact}$ for each ratio calculated for $\Delta_E = 0.2$ and $\Delta R_{e_E} = 0.2000 \times 10^{-10}$ m. The numerical values are listed in column 3 of Table 4.3. (b) The bar-plot of $\frac{\nu^{o^2}}{L_{(v'-1, o')}}, \text{LLS}$ for each ratio calculated for $\Delta_L = 0.2341$ and $\Delta R_{e_L} = 0.2108 \times 10^{-10}$ m. The numerical values are listed in column 4 of Table 4.3. ........................................ 82

Figure 4.6 A plot of $\Delta R_{e_Q}$ from Table 4.4 for $\Delta = 0.2$ and $\Delta R_{e_E} = 0.2 \times 10^{-10}$ m in the quadratic approximation, Equation 2.17. ........................................ 85

Figure 4.7 A plot of $\Delta R_{e_Q}$ from Table 4.5 for $\Delta = 0.4$ and $\Delta R_{e_E} = 0.2 \times 10^{-10}$ m in the quadratic approximation, Equation 2.17. ........................................ 87

Figure 4.8 The bar-plot of $\frac{\nu^{o^2}}{L_{(v'-1, o')}}, \text{Exact}$ for $\Delta = 0.6$ and $\Delta R_{e_E} = 0.2 \times 10^{-10}$ m ...... 90

Figure 5.1 Schematic Franck-Condon intensities illustrating differences between converse processes and inverse $\beta$-parameters. ........................................ 92

Figure 5.2 Schematic Franck-Condon intensities illustrating differences between converse processes and inverse $\beta$-parameters. ........................................ 93

Figure 5.3 A specification of the ranges of $|\Delta R_e|$ for $\Delta = 0.3$ within which different pattern sets of vibronic intensities occur. These ranges remain essentially unchanged for all values of $\Delta$ in the range $0 \leq \Delta \leq 0.6$. ........................................ 95
Figure 5.4 Theoretical FCI intensities from Figure 3.1(a) for $\Delta = 0.1$, configured for pattern recognition.
(a) A selection of spectra extracted at intervals of $|\Delta R_e| = 0.1 \text{Å}$
(b) A close-up of Figure 3.1(a) in the region of small $|\Delta R_e|$.
(c) Close-up of the lower part of the spectrum at $|\Delta R_e| = 0 \text{Å}$ in (a) above. The $S^2_{00'}$ (red bar) extends all the way up to $\sim 1$ ........................................ 97

Figure 5.5 Theoretical FCI intensities from Figure 3.1(b) for $\Delta = 0.2$, configured for pattern recognition.
(a) A selection of spectra extracted at intervals of $|\Delta R_e| = 0.1 \text{Å}$
(b) A close-up of Figure 3.1(b) in the region of small $|\Delta R_e|$.
(c) Close-up of the lower part of the spectrum at $|\Delta R_e| = 0 \text{Å}$ in (a) above. The $S^2_{00'}$ (red bar) extends all the way up to $\sim 1$ ........................................ 98

Figure 5.6 Theoretical FCI intensities from Figure 3.1(c) for $\Delta = 0.3$, configured for pattern recognition.
(a) A selection of spectra extracted at intervals of $|\Delta R_e| = 0.1 \text{Å}$
(b) A close-up of Figure 3.1(c) in the region of small $|\Delta R_e|$.
(c) Close-up of the lower part of the spectrum at $|\Delta R_e| = 0 \text{Å}$ in (a) above. The $S^2_{00'}$ (red bar) extends all the way up to $\sim 1$ ........................................ 99

Figure 5.7 Theoretical FCI intensities from Figure 3.1(d) for $\Delta = 0.4$, configured for pattern recognition.
(a) A selection of spectra extracted at intervals of $|\Delta R_e| = 0.1 \text{Å}$
(b) A close-up of Figure 3.1(d) in the region of small $|\Delta R_e|$.
(c) Close-up of the lower part of the spectrum at $|\Delta R_e| = 0 \text{Å}$ in (a) above. The $S^2_{00'}$ (red bar) extends all the way up to $\sim 1$ ........................................ 100

Figure 5.8 Theoretical FCI intensities from Figure 3.1(e) for $\Delta = 0.5$, configured for pattern recognition.
(a) A selection of spectra extracted at intervals of $|\Delta R_e| = 0.1 \text{Å}$
(b) A close-up of Figure 3.1(e) in the region of small $|\Delta R_e|$.
(c) Close-up of the lower part of the spectrum at $|\Delta R_e| = 0 \text{Å}$ in (a) above. The $S^2_{00'}$ (red bar) extends all the way up to $\sim 0.5$ ........................................ 101

Figure 5.9 Theoretical FCI intensities from Figure 3.1(f) for $\Delta = 0.6$, configured for pattern recognition.
(a) A selection of spectra extracted at intervals of $|\Delta R_e| = 0.1 \times 10^{-10} \text{Å}$.
(b) A close-up of Figure 3.1(f) in the region of small $|\Delta R_e|$.
(c) Close-up of the lower part of the spectrum at $|\Delta R_e| = 0$, 0.1 and 0.2Å in (a) above. The $S^2_{00'}$ (red bar) extends up to $\sim 0.9, 0.53$ and $0.10$, respectively. ......................................................... 102

Figure 5.10 The theoretical spectrum for $\Delta = 0$ and $\Delta R_e = 0$, Pattern 1. This is the only case where the intensity is totally resident in the
0' - 0'' band. The intensity is exactly one: \( I_{0'0''} = 1 \). No alternation exists in this case. ............................................................................................................... 103

Figure 5.11 Typical Pattern 2 spectrum. This particular example has the parameters of \( \Delta = 0.1 \) and \( \Delta R_e = 5.1 \times 10^{-11} \) m. There is no discernible alternation in this region. ............................................................................................................... 105

Figure 5.12 Typical Pattern 3 spectra. The x-axes are labeled with each \( |\Delta R| \) value. As \( |\Delta R| \) increases, the intensity in the lower energy vibronic bands diminishes, that in the higher energy vibronic bands increases, the spectrum flattens out, and the overall width increases. This widening is not noticeable here because we extend our considerations only as far as \( I_{0'0''} \) ........ 106

Figure 5.13 Typical Pattern 4 vibronic spectra for \( \Delta = 0.3 \) The first spectrum on the left illustrates the diminishing intensity of the \( 0'0'' \) and \( 1'0'' \) transitions. ....................................................................................................... 107

Figure 5.14 Schematic Overview of Patterns. (FCIM Model from Table 6.1, 40: SnO, \( \Delta = -0.4 \)) ............................................................................................................... 110

Figure 6.1 The spectrum computed for \( \Delta R_{eR} = 1.940E-11m \) ......................... 121

Figure 6.2 (a) The Experimental Spectrum, Emission. ........................................ 121

Figure 6.2 (b) The spectrum of 2 (a) divided by \( v^3 \). ........................................ 121

Figure 6.3 The spectrum computed for \( \Delta R_{eL} = 2.101E-11m \) ......................... 121

Figure 6.4 The spectrum computed for \( \Delta R_{eQ} = 1.892E-11m \) ......................... 121

Figure 6.5 The spectrum computed for \( \Delta R_{eCFW} = 1.895E-11m \) ......................... 121

Figure 6.6 The spectrum computed for \( \Delta R_{eBestFit} = 1.890E-11m \) ......................... 121

Figure 6.7 \( \Delta R_{BestFit, A} \) versus \( \Delta R_{eR, A} \) .......................................................... 122

Figure 6.8 \( \Delta R_{eL, A} \) versus \( \Delta R_{eR, A} \) .......................................................... 123

Figure 6.9 \( \Delta R_{eQ, A} \) versus \( \Delta R_{eR, A} \) .......................................................... 124

Figure 6.10 \( \Delta R_{eCFW, A} \) versus \( \Delta R_{eR, A} \) .......................................................... 125

Figure 6.11 The Schumann-Runge (S-R) Bands of Oxygen, \( B^3\Sigma_u \leftarrow X^2\Sigma_g^+ \) [26]. (a) The experimental absorption spectrum is the upper spectrum, and is labeled by \( v' \) from the designation \( v' \leftarrow 0'' \). The smooth curve represents an attempt to extrapolate the absorption intensity of the higher energy electronic transition to lower energies. The lower spectrum .......
is obtained by subtracting the extrapolated intensity from the upper spectrum; this spectrum is thought to be the "isolated" S-R absorption spectrum of O₂.

(b) The experimental intensities for the "isolated" S-R bands in bar-graph form; taken from (a) above.

(c) The graph of ratio of experimental intensities for O₂ : B³Σ_u⁺, ν' → X³Σ_g⁻, 0'' from integrated areas under the spectrum for the individual transitions. This spectrum is unusable for either linear or quadratic processing. Whether this is due to an improper subtraction procedure or to spectroscopic perturbation by other electronic states is unknown at this time. .......................................................................................................................... 129
ABSTRACT

An exact power series expression has been obtained for the Franck-Condon integral (FCI) in the harmonic approximation. This expression is a function of a parameter $A$ where $A \to 0$ as the frequencies of vibration in the two combining electronic states approach equality. These two characteristics, that of a power series in $A$ and the fact that $A \to 0$ in certain situations, permit truncation of various functions involving FCI's. Such truncation was performed for the ratio $S_{v'}^2/S_{(v-1)^0}^2$, where the $S_{v'}^2$ are the FCI's, and the subscripts, in the usual notation, denote the vibrational quantum numbers in the two different electronic states. As a result, two approximations to the $S_{v'}^2/S_{(v-1)^0}^2$ ratio were obtained: a linear approximation in $A$ and a quadratic expression in $A^2$.

Maps of the Franck-Condon integrals, FCIM's, were found to be very useful. An FCIM is a plot of $S_{v'}^2(\Delta R_a)$ versus $\Delta R_a$ for various values of the parameter $v'$. These FCIM's facilitated a test of the linear and quadratic approximations and led to a precise specification of the ranges of $A$ within which they are valid. They resulted in the concept of a "Franck-Condon window". A Franck-Condon window (FCW) is that specific region of the FCIM (i.e., the range of $\Delta R_a$) in which the gross (i.e., non-numerical, vibronic intensity) pattern of some vibronic spectrum is represented.

The vibrational intensity distributions in 60 different electronic transitions were subjected to Franck-Condon analysis using (i) the linear approximation, (ii) the quadratic approximation, (iii) the FCW approach, and (iv) the best fit to the FCIM. It was found that method (ii), (iii) & (iv) provided excellent agreement with experiment whereas method (i) produced mixed results.
The analysis had some incidental benefits: it caused a reassignment of one vibronic spectrum and permitted a choice between two proposed alternative assignments for another vibronic spectrum.
CHAPTER I
THE FOUNDATION

This work begins with the essentials that are the foundation of our knowing about spectra and molecular properties. These include issues of transition in molecular species [1,2], electronic versus nuclear motion [3], associate quantum mechanical (physical and mathematical) fundamentals [4,5,6,7,8,9,10,11], and illustrative experimental spectra [12,13].

The molecular properties are deduced from absorption and emission spectra in a variety of ways. The spectral frequencies of the absorption maxima provide information on the energy levels of the molecular excited state. The observed spectral intensities provide a basis for the determination of symmetries and multiplicities of those states. Analysis of the intensity distribution permits the identification of excitation modes, which in turn differentiates the assignment of rotational, vibrational, and electronic transitions. The splittings and broadenings of the spectral bands detail the presence of intramolecular rotations and other types of conformational processes and interactions; these particular details may contain the information required to estimate barrier heights for such processes. One can deduce electric or magnetic moments of the molecule in the ground state as well as in the excited states from splittings or broadenings of spectra induced by external electric or magnetic fields. Finally, the spectra of molecules in condensed phases provide some access to the question of intermolecular interactions.

Many other molecular properties can be estimated from spectral data. In fact, if one considers the vast variety of conditions under which spectra can be measured,
one can find some information about almost every molecular characteristic. Yet we
still extract from spectra only a small portion of the information they contain. Such
limitations involve basically two aspects: the rigor of quantum mechanics and the
conformity of real systems to that theory. The strategy we propose serves to
circumvent this problem in one specific area.

Information contained in spectra is complex. Any one spectrum may
simultaneously reflect many facets of the molecular structure. In order to decipher
this information, we require physical models. The connection between frequencies of
intensity maxima, for example, and the energies of stationary states requires a
nontrivial analysis of the interaction of the molecule with electromagnetic radiation.
Symmetries and multiplicities of the excited states are examples of the type of data
that one might seek. Indeed, the fact that a large portion of spectroscopic information
is not processed any further, justifies a search for reliable, simple models. Such a
search is the objective of this thesis.

1.1 Geometry of Electronically-Excited States

We wish to present a model that permits the estimation of molecular geometry
in an electronically-excited state.

Ground-state geometry is one of the most basic molecular characteristics. It
provides the experimental basis for concepts of molecular architecture, and it is
mandatory for any understanding of molecular behavior. Since it is now known that
many physicochemical processes involve electronically excited states, the
determination of the molecular geometry in such states no longer requires
justification. However, although several well-developed techniques exist for
ground-state geometry studies, the means for the determination of geometries in
electronically exited states are rather limited [7]. In order to understand this, we will
now discuss the extent to which the techniques for ground-state geometry
determination might be applied to electronically excited states.

There are basically two types of useful techniques: diffraction and rotational
spectroscopic methods.

1.2 Diffraction Techniques

The diffraction techniques estimate the molecular geometry from a diffraction
pattern produced by the scattering of X-rays, neutrons, or electrons by the individual
molecules. The scattering cross section of both X-rays and neutrons is very small for
a single molecule; therefore, the efficiency of X-ray and neutron diffraction techniques
is crucially dependent on the interference amplification of weak scatterings from
individual molecules in a large sample of regularly distributed molecules, as in, for
example, monocrystals. The scattering cross section of electrons, however, is large
enough to permit the observance of the diffraction from molecular vapors.
Nonetheless, in order to obtain a sufficiently large signal-to-noise ratio, the
concentration must lie above certain limits. Consequently, all diffraction methods
require a relatively large concentration of the molecules under study.

Because of the short life-time of electronically excited states, it is not generally
possible to generate a high enough concentration of molecules in these states.
Consequently, diffraction techniques are not usually applicable to excited states.

1.3 Rotational Spectroscopic Methods

The common spectroscopic method for the determination of molecular
geometry is based on an analysis of the rotational structure of a spectral band. In
many cases, it is possible to treat the motions of the electrons and nuclei of an
isolated molecule as a superposition of the following four types of motions: the
translation and rotation of the whole molecule; the small oscillations of nuclei around
their equilibrium positions; and the motions of electrons within the nuclear framework. With the exception of translation, the movement of the entire molecule from one place to another, all these forms of motion are quantized. The consequences of quantization is demonstrated by the energies of the molecular stationary states, as shown in Figure 1.1.

The gross features of the energy-level pattern are determined by the electronic levels that are usually separated by many electron-volts. Each electronic level is accompanied by a family of vibrational levels that are separated by energies of the order of tenths of electron-volts. Finally, with every vibrational level, there is associated a dense manifold of rotational levels with energy separation of about one one-hundredth of an electron-volt or lower.

The spectral transitions within the ground-state rotational manifold are termed "pure rotational transitions," and the corresponding rotational spectra are observed in the microwave region. The transitions between the rotational-vibrational states of the electronic-ground state are termed "rovibronic transitions." The presence of separated rotational lines in the microwave, infrared, visible, or UV spectrum constitutes the rotational structure that is said to be present in these spectra. An example of such a spectrum is given in Figure 1.2.

Quantum mechanical analysis of the molecular rotations shows that the separation of the rotational spectral lines is determined by the inertial moments of the molecule. The inertial moments are dependent on the masses and relative positions of the nuclei in the molecule. For example, the moment of inertia, I, of a diatomic
Figure 1.1 The energy separations for individual types of energy states are

- electronic levels, many eV
- vibrational levels, tenths of an eV
- rotational levels, hundredths of an eV
Figure 1.2 The spectrum of the \( \text{O}_2 \) Schumann-Runge region [12]. The \( \nu' = 8', 7', 6', 5', 4' \) vibrational electronic transitions are accompanied by rotational transitions. The electronic excitation, from ground to excited state, is \( A^3 \Sigma_u^+ \rightarrow X^3 \Sigma_g^- \).
molecule is defined as

\[ l = \frac{m_1 + m_2}{m_1 m_2} R^2 = \mu R^2 \]  

(1.1)

where \( m_1 \) and \( m_2 \) are the masses of the nuclei, \( R \) is their separation, and \( \mu \) is the reduced nuclear mass. For a nonlinear polyatomic molecule, the moment of inertia has three components; these are usually associated with the perpendicular cartesian axes of the center of mass of the molecule. Each component remains a simple function of the nuclear masses and their individual separations. The inertial moment of a polyatomic is

\[ l = \Sigma m_j r_j^2 \]  

(1.2)

Thus, from the separation of rotational lines in the microwave or infrared spectra, the components of the inertial moments can be evaluated and the ground state molecular geometry can be estimated. Because of the high accuracy with which it is often possible to measure the positions of such rotational lines, the geometry obtained may be very precise. Similarly, from the rotational structure of the spectra in the optical and UV regions, we can determine the molecular geometry in electronically excited states.

The spectroscopically estimated ground and excited state equilibrium geometries, \( R'_0 \) and \( R'_e \), for the diatomic molecules of this study are listed in Chapter 6, Table 6.1, Columns 7 and 8. A brief inspection of these data shows that the molecular structure in the electronically excited states can be substantially different from that in the ground state.

Unfortunately, several factors restrict the applicability of this rotational spectroscopic method. First, the inertial moment is a symmetric tensor which, as already mentioned, contains at most three independent components. Consequently,
only three geometric parameters, such as the bond lengths and angles, can be determined. For molecules whose geometry is specified by more than three parameters, the inertial moment is not, therefore, sufficient for a unique determination of structure. The consideration of the spectra of isotopic molecules removes this restriction partially. However, even then, the spectroscopic method is suitable only for relatively small, simple molecules.

The second limitation arises from the necessity for highly resolved rotational structure. This can usually be achieved only in the vapor phase since, in the condensed phase, intermolecular interactions broaden the spectral lines and smear out the rotational structure. In addition to this, the rotational lines for multiatomic molecules are so closely packed that they are not often resolved even in the vapor phase. Thus, the usefulness of the spectroscopic method is further restricted to light volatile species. Finally, the various intramolecular coupling mechanisms which tend to broaden the spectral lines are more efficient in electronically excited states. This latter fact explains the smaller probability of finding resolved fine structure in the visible and UV regions. Therefore, the number of molecules for which the geometry of an electronically excited state can be determined from rovibronic structure is relatively small.

All techniques for the quantitative determination of molecular structure fall within one or the other of these two classifications. Consequently, the number of molecules for which geometric data are known for electronically excited states is small.

1.4 The Quantitative Discussion of Vibronic Spectra

Despite these limitations, many molecules yield vibronic spectra that are well-resolved and well-understood. These well-known examples form the basis for all
the correlations deduced by researchers in theoretical and experimental quantum chemistry. These spectra exhibit a number of peaks separated by several hundreds of reciprocal centimeters, cm⁻¹, wavenumbers; each of these peaks represents a family of unresolved rovibronic lines with the same common initial and final vibrational levels. In many instances the vibrational structure can be resolved in the solid or liquid phases, a circumstance that opens the possibility for a study of highly polar or even ionic molecules. Figure 1.3 reproduces an example of a vibronic spectrum for the permanganate ion. The individual vibrational peaks are detectable in this case, in both the solution and crystal. Because of the abundance of such vibronically structured spectra, it is mandatory to ask whether information on the molecular structure in electronically excited states can be extracted from these types of spectra.

The answer is affirmative and is based on the following statement: The vibronic distribution of the spectral density is strongly dependent on the differences in equilibrium geometries of a molecule in the ground and excited states. From this it follows that, if we can find a quantitative relation between the vibronic intensity distribution and the difference in the geometry, the latter can be estimated from observed spectra. If, in addition, the ground-state geometry is known, the excited state geometry can then be evaluated.

The difference in geometry is not the only factor which influences the vibronic intensity distribution. In order to develop a technique which will elicit the geometry changes from the vibronic intensity pattern, a suitable model must be formulated. Such a model must specify, in a quantitative form, the manner in which the various molecular properties affect the vibronic distribution of intensity; it must identify those particularly critical properties that cannot be neglected; and, finally, it must determine...
Figure 1.3 The vibronic spectrum of the permanganate ion. The individual vibronic bands are detectable in both the solution (---) and the crystal (-----); the rovibronic components of the spectrum are unresolved [13].
the limitations of the technique. The construction of such a model requires a rather involved quantum mechanical analysis of the processes accompanying the electronic excitation of a molecule. However, the basic ideas can be illustrated in a simple visual way.

1.5 The Model

From the point of view of geometry, the simplest molecule is the diatomic. It has only one geometric parameter, the bond length. For this reason, the steps which lead to the model will be illustrated using the diatomic example. In order to obtain a description of the molecular behavior, we must solve the Schrödinger equation

\[ \hat{H} \psi = E \psi \]  

Equation 1.3

where \( \hat{H} \) is the molecular Hamiltonian. Unfortunately, even for molecules as simple as the diatomics, the Hamiltonian is far too complex to permit the exact solution of Equation 1.3. However, in view of the restricted goal of this work, namely the relationship between the spectral intensity distribution and the geometry changes, we can simplify the problem by introducing a sequence of approximations. These approximations allow us to neglect factors of secondary importance and lead to the desired model.

1.6 The Separation of Molecular Motions

First, unless the molecule consists of very heavy atoms, we can neglect all spin-dependent interactions.

Second, we will assume that the translational, rotational, vibrational, and electronic components of the molecular motion are mutually independent. This assumption is crucial, and the quantum mechanical conditions for its validity are formulated in the Born-Oppenheimer approximation. The rigorous form of the
Bom-Oppenheimer approximation involves rather abstract concepts. However, when interpreted in a classical language, it yields the following separability conditions: If the intramolecular forces permit only small displacements of the nuclei within the molecule and if the external forces to which the molecule is subjected are much smaller than the intramolecular forces, the various components of the molecular motion become highly independent.

The requirement of small nuclear displacements assumes a rigid molecular structure and thus eliminates from consideration particular molecules that are characterized by a low dissociation energy as well as molecules whose structure permits an internal rotation or other types of stereochemical conversions occurring at low activation energies. For stable and rigid molecules, the intramolecular forces dominate the external ones not only in the vapor phase but also in those condensed media which exhibit only weak solvent-solute interactions. In the condensed phase, the molecular translations and rotations become vibrations and librations of the whole molecule around its equilibrium position. In the crystalline state these whole-molecule vibrations-librations are coupled with similar motions of the other molecules, giving rise to the lattice vibrations. This coupling represents one of the mechanisms which tend to broaden spectral bands.

Consider the case when the Bom-Oppenheimer approximation is applicable. The Hamiltonian $\hat{H}$ of a free molecule, for example a molecule in the dilute vapor phase, separates into four parts corresponding to the four components of the molecular motion

$$\hat{H} = \hat{H}_T + \hat{H}_R + \hat{H}_O + \hat{H}_S.$$  

(1.4)
where $\hat{\mathbf{R}}_t$ specifies the translations of the molecular center of mass. Since we assume that the molecule has a rigid structure, the motion of the center of mass causes only negligible broadening of the spectral lines. Therefore, we disregard them completely. The operator $\hat{\mathbf{R}}_R$ specifies the rotation of the molecule around its center of mass. A more explicit form of $\hat{\mathbf{R}}_R$, for example that for the rigid rotor approximation, is

$$\hat{\mathbf{R}}_R = \frac{\hat{P}_A^2}{2I_A} + \frac{\hat{P}_B^2}{2I_B} + \frac{\hat{P}_C^2}{2I_C}$$

(1.5)

where $I_A$, $I_B$, and $I_C$ are the components of the inertial moment and $\hat{P}_A$, $\hat{P}_B$, and $\hat{P}_C$ are the angular momentum operators.

1.7 Intramolecular Motions

The operators $\hat{\mathbf{R}}_o$ and $\hat{\mathbf{R}}_e$ specify the motions of the nuclei and electrons within the translating and rotating molecule and they determine the main features of the vibronic spectra. We will, therefore, discuss these in more detail, at first focusing on their separability. For this purpose we introduce the Hamiltonian $\hat{\mathbf{R}}_\text{in}$ that specifies the intramolecular motions of the electrons and nuclei without assuming their separability. The partitioning of the molecular Hamiltonian of Equation 1.4 is now

$$\hat{\mathbf{H}} = \hat{\mathbf{R}}_t + \hat{\mathbf{R}}_R + \hat{\mathbf{R}}_\text{in}$$

(1.6)

where $\hat{\mathbf{R}}_t$ and $\hat{\mathbf{R}}_R$ retain their original meaning. The operator $\hat{\mathbf{R}}_\text{in}$ can be written as the sum of three parts,

$$\hat{\mathbf{R}}_\text{in} = \hat{\mathbf{T}}_e + \hat{\mathbf{T}}_n + \mathbf{V}$$

(1.7)
where $\hat{T}_e$ and $\hat{T}_n$ represent the kinetic energy of intramolecular electronic and nuclear motions, respectively, and $V$ is the potential energy of interaction among electrons and nuclei. This potential energy depends only on the relative distances between electrons and nuclei. For the diatomic molecule, it can be written as

$$V = V(r, R)$$

where $r$ is the set of electron coordinates and $R$ is the set of nuclear separations.

For polyatomic molecules, $V$ remains similar to that of a diatomic molecule, except that instead of one geometric parameter $R$, it will depend on all geometric parameters such as bond lengths, bond angles and dihedral angles. Thus, the Hamiltonian $\hat{H}_R$ is also geometry-dependent and we can expect that those spectral features that are determined by $\hat{H}_R$ will, in some fashion, reflect the molecular structure. However, while within the approximations accepted here, the rotational Hamiltonian $\hat{H}_R$ depends only on the equilibrium molecular geometry, the Hamiltonian $\hat{H}_{\alpha\omega}$ is dependent on the instantaneous values of the geometric parameters, values that do vary about their equilibrium value. The variances are small for rigid molecules.

The deduction from these considerations is that the relations between the intramolecular motions, equilibrium geometry, and spectra may be less straightforward than those which we found for the molecular rotations. In order to elucidate these relations, let us analyze the intramolecular motions of the electrons and nuclei.

Since the nuclei are at least 1860 times heavier than the electrons, their motions internal to the molecule possess much lower velocities. Therefore, during any period sufficient for electrons to execute many revolutions around the nuclear framework, the internuclear distances change insignificantly. In other words, if we take for the time unit an average period of the electron revolution, then for a
very long time interval, the electrons may be considered to revolve around the motionless nuclei.

The description of the electronic motions can be obtained in the following manner. The large disparity between the nuclear and electronic velocities permits us to neglect the operator $\hat{T}_m$ in Equation 1.7. The resulting simplified Hamiltonian

\[ \hat{H}_e = \hat{T}_e(r) + V(r; R) \]  

(1.9)

specifies the electronic motions about the framework of static nuclei. The solution of the Schrödinger equation with the Hamiltonian $\hat{H}_e$ gives the electronic functions and energies for a particular stationary nuclear configuration of the molecule.

In the diatomic case, this means that the internuclear distance has some fixed value, $R$, and the Schrödinger equation for the electronic motion becomes

\[ \hat{H}_e(r; R) \psi(r; R) = \varepsilon(R) \psi(r; R) \]  

(1.10)

an equation that yields many solutions. These comprise the lowest energy corresponding to the electronic ground state $\varepsilon_0(R)$, and those with higher energies corresponding to the various electronically excited states $\varepsilon_e(R)$.

1.8 Potential Energy Curves

It is important to realize that the energy $\varepsilon(R)$ and the wave function $\psi(r; R)$ characterize the electronic motions for only one particular value of the internuclear distance. In order to obtain a complete description of the electronic motion, we must solve Equation 1.10 for various values of $R$ and fit those piecewise descriptions together. This fitting produces curves known as electronic potential wells. Examples of these are shown in Figure 1.4.
Figure 1.4  The fitting together of the solutions of Equation 1.10 for various values of $R$ generate the manifold of potential energy curves. Only three of these are shown.
Those states for which the electronic potential possesses a minimum are known as bound states. The internuclear distance at the minimum of such a state represents the equilibrium bond length associated with this state. The electronic energy at the minimum of the potential well specifies the position of the "pure" electronic level in the rotation-vibration-electronic energy diagram. The shapes of the potential curves may be quite different for different electronic states, as indicated in Figure 1.4. In particular, if two potential curves reach their minima at different values of $R$, the corresponding electronic states will have different values for the equilibrium bond lengths.

For a polyatomic molecule, the electronic potential in a given electronic state may be characterized by a family of potential curves that yield a potential surface. One potential energy curve similar to those for a diatomic molecule is associated with each independent geometric parameter. The positions of minima for these curves will then specify the equilibrium geometry of the corresponding excited state. This is as far as consideration of the separated electronic motions will take us.

1.9 Vibrational Motions and Spectra

In order to describe the motions of nuclei, let us now return to the picture of very fast electrons and rather slow nuclei. The motion of the nuclei is determined by their mutual repulsion and by their attraction to all of the electrons. The electrons traverse all possible positions relative to the nuclear framework many times before the nuclei change their locations. Therefore, the nuclei experience an interaction with the electrons that is an average over all the instantaneous positions of the electrons. The resulting average potential depends on the character of the electronic motion and is, therefore, different for different electronic states. The electronic potential curves shown in Figure 1.4 for the case of a diatomic molecule are nothing less than these
average potentials. Therefore, the Hamiltonian $\mathcal{H}_o$, which characterizes the nuclear motions associated with the $x$th electronic state, will be

$$\mathcal{H}_o = \mathcal{T}_m + \varepsilon_x(R) \quad (1.11)$$

A result similar to that shown in Figure 1.5 is obtained when the Schrödinger equation for nuclear motion in such a potential is solved.

$$\mathcal{H}_o \chi(R) = E \chi(R) \quad (1.12)$$

for nuclear motion in such a potential is solved.

The possible modes of nuclear motion are restricted by energy quantization. For a diatomic molecule, this result can be visualized by assuming that a single particle with a mass equal to the reduced mass of the two nuclei vibrates within a potential well with an energy equal to one of the quantized values. The allowed values of the vibrational energy specify the energy distribution of vibrational levels associated with the given electronic state. In general, the separation between adjacent vibrational levels decreases as we ascend the potential well until finally these levels merge into a continuum of allowed states. The edge of the continuum corresponds to the dissociation of the molecule.

The transitions between vibrational levels of different electronic states, the vibrational transitions, determine the gross features of the observed vibronic spectrum. An important characteristic of vibronically structured spectra is the vibrational progression. They represent families of vibronic peaks that exhibit a constant or regularly decreasing separation as well as a regular intensity variation. The vibrational progression results from vibronic transitions that initiate in a common vibrational level but terminate on different members of the vibrational manifold.
Figure 1.5 The vibrational levels obtained when the Schrödinger equation, $\hat{H}_v \chi(R) = E \chi(R)$ where the Hamiltonian, $\hat{H}_v = \hat{T}_m + \varepsilon_v(R)$, for nuclear motion is solved. The harmonic potential is indicated by the dotted lines, see Figure 1.6. The solid line is a Morse potential. The edge of the continuum, drawn as a series of connected diagonals, denotes the dissociation energy of the molecule.
associated with the final potential well. Therefore, the separation of the peaks within the vibrational progression yields the separation of the vibrational levels in the terminal electronic state.

The electronic potential curves for a large number of molecules in the vicinity of their minima can be approximated by a parabola; this leads us to the harmonic approximation, shown in Figure 1.6. The use of this approximation has several advantages. First, the Schrödinger expression, Equation 1.12, for the nuclear motions in the parabolic potential can be solved exactly, and the resulting wave functions for the individual vibrational states turn out to have a simple analytical form. For the harmonic potential, the vibrational levels are equidistant. Indeed, the fact that the frequency increment of successive vibrational progression members observed for many molecules is nearly constant indicates the broad applicability of the harmonic approximation. Second, the parabolic potential is uniquely specified by the curvature at its minimum, and this also bears a simple relation to the force constant \( k_x \) of the harmonic vibrations and to the fundamental vibrational frequency \( \nu_x \). Consequently, both the energies \( E \) and wave functions \( \chi(R) \) depend on a single parameter, \( k_x \).

1.10 The Vibronic Intensity Distribution

Now that we have described the intramolecular motions, we can approach the main problem of the dependence of the vibronic intensity distribution on the change in molecular geometry. To do this, let us consider the manifold of vibrational states associated with the electronic ground state and that associated with one of the electronically excited states of a diatomic molecule. The low-energy portions of these manifolds are presented schematically in Figure 1.7, where the corresponding harmonic potential curves are also plotted. In this particular case, the curvature of the ground-state potential is larger and the ground-state bond length is shorter than for
Figure 1.6 Parabolic Model

\[ k_x = \frac{d^2 u_x(R)}{dR^2} \bigg|_{R = R_x} \]

\[ \nu_x = \frac{1}{2} \pi \sqrt{\frac{\hbar}{\mu}} \]

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

\[ \hbar = \text{Planck's constant} \]

The harmonic approximation to the potential curve where \( k_x \) is the force constant, \( \nu_x \) is the fundamental vibrational frequency. The relations between the curvature of the harmonic potential, the vibrational force constant, and the fundamental vibrational frequency are also shown.
Figure 1.7 The schematic of potential energy curves, low-energy manifold of vibrational states, and a typical pattern observed experimentally in the expected distribution of probabilities. The notation is

Ground-state: $0''$, $1''$, ..., $v''$

Excited-state: $0'$, $1'$, ..., $v'$
the excited state. This is the most typical pattern observed experimentally. The reverse situation, however, is possible. Based on the current spectroscopic notation, the vibrational states of the ground and excited states are labeled by double primed indexes $0^{''}, 1^{''}, ..., \nu^{''}$ and single primed indexes $0', 1', ..., \nu'$, respectively.

Let us now try to anticipate what sort of absorption spectrum we should obtain for a diatomic molecule when this simplified model is used. We must now consider the frequencies in the electromagnetic spectrum that will be absorbed as well as the rate with which the energy at these frequencies is removed from the incident beam.

The first part of the problem is relatively simple. Under ordinary experimental circumstances, electromagnetic radiation is absorbed only if its frequency is equal to the energy difference between two stationary states of the system. Such a frequency is termed the resonance frequency. Since we are concerned with a situation in which the initial state is one of the vibrational states of the ground-state manifold and the final state belongs to the vibrational manifold of an electronically excited state, we obtain the following values for the resonance frequencies

$$v_{\nu'^{''}} = \frac{E_{\nu'} - E_{\nu^{''}}}{h} \quad (1.13)$$

However, even if the light interacting with the molecule contains the resonance frequencies, two additional criteria must be met in order to produce a measurable absorption. First, the sample must contain a sufficiently large concentration of molecules in the initial state. Second, the probability of the transition $\nu' - \nu^{''}$ that is induced by interaction of the molecule with the resonant photon must be sufficiently high. In the majority of spectroscopic experiments, the sample is usually at or near thermodynamic equilibrium, and the concentration of molecules in the individual stationary states can be estimated using the Boltzmann distribution law. It follows
from this law that, if the sample temperature is not very high or the energy separation of the vibrational levels in the electronic ground state is not very small, the majority of the molecules will be in the 0" vibrational state. Consequently, in the absorption spectrum, we will only observe those bands that represent \( v' - 0" \) transitions. The probabilities of these transitions can be evaluated correctly only by quantum mechanical methods. However, qualitative estimates of magnitude can be obtained using a set of classical ideas that were formulated by James Franck in 1925 [1].

1.11 Franck's Ideas

Let us investigate the changes which electronic and nuclear motions undergo when a molecule absorbs a photon. The absorption of the photon of energy,

\[
 h\nu = E_v - E_{v'}
\]  

(1.14)

represents a relatively large increase of molecular energy. Thus, it causes a considerable reorganization of both the electronic and nuclear motions. The motion of the electrons rearranges almost instantaneously with the act of photon absorption due to their very small inertial mass. The converse is true of the nuclei. The force field experienced by the nuclei because of their attraction by the electrons is strongly dependent on the mode of the electronic motion. Consequently, during the absorption process the force field changes suddenly from that specified by the ground-state potential curve to that specified by the excited state potential curve. However, since the large inertial mass of the nuclei makes them resistant toward any rapid change in their motions, these motions remain more or less the same as that of the initial vibrational state for some time after photon absorption. Upon excitation, the electron due to its small size will sample the energy change in its environment and respond quicker than the sluggish nuclei.
Two important characteristics of the $0''$ type of nuclear vibrations must now be emphasized. These are shown in Figure 1.7. First, the amplitude of oscillation is relatively small and, therefore, the nuclear positions are restricted to a narrow region of internuclear distances. Second, the kinetic energy of nuclear vibrations is very small.

Let us now determine which of the terminal $v'$ states permits the nuclei to retain these characteristics that appear to be typical for the initial $0''$ state. The restriction of the nuclear positions eliminates all those states that do not lie directly above the vibratory region of the $0''$ state. The low-velocity requirement infers that the nuclei will tend to start their newly excited life close to the walls of the terminal potential well. The transitions to states that simultaneously satisfy both of these conditions are termed vertical transitions. They are the most probable transitions. Thus, for the potentials shown in Figure 1.7, the most probable transition is $2'\leftarrow 0''$ or $1'\leftarrow 0''$ and photons of frequency $\nu$ will exhibit the highest absorption rate at the frequencies

$$
\nu_{2'\leftarrow 0''} = \frac{E_{2'} - E_{0''}}{h} \quad \text{and} \quad \nu_{1'\leftarrow 0''} = \frac{E_{1'} - E_{0''}}{h}
$$

This will be reflected in maximum values of the absorption coefficients for the region of frequencies $\nu_{2'\leftarrow 0''}$ and $\nu_{1'\leftarrow 0''}$. For simplicity, we have shown $\nu_{2'\leftarrow 0''}$ to be the highest intensity transition.

A more detailed analysis shows that these restrictions, nuclear velocity and position, are not absolute and that transitions to other states are also possible. However, their probabilities are smaller than that of the vertical transition, and probabilities decrease rapidly with departure from the vertical transition region in
directions of both increasing and decreasing excitation energies. An expected
distribution of probabilities is depicted qualitatively in Figure 1.7.

1.12 Geometry and Force Constant Changes

Figure 1.8 displays three pairs of harmonic potentials, all of which possess a
common ground-state potential. The concept of nuclear resistance to change of
motion suggests that the $3' \leftarrow 0''$, $2' \leftarrow 0''$, and $1' \leftarrow 0''$ transitions are the most
probable transitions for Set I. In Set II, the minimum of the excited-state potential is
located at an internuclear distance that is larger than the minimum for Set I. The
maximum transition probability now occurs in the region of the $5', 4', 3', 2' \leftarrow 0''$
transitions. Comparison of the potential curves of Sets I and II indicates that the
transition probability distribution depends on the difference
\[
\Delta R_e = R_{e'} - R_{e''} = R_e - R_g
\]
that is, the difference between the bond lengths $R$ of the electronically excited and
ground states, respectively. Equation 1.16 also portrays the various notations that
are used to represent equilibrium distances in different texts.

In Set III, the difference of the equilibrium bond lengths is the same as in Set
II. However, the curvature of the upper potential and, consequently, the separation of
the upper vibrational levels is smaller than that in Sets I and II. As a result, the
maximum transition probability shifts relative to both Sets I and II. Therefore, the
difference in the curvature of the potential wells, that is, the difference in the
vibrational force constants $k_g$ (or $k''$) of the electronic ground and $k_e$ (or $k'$) of the
electronic excited states, also influences the probability distribution.

Thus, the very simple classical model used here to estimate the vibronic
transition probability reveals that two characteristics of a diatomic molecule are
Figure 1.8 The schematic of vibronic excitations. Three sets of harmonic potential energy curves in various relationships.
influential. These are the bond length difference, $R_e^0 - R_e^n$, and the difference between the vibrational force constants in the excited and ground electronic states. Analogous results can be obtained for polyatomic molecules. In this latter case, the transition probability distribution depends on the differences between all independent geometric parameters and associated force constants in the ground state and the excited state.

1.13 Quantum Mechanical Models of Intensity Distribution

The arguments provided above justify an attempt to estimate the molecular geometry in electronically excited states by analyzing the vibronic structure of absorption spectra. The intent, however, is to develop an operative method for geometry determination that demands a more precise formulation of the problem. A more exact analysis of the processes which accompany photon absorption is necessary. For example, the qualitative discussion given above does not guarantee that the geometry and force constant differences are the only factors which exert critical influence on the vibronic structure of spectra. Moreover, it does not yield any quantitative relation between these factors and the intensity distribution that will be used to extract the geometric parameters. These kinds of problems require a quantum mechanical approach. Fortunately, the quantum mechanics verify that our simplistic conclusions are in fact quantitatively correct. As early as 1926, Edward U. Condon [2] proved that the most probable vibronic transition within an intense electronic absorption band will be the vertical one. Similarly, the supposition that the electronic and nuclear motions are nearly independent of each other was confirmed by Max Born and Robert Oppenheimer [3]. Thus, we will evade the technicalities of the rigorous problem and present only an overview.
1.14 Requirements of a Model

We must construct models that facilitate the computation of spectral intensity distributions from molecular properties. Constituents of such a model must be analogous to properties of the real molecule that are critical to the vibronic intensity distribution. A determination of a critical molecular property is a correlative problem: First, we must ascertain to what extent an approximate geometry can be ascribed to the real system, and second, we need to know the nature of the electronic transition. For example, the geometry and force-constant differences are the only critical parameters for transitions that yield high-intensity absorption bands, providing that the nuclear vibrations are nearly harmonic. Oftentimes, the electronic potential may deviate strongly from the parabolic. Under these conditions, the anharmonicity constants also become a critical molecular property. For a weak electronic transition, such as symmetry or multiplicity-forbidden transitions, parameters relating to the magnitude of vibronic and/or spin orbital coupling may become important.

A model must also specify the mechanism that governs light absorption. In the majority of the cases, the electric dipole mechanism is the most important. Yet the electric quadrupole or magnetic dipole mechanism may contribute most significantly to the overall absorption intensity for very weak transitions.

As a result, we can fabricate different models by making different selections of the critical molecular properties and of the transition mechanisms. Each of these models reflects some specific physical situation, and it is possible to prepare a family of them that will cover the majority of important cases.

Each model represents, in an operational sense, an algorithm whose input is the characteristics of the hypothetical molecule and whose output is the computed transition probability distribution, that is, the theoretical spectrum. Thus, the
theoretical model solves the problem in a direction that proceeds from molecular properties to the molecular spectrum. In order to infer the molecular properties from the experimental spectrum, we must reverse this direction. This can be achieved by fitting the theoretical to the experimental spectrum. The theoretical spectrum will resemble the observed spectrum if the theoretical model is a high fidelity map of the physical processes that accompany the spectral transitions in the molecule of interest and if the imputed characteristics of the hypothetical molecule lie close to those of the real molecule. For a selected theoretical model, the imputed molecular characteristics can be varied until the best possible fit of the theoretical and experimental spectrum is achieved.

When such a best possible theoretical spectrum is obtained, two situations are possible. First, the difference between the theoretical and experimental spectrum might be insignificant. In this case, we can conclude that the physical processes implicit in the model are sufficient to explain the spectral behavior of the molecule under study. Moreover, the values of the optimized molecular characteristics, for example, the geometry in the electronically excited state, may have a physical significance. On the other hand, if the best achievable fit obtained with a specific model is unsatisfactory, we must conclude that the transition is not adequately matched by the model. In this instance, we must search for a better model. Such an optimization procedure, one pertinent to the particular case of Equation 2.10, is schematized in Figure 1.9.

Thus, the optimization of the match between the theoretical and experimental spectra provides the values of interesting molecular properties as well as a quantitative test of the validity of the assumed spectroscopic processes.
Figure 1.9 A schematic of the optimization procedure, one used with Equation 2.10 to assay the degree of fit of the linear and quadratic approximations, and the "best fit" procedure to the experimental results.
1.15 The Diatomic Model Specification

This approach will now be investigated for a simple model of a diatomic molecule, Figure 1.10. In this model the following assumptions specify the diatomic molecule and the mechanism of light absorption:

The nuclear vibrations are harmonic in both the ground and electronically excited states. Therefore, two harmonic potentials, \( \varepsilon_g(R) \) and \( \varepsilon_e(R) \), must be specified. Each of these is fully characterized by its curvature

\[
\frac{d^2 \varepsilon_x(R)}{dR^2} \bigg|_{R=R_x}
\]

Alternatively, we can specify the harmonic potentials by the force constants, \( k_x \), or by the vibrational fundamental frequency, \( \nu_x \), and the reduced mass, \( \mu \).

The relative location of these potential curves is specified by two additional parameters: The energy separation, \( T_\varepsilon \), of their minima and the displacement, \( \Delta R \), of these minima on the internuclear separation scale. This energy bears a simple relation to the frequency \( \nu_0 \) of the \( 0' \leftarrow 0'' \) transition, and is given by

\[
h \left[ \nu_0 + \frac{1}{2}(\nu_e - \nu_g) \right]
\]

Consequently, the frequency \( \nu_0 \) can be used to specify the separation of the initial and terminal potential wells.

The vibronic transitions are assumed to be electric dipole allowed. This assumption introduces as a parameter the quantity \( |M|^2 \) which is the electronic transition probability. We will restrict ourselves to low-temperature spectra and, therefore, only the \( \nu' \leftarrow 0'' \) transitions (or in the case of emission, \( 0' \rightarrow \nu'' \)) must be considered.
Figure 1.10 The parameters $v_o$, $v_g$, $v_e$ and $\Delta R_e$ are schematized.
Thus, within this model the vibronic spectral activity of a diatomic molecule is characterized by six parameters: \( v_o, v_e, v_s, \Delta R, \mu, \) and \( |\vec{M}|^2 \). The parameters \( v_o, v_e, v_s \) and \( \Delta R \) are schematized in Figure 1.10. The relations between the curvature of the harmonic potential, the vibrational force constant, and the fundamental vibrational frequency are also shown in Figure 1.6.

For a given diatomic molecule, the reduced mass \( \mu \) can be evaluated from the known nuclear masses. The ground state fundamental vibrational frequency, \( v_o \), can be estimated from infrared or Raman spectra. If the vibronic structure of the electronic absorption band is sufficiently resolved, the pure electronic frequency, \( v_o \), and the fundamental vibrational frequency in the excited state \( v_s \), can be derived in a straightforward manner. Thus, under optimal circumstances, the only unknown molecular properties are the bond length differences, \( \Delta R \), and the electronic transition probability, \( |\vec{M}|^2 \). The probability of the \( v' \leftrightarrow 0'' \) vibronic transitions can be shown to be

\[
P_{v'\rightarrow 0''} = C |\vec{M}|^2 S_{v'\rightarrow 0''}^2
\]

where the factor \( C \) depends only on universal constants, and the \( S_{v'\rightarrow 0''}^2 \) terms are the Franck-Condon integrals, FCI's. It can be shown that

\[
\sum_{v'} S_{v'\rightarrow 0''}^2 = 1
\]

which, in turn, yields the relation

\[
\sum_{v'} P_{v'\rightarrow 0''} = C |\vec{M}|^2
\]
Therefore, the electronic transition probability $|M|^2$ is proportional to the total probability of all transitions from the 0''-state to the various excited $v'$-states. Its magnitude may vary strongly for different electronically excited states. The various degrees of electronic allowedness of a transition is reflected in the spectrum by a relatively large variation of molar extinction coefficients.

Equation 1.19 for $P_{v'-0''}$ is correct only for a strongly allowed transition. For weakly allowed transitions, additional terms must be introduced.

1.16 Franck-Condon Integrals, FCI's

The Franck-Condon integrals or FCI's, $S^2_{v'-0''}$ specify the manner in which the total transition probability, $C|\vec{M}|^2$, is distributed over the individual vibronic transitions, $v' \rightarrow 0''$. The expression $C|\vec{M}|S^2_{v'-0''}$ represents that portion of the total intensity which is associated with the $v' \rightarrow 0''$ transition. Since the previous qualitative discussion indicates that the geometry difference affects the intensity distribution within the manifold of $v' \rightarrow 0''$ transitions, it is the FCI's, which serve this function in Equation 1.19, that are the obvious quantities of primary interest for geometry purposes.

The FCI's are the squares of the overlap integrals, $S_{v'-0''}$, between the vibrational wave function $\chi_{0''}$ of the 0''-state and the vibrational wave function $\chi_{v''}$ of the $v''$-state. The overlap is generally represented by

$$S_{v'-0''} = \int_0^\infty \chi_{v''}(R') \chi_{0''}(R') \, dR \quad (1.22)$$

These wave functions, in the case of the harmonic potential, are simple enough so that their overlap integrals can be evaluated easily. Their evaluation shows that they depend on two parameters, $\beta$ and $\gamma$ (or $\gamma$), which in turn are related in a simple way.
to the characteristics of the hypothetical diatomic molecule undergoing the absorption transition

$$\gamma = \left( \frac{2 \frac{c \mu}{R}}{h} \right)^{\frac{1}{2}} |\Delta R_0|$$

The dependence of the overlap integrals on $\beta$ and $\gamma$ is detailed in Chapter 3 and Appendix I.

The values of the FCI's are largest for the vertical transitions. This result is known as the Franck-Condon Principle and it can be understood from a simple inspection of the shapes of the vibrational functions $\chi_0^v$ and $\chi_v^v$, which are quantitatively plotted in Figure 1.11. It is clear that, for the vibronic transitions which are of lower energy than the vertical transition, the overlap integrals, the FCI's, are small because of the relative displacement of the maxima of the wave functions. For the transitions of energy higher than vertical, the overlap integrals, the FCI's, are again small, although now it is the rapid sign alternation of the wave function $\chi_v^v$ that is primarily responsible.

The FCI's are plotted as a function of the quantum number $v'$ in Figure 1.12. The regular change of the probability distribution pattern with the value of $\gamma$ is quite apparent. In this example, $v_o = 1000 \text{ cm}^{-1}$; $\mu = 10^{-26} \text{ kg}$; $\gamma$ is approximately equal to $|\Delta R| \times 10^{-11} \text{ m}$; and $0.0 \leq \gamma \leq 4.0$, (which corresponds to a variation of $0 \text{ Å} \leq |\Delta R| \leq 0.4 \text{ Å}$.) The sensitivity of the pattern of the vibronic transition probability distribution to the equilibrium bond length difference is clearly illustrated.

The dependence of the probability distribution on the value of the ratio, $\frac{\Delta r}{r_o}$, is shown in Figure 1.13.

36
Figure 1.11 An illustration of vertical transition probability. The impact of the Franck-Condon Principle is depicted by the vertical column that traverses the vibrational functions, $\chi_{0''}$ and $\chi_{v'}$. 

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Figure 1.12 The Franck-Condon factors (unnormalized) are plotted as a function of the quantum number $\nu'$. The regular change of the probability distribution pattern with the value of $\gamma$ is quite apparent.
Figure 1.13 The dependence of the probability distribution (unnormalized) on the value of the ratio, $\frac{V_e}{V_g}$, is shown. In this case, the $\gamma$ parameter is held constant at $\gamma = 2$. 

$$\gamma = \left(\frac{4\pi c\mu V_g}{h}\right)^{1/2} \Delta R$$
1.17 Observed and Calculated Transition Probabilities

The calculated transition probability patterns must now be compared with the measured absorption spectra. The intensity distribution in the absorption spectrum is usually specified by the frequency dependence of the molar absorption coefficient. The value $a(v)$, the absorption coefficient at frequency $v$, is related to the probability of the transition $P_v$ induced by the absorption of a photon of frequency $v$ by

$$ \frac{a(v)}{v} = AP_v $$

where $A$ is a numerical constant. This relation assumes that only one transition exists at frequency $v$. This condition is not satisfied when transitions originate or terminate in a degenerate state or when a 'hot' band overlaps a standard vibronic band. In these cases, a more general relation is required and is given by

$$ \frac{a(v)}{v} = A \sum P_v $$

where $\sum P_v$ is the sum of transition probabilities for all transitions of excitation energy $\Delta E = hv$. The simpler relation in Equation 1.24 is applicable to our model and, when the transition probabilities are taken from Equation 1.19, this relation becomes

$$ \frac{a(v)}{v} = \tilde{A} |\tilde{M}|^2 S_{\alpha \beta}v $$

where $\tilde{A}$ is a proportionality constant equal to $AC$.

Two problems still complicate this issue. First, the value of the electronic transition probability $|\tilde{M}|^2$ is unknown. Quantum mechanics yields for $|\tilde{M}|^2$ the following expression:
\begin{align}
|\vec{M}|^2 &= \left| \left\langle \varphi_g(r;R_g) \bigg| \sum_{i=1}^{n} \hat{r}_i \bigg| \varphi_e(r;R_g) \right\rangle \right|^2 
\end{align}

where \( \hat{r}_i \) is the electric dipole operator and where \( \varphi_g(r;R_g) \) and \( \varphi_e(r;R_g) \) are the wave functions of the electronic ground state and excited state, as evaluated from Equation 1.10 at the ground state equilibrium geometry. However, in order to evaluate \( |\vec{M}|^2 \) with sufficient accuracy, both wave functions must be known with a precision that is accessible only for the very simplest molecules. Therefore, we can either treat the total transition probability as another semiempirical parameter which must be estimated from experimental spectra or, since we are only interested in the distribution of vibronic intensity within the electronic absorption band, and not in the absolute intensity of this band, we can view this parameter as totally unimportant to our efforts.

The second complication arises from the fact that the model provides values of absorption coefficients only for the resonance frequencies, \( \nu \nu^* \), of vibronic transitions. That is, the theoretical spectrum consists of discrete lines, whereas the observed absorption spectrum contains broad bands. This discrepancy originates primarily in our complete neglect of molecular rotations. As already pointed out, every vibrational level of the molecule actually consists of a large family of densely packed rotational sublevels. Even for temperatures for which the concentration of molecules in the \( 1^\nu \)-state and the higher vibrational states is negligible, the lower portion of the rotational sublevels in the \( 0^\nu \)-state is highly populated. Consequently, every pure vibronic transition is accompanied by a large number of rovibronic transitions, each with a specific transition probability. A vibronic band with and without the accompaniment of rovibronic transitions is schematized in Figure 1.14.
Figure 1.14 The schematic of a vibronic band with (lower) and without (upper) accompanying rotational excitations.
The interest of this work resides in spectra with unresolved rotational structure, in other words, spectra that are observed when individual rovibronic bands strongly overlap. In this case, we cannot accurately estimate the experimental value of the absorption coefficient of the pure vibronic transition $a(\nu \nu')$. Fortunately, it is possible to show that the probability of a pure vibronic transition, as provided by the model in Figures 1.12-1.13, is proportional to the sum of the transition probabilities of all the rovibronic transitions associated with a given vibronic transition [9].

Therefore, Equation 1.26 can be modified to

$$W = \frac{\beta}{A} \int dv = \tilde{A} |\tilde{M}|^2 S_{\nu-0} (1.28)$$

where $l_{\nu \nu'}$ is the sum of the rovibronic transition probabilities and the integration is carried over the whole vibronic band. $\tilde{A}$ is a new proportionality constant, and it depends only on the temperature. When the energies of the rotational sublevels of the $0''$-state are known, $\tilde{A}$ can be evaluated from statistical considerations. Otherwise, it must be estimated from the temperature dependence of the vibronic band shape. Thus, Equation 1.28 formulates a bridge between the discrete theoretical and continuous observed spectra. Combining Equation 1.28 with the sum rule of Equation 1.20 yields the following expression for the electronic transitions probability:

$$\left|\tilde{M}\right|^2 = \frac{1}{\tilde{A}} \sum \nu' l_{\nu \nu'} = \frac{1}{\tilde{A}} \int \frac{\beta}{\nu} dv \quad (1.29)$$

where the integration now sweeps over the entire electronic band.
1.18 Emission and Absorption of Radiation

There are generally three types of transitions of interest [5,11]: induced absorption, spontaneous emission and induced emission. We assume that the first two of these processes dominate the spectra that will be analyzed in Chapter 6.

A transition from one state to the other is accompanied by emission or absorption of radiation at frequency

\[ \nu_{\nu'\nu} = \frac{E_{\nu'} - E_{\nu}}{h} \]  \hspace{1cm} (1.13)

The probability of absorbing a quantum of energy and undergoing a transition to the upper state in unit time is

\[ B_{\nu \rightarrow \nu'} \rho(\nu_{\nu'\nu}) \]  \hspace{1cm} (1.30)

where \( B_{\nu \rightarrow \nu'} \) is the Einstein coefficient of absorption and \( \rho(\nu_{\nu'\nu}) \) is the radiation density in which the system is bathed. The probability that the upper state will undergo transition to the lower state, with corresponding emission of radiant energy, is

\[ A_{\nu \rightarrow \nu'} + B_{\nu \rightarrow \nu'} \rho(\nu_{\nu'\nu}) \]  \hspace{1cm} (1.31)

where \( A_{\nu \rightarrow \nu'} \) is Einstein's coefficient of spontaneous emission and \( B_{\nu \rightarrow \nu'} \) is Einstein's coefficient of induced emission. At equilibrium, the rates of emission and absorption are equal. Consequently,

\[ \frac{N_{\nu'}}{N_{\nu}} = \frac{A_{\nu \rightarrow \nu'} + B_{\nu \rightarrow \nu'} \rho(\nu_{\nu'\nu})}{B_{\nu \rightarrow \nu'} \rho(\nu_{\nu'\nu})} \]  \hspace{1cm} (1.32)

We now use statistical mechanics, namely

\[ \frac{N_{\nu'}}{N_{\nu}} = \mathcal{E}^{\frac{E_{\nu'} - E_{\nu}}{kT}} = \mathcal{E}^{\hbar \nu_{\nu'\nu}/kT} \]  \hspace{1cm} (1.33)

and Planck's radiation law.
The experimental emission spectra of this work are presumed to be spontaneous in nature, whereas the absorption spectra are all induced in nature. These differences will be reflected in the manner in which emission and absorption spectra are subjected to Franck-Condon analyses.

\[ p(v,v') = \frac{8\pi h^3}{c^3} \frac{1}{e^{2h\nu/k_B T} - 1} \quad (1.34) \]

to find

\[ A_{v'\rightarrow v} = \frac{8\pi h^3}{c^3} B_{v'\rightarrow v} \quad (1.35) \]

and

\[ B_{v'\rightarrow v} = B_{v'\rightarrow v} \quad (1.36) \]

The experimental emission spectra of this work are presumed to be spontaneous in nature, whereas the absorption spectra are all induced in nature. These differences will be reflected in the manner in which emission and absorption spectra are subjected to Franck-Condon analyses.
CHAPTER 2
THE THEORETICAL EQUATIONS

The purpose of this chapter is to present an equation for the Franck-Condon integral in a power series form and in terms of a parameter that, in certain cases, will permit truncation [5]. A series solution in an appropriate form has been found and is given in Equation 2.5. As far as we know, this solution is unique to this work; see, however, Appendix V. The truncation parameter that developed from the series solution is based on the ratio of the fundamental vibrational frequencies of the two electronic states involved in the electronic transition. When this ratio, \( \frac{\nu'}{\nu''} \), is close to unity, one may truncate the ratio, \( \frac{I_{\nu''}^{\nu'}}{I_{\nu''"}^{\nu''}} \) (the ratio of the two vibronic intensities) to a quadratic form in the truncation parameter, Equation 2.17, or to a simple linear form in the truncation parameter, Equation 2.19. Whether these two approximate forms, both of which are unique to this work, will have any useful applicability remains to be determined. That determination will be the subject of Chapters 3-7.

2.1 Franck-Condon Integral, FCI

The Franck-Condon integral, FCI = \( S_{\nu''}^{\nu'} \), is defined as the absolute value squared of the overlap integral between the vibrational wavefunction \( \chi_{\nu'}(R') \) of the ground state \( \nu'' \) quantum level, with equilibrium bond distance \( R'' \), and \( \chi_{\nu'}(R') \) of the excited state \( \nu' \), with equilibrium bond length \( R' \) [4]. The values of \( S_{\nu''}^{\nu'} \) specify the distribution of the total electronic intensity over the individual vibronic transitions, \( \nu' \leftrightarrow 0'' \), where \( \nu' = 0', 1', 2', 3', .... \) For the case of light absorption, the Franck-Condon integral is given by
\[ S^{2}_{\nu 0''} = \left| \int_{0}^{\infty} \chi_{\nu'}(R)\chi_{\nu''}(R')dR \right|^{2} \]  \hspace{1cm} (2.1)

or, for the case of light emission, by

\[ S^{2}_{\nu 0'} = \left| \int_{0}^{\infty} \chi_{\nu'}(R)\chi_{\nu''}(R')dR \right|^{2} \]  \hspace{1cm} (2.2)

The primary result of this work will evolve directly from the formal equation, Equations 2.1 or 2.2, where \( \Delta R = R' - R'' \), \( \Delta R_{e} = R'_{e} - R''_{e} \) and \( R \) is the integration variable.

This integral may be re-expressed for the absorption case [Appendix I] as

\[ S^{2}_{\nu 0''}(\Delta \xi; \nu', \nu'') = \left| \langle \chi_{\nu''}(\xi; \nu'')\chi_{\nu'}(\xi + \Delta \xi; \nu') \rangle \right|^{2} \]  \hspace{1cm} (2.3)

The general form of the integral (Appendix I) is

\[ S^{2}_{\nu 0''} = C_{3} \frac{1}{2\nu'!\nu''!} \left| \int_{-\infty}^{\infty} \exp(-a \xi^{2} - b \xi)H_{\nu'}(\sqrt{a \xi + b})d\xi \right|^{2} \]  \hspace{1cm} (2.4)

This latter equation was initially solved for the absorption case in which excitation occurs from the ground state vibrational level of quantum number \( 0'' \) to the levels of the excited state, \( \nu' = 0', 1', 2', 3', 4', 5', 6', \) and \( 7' \) [Appendix II,6,14,15]. The trends that were evident in the resulting equations, Appendix III, lead to the compact, exact analytical equation

\[ S^{2}_{\nu 0''} = \frac{1}{2\nu'!\nu''!} S^{2}_{\nu 0''} \left| \sum_{n=0}^{\left[ \frac{\nu'}{2} \right]} (-1)^{n} \frac{\nu'!}{n!(\nu' - 2n)!} (-\sigma + 2)^{\nu' - 2n}(-\sigma + 1)^{n} \gamma^{\nu' - 2n} \right|^{2} \]  \hspace{1cm} (2.5)

where \( \left[ \frac{\nu'}{2} \right] \) is the largest positive integer \( \leq \frac{\nu'}{2} \), and the FCI = \( f(\Delta R_{e}; \nu', \nu'') \). The parameters \( \nu' \) (or \( \nu_{\text{excited}} \) or \( \nu_{e} \)) and \( \nu'' \) (or \( \nu_{\text{ground}} \) or \( \nu_{g} \)) are excited- and ground-state frequencies, respectively, and are part of the fundamental expressions of the parameters \( a' \) and \( a'' \) that come into play in the \( \sigma \) and \( \Delta \) terms. The term \( \Delta R_{e} \).
is the change in $R_e$, and it is to be distinguished from the parameter $\Delta$. Critical definitions are

$$\gamma = \sqrt{\alpha'} |\Delta R_e| \quad \text{where} \quad \alpha' = \frac{2\alpha' \mu}{\hbar} \quad (2.6)$$

$$\sigma = \frac{\alpha}{\beta} \quad \text{where} \quad \alpha = \frac{\alpha'+\alpha''}{2} \quad (2.7)$$

and $\Delta = 1 - \beta \quad (2.8)$

$$= 1 - \frac{\alpha'}{\alpha} = 1 - \frac{\gamma}{\beta} \quad (2.9)$$

The parameters known from experiment are $\alpha'$, $\alpha''$, $\alpha$, $\Delta$, $\beta$, and sometimes $\Delta R_e$.

The various values of $\Delta R_e$ that are source- or computation-dependent will be distinguished later in Chapter 3. The significance of $\gamma$ and $\sigma$ is elaborated in Appendix I and in the subsequent development of the linear and quadratic approximations to the exact equation.

The photoelectron spectrum of the hydrogen diatomic molecule, Figure 2.1, exemplifies an absorption of energy from the lowest level of the ground state of the neutral molecule to the first ten or so levels of the ground state of the ionized molecule [16]. This spectrum is shown here only for illustrative purposes. Its analysis will be discussed in Chapter 6. The transitions

$$0' \leftarrow 0'', 1' \leftarrow 0'', 2' \leftarrow 0'', \ldots, 9' \leftarrow 0''$$

occur proceeding from left to right, with the most intense being the $2' \leftarrow 0''$ transition.

The intensity of these individual transitions, $I_{0''}$, is the experimental equivalent of $S_{0''}^2$ in the reformulated expressions for the ratio equation, Equation 2.10.

2.2 The Ratio Equation

The exact, general ratio of FCI's for neighboring vibronic transitions are used in the development of linear and quadratic approximations. The FCI's, $S_{\nu''-\nu}'$, are needed for use in the equivalent expression.
Figure 2.1 The photoelectron spectrum of the hydrogen diatomic molecule for the transition [16]

\[ \text{H}_2 : \bar{X}^2 \Sigma_g^+ (\nu' = 0, 1, 2, \ldots) \leftarrow \text{H}_2 : \bar{X}^1 \Sigma_g^+ (\nu'' = 0) \]

This spectrum is shown here only for illustrative purposes. Its analysis will be discussed in Chapter 6. The transitions

\[ 0' \leftrightarrow 0'', 1' \leftrightarrow 0'', 2' \leftrightarrow 0'', \ldots, 9' \leftrightarrow 0'' \]

occur proceeding from left to right, with the most intense, according to Lee & Rabalais [16], being the \( 2' \leftrightarrow 0'' \) transition. The small numbers at the base of each transition are the relative intensities. The excitation source was the He II transition at 40.82 eV.
or, when reformulated, for \( \frac{I_{v'} - I_{v'-1}}{I_{v'} - I_{v'-1} - S_{v'}^{2} - S_{v'-1}^{2}} = 0 \). A derivation for the ratio of the Franck-Condon overlap integrals of neighboring spectral peaks is now given:

\[
\frac{S_{v'}^{2}}{S_{v'-1}^{2}} = \frac{\frac{1}{2^{v}} \sum_{n=0}^{\frac{v}{2}} (-1)^{n} \left( \frac{\nu_{1}}{m(v-2n)} \right) (-\sigma + 2)^{v-2n}(-\sigma + 1)^{n}y^{v-2n}}{\frac{1}{2^{v'-1}} \sum_{n=0}^{\frac{v'-1}{2}} (-1)^{n} \left( \frac{\nu_{1}}{m((v-1)-2n)} \right) (-\sigma + 2)^{(v-1)-2n}(-\sigma + 1)^{n}y^{(v-1)-2n}}^{2} \tag{2.11}
\]

Since \( \frac{1}{2^{v}} \frac{S_{v'}^{2}}{S_{v'-1}^{2}} = \frac{1}{2^{v}} \), it follows that

\[
\frac{S_{v'}^{2}}{S_{v'-1}^{2}} = \left\{ \begin{array}{c}
(-1)^{0} \frac{\nu_{1}}{m(v-2n)} (-\sigma + 2)^{v-2n}(-\sigma + 1)^{0}y^{v-2n} \\
+ (-1)^{1} \frac{\nu_{1}}{m((v-1)-2n)} (-\sigma + 2)^{(v-1)-2n}(-\sigma + 1)^{1}y^{(v-1)-2n}
\end{array} \right\}^{2} + ... \tag{2.12}
\]

In order to derive working approximations of the ratio equation, certain elements of the exact results for the FCI's are re-expressed in terms of the ratio of frequencies, Equation 2.9. Now, as \( \beta = \frac{\nu'}{\nu} \to 1, \Delta \to 0 \). Therefore, if the \( \frac{S_{v'}^{2}}{S_{v'-1}^{2}} \) can be formulated as a power series in \( \Delta \), higher powers of \( \Delta \) may be neglected as \( \Delta \to 0 \).

The task now is to formulate the ratio equation as a power series in \( \Delta \). First, expand in \( \Delta \): From Equation 2.7, and since \( \frac{\nu'}{\nu} = \frac{\nu'}{\sigma} = \beta \) from Equation 2.8, we solve for \( -\sigma + 2 \), to find

50

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\[ (-\sigma + 2) = -\frac{q'}{\beta} + 2 = -\frac{2\mu'}{\alpha + \mu'} + 2 = \frac{2\mu'}{\alpha + \mu'} = \frac{2}{1+\beta} = \frac{2}{2-\Delta} = \frac{2}{2} + \frac{\Delta^2}{4} \]  

(2.13)

which possesses no truncation capability because of the presence of unity. However,

\[ (-\sigma + 1) = -\frac{q'}{\beta} + 1 = -\frac{2\mu'}{\alpha + \mu'} + 1 = -\frac{2\beta}{\beta + 1} + 1 = \frac{1-\beta}{1+\beta} = \frac{\Delta}{2-\Delta} = \frac{2}{2} + \frac{\Delta^2}{4} \]  

(2.14)

and, since the leading term in this expression is \( \Delta \), it does facilitate truncation. Thus,

truncation at various powers of \( -\sigma + 1 \) leads to the following orders in \( \Delta \)

\[ (-\sigma + 1) \Rightarrow 1st \ order \ in \ \Delta \]

\[ (-\sigma + 1)^2 \Rightarrow 2nd \ order \ in \ \Delta \]

\[ (-\sigma + 1)^3 \Rightarrow 3rd \ order \ in \ \Delta \]

etc.

To the 2nd order in \( \Delta \), one finds

\[
\left[ 1 + \Delta + \frac{3}{4} \Delta^2 \right] y^4
\]

\[
\left[ -2\nu \frac{S_{\nu}^2 \varphi}{S_{(\nu-1)\nu}^2} - \left( \frac{\nu}{\nu-2} - \frac{\nu-1}{\nu-3} \right) \Delta + \left( \frac{1}{2} \frac{\nu}{(\nu-2)} + \frac{1}{2} \frac{(\nu-1)}{(\nu-3)} \right) \Delta^2 \right] y^2
\]

\[
+ \frac{1}{4} \left[ \frac{\nu}{(\nu-4)} + \frac{\nu}{(\nu-2)} - \left( \frac{\nu-1}{\nu-5} - \frac{\nu-1}{\nu-3} \right) \left( \frac{\nu}{\nu-2} - \frac{\nu-1}{\nu-3} - \frac{\nu-1}{\nu-3} \right) \right] \Delta^2 = 0
\]

(2.15)

After much algebra and the transformation \( \gamma \) to \( \gamma' \), where \( \gamma = \sqrt{a''} \Delta R_0 \), and using

Equation 2.8 in the form

\[ (1 - \Delta) a'' = a' \]

and Equation 2.6 in the form

\[ \gamma = \sqrt{a} \Delta R_0 \]

one finds

\[ \gamma = \sqrt{(1 - \Delta) a''} \Delta R_0 \]

\[ \gamma^2 = (1 - \Delta) a'' R_0^2 = (1 - \Delta) \gamma'^2 \]

\[ \gamma^4 = (1 - \Delta)^2 a''' R_0^4 = (1 - \Delta)^2 \gamma'^4 \]

(2.16)
The final outcome for the absorption case is

\[ \gamma^4 - \frac{2v}{1-v^2} \left[ \frac{s_{H_1}^2 \sigma_{v''}}{s_{H_1}^2 \sigma_{v''-1 \Delta}} + \frac{(v'-1)}{v} \Delta + \frac{1}{2} \frac{(v'-1)}{v} \Delta^2 \right] \gamma^2 - (v'-1)(v'-3)\Delta^2 = 0 \]

(2.17)

This result is a quadratic in \( \Delta R^2 \) that is easily solvable for \( \Delta R \) of the term

\[ \gamma = \sqrt{a'} \Delta R', \]

where the coefficients of the quadratic equation are

\[ a = 1, \]
\[ b = -\frac{2v}{1-v^2} \left[ \frac{s_{H_1}^2 \sigma_{v''}}{s_{H_1}^2 \sigma_{v''-1 \Delta}} + \frac{(v'-1)}{v} \Delta + \frac{1}{2} \frac{(v'-1)}{v} \Delta^2 \right] \]

and

\[ c = -(v'-1)(v'-3)\Delta^2 \]

(2.18)

The linear case is obtained by truncation of all powers of \( \Delta \) greater than 1:

\[ \gamma^2 - 2v' \left[ \frac{s_{H_1}^2 \sigma_{v''}}{s_{H_1}^2 \sigma_{v''-1 \Delta}} + \frac{(v'-1)}{v} \Delta \right] = 0 \]

(2.19)

The linear approximation to \( \Delta R^2 \) may be solved by linear least-squares regression analysis, using Equation 2.10:

\[ \frac{I_{v''} \sigma_{v'}}{I_{v''-1 \Delta}} = \left[ (\Delta R)^2 - \frac{\Delta}{2} \right] \frac{1}{v' - \Delta_L} \]

(2.20)

where each \( I \) is an experimental intensity and \( \Delta_L \) is the linear (L) least-squares value of \( \Delta \). One merely solves for

\[ \Delta R = \left( (m - \Delta_L) \frac{2}{e^2} \right)^{\frac{1}{3}} \]

(2.21)

where \( m \) is the slope. It is important to emphasize that one finds \( \Delta R^2 \) and not \( \Delta R \); thus, the sign of \( \Delta R \) remains ambiguous.

Task 3 is the test of these theoretical results by comparison to both exact theoretical and good experimental spectra. As indicated, \( \Delta R \) has often been determined from absorption, emission, or PES spectra, but the accuracy of the
approach has never been tested in any general way. The present strategy may well provide both that test and, in addition, generate a very simple method of estimating $\Delta R_e$.

Many works pertaining to the Franck-Condon integrals that are of interest in this dissertation have appeared in the literature. The most trenchant we discovered were authored by Ballhausen [4], Schleich and Wheeler [17], and Wagner [18]. These works, their relationship to each other and to this dissertation are discussed in Appendix V.
CHAPTER 3

THE THEORETICAL SPECTRA: PRELIMINARIES

The purpose of this chapter is to introduce the concepts and define the terminology that will be used in succeeding chapters. No specific analyses will be presented in this chapter. However, while concepts proceeding from such analyses, ones found to be generally useful, will be presented here, they will not be justified at this point. It is well to remember that the theoretical expression of Equation 2.5 for the Franck-Condon integral(s), may be used in both exact and approximate ways. However, regardless of how used, the aim is to obtain values of $\Delta R_e$ in which one can have a high degree of trust.

Equation 2.5 is used to generate maps of vibronic intensities as a function of $\Delta R_e$. Such maps are shown in Figure 3.1, one map for each selected value of $\Delta$. These maps are referred to as "Franck-Condon Integral Maps", FCIM's. An FCIM is a plot of the FCI's for a group of vibronic transitions for a particular value of $\Delta$ over the entire range of $\Delta R_e$. Details of the regions marked by an ellipse on these maps are shown in Figures 3.2, 3.3, 3.4 and 3.5. The elliptical figure encloses that region of $\Delta R_e$ that incorporates (vide infra) $\Delta R_e L$, $\Delta R_e q$, $\Delta R_e_{CFW}$, and $\Delta R_e_{Best FR}$.

A vertical line on any one of the maps of Figures 3.1-3.5 selects a particular vibronic spectrum, one determined by specific values for both $\Delta$ and $\Delta R_e$. Such a particular value of $\Delta R_e$ is referred to as $\Delta R_e E$, where the subscript $E$ indicates "exact." Examples of such theoretical spectra are shown in Figure 3.6 (a, b and c). These spectra are then subjected to analyses by Equations 2.10, 2.17 and 2.19 in order to find the degree to which the values of $\Delta R_e$ calculated from them correspond...
Figure 3.1 The Franck-Condon Integral Maps, FCIM's, FCI versus $\Delta R_e$, where $-\infty < \Delta R_e < \infty$, for $\Delta = 0.1$, 0.2, 0.3, 0.4, 0.5 and 0.6 and for the FCI's denoted on the right side of Figure 3.1 (f). The ellipses demark the Franck-Condon region, FCR. The FCR encloses all the values $\Delta R_e$, $\Delta R_e$, $\Delta R_e$ $C_{FCW}$, and $\Delta R_e$ $BestFitt$. 

55
Figure 3.2 A close-up of the regions marked by ellipses in Fig. 3.1(b, d and f). As indicated in the caption for Figure 3.1, these are the Franck-Condon regions. The FCR encloses all $\Delta R_e$ that are relevant to the discussion.
Figure 3.3 The Franck-Condon region (FCR) in Figure 3.2(a) on which are marked all values of $\Delta R_0$ that are relevant to the discussion. The gross intensity pattern defining the Franck-Condon window (FCW) is

$$S^2_{30''} > S^2_{20''} > S^2_{40''} > S^2_{10''} > S^2_{50''} > S^2_{60''} > S^2_{00''} > S^2_{70''} > S^2_{80''}$$

Its limits are determined by the circled crossings (see Legend at right):

$$0' \leftarrow 0'' \text{ and } 6' \leftarrow 0''$$
$$5' \leftarrow 0'' \text{ and } 1' \leftarrow 0''$$

The following values of $\Delta R_0$ are labeled
1. FCR low extremum = FCW low extremum:
$$\Delta R_0 = 1.948 \times 10^{-11} \text{ m}$$
2. FCW center: $\Delta R_{0, FCW} = 1.987 \times 10^{-11} \text{ m}$
3. Quadratic approximation: $\Delta R_{0, Q} = 1.991 \times 10^{-11} \text{ m}$
4. Exact value: $\Delta R_{0, E} = 2.000 \times 10^{-11} \text{ m}$
5. FCW high extremum: $\Delta R_0 = 2.030 \times 10^{-11} \text{ m}$
6. FCR high extremum = $\Delta R_0$ of the Linear approximation:
$$\Delta R_{0, L} = 2.108 \times 10^{-11} \text{ m}$$

The width of the FCW is $8.20 \times 10^{-13} \text{ m}$ or 0.008 Å.
The width of the FCR is $1.597 \times 10^{-12} \text{ m}$ or 0.016 Å.
Figure 3.4 The Franck-Condon region (FCR) in Figure 3.2(b) on which are marked all values of $\Delta R_\sigma$ that are relevant to the discussion. The gross intensity pattern defining the Franck-Condon window (FCW) is

$$S_{2'0''} > S_{3'0''} > S_{1'0''} > S_{4'0''} > S_{5'0''} > S_{6'0''} > S_{5'0''}$$

Its limits are determined by the circled crossings (see Legend at right):

1. $1' \leftarrow 0''$ and $3' \leftarrow 0''$
2. $5' \leftarrow 0''$ and $0' \leftarrow 0''$

The following values of $\Delta R_\sigma$ are labeled

1. FCR low extremum = FCW low extremum:
   $$\Delta R_\sigma = 1.880 \times 10^{-11} \text{ m}$$
2. Quadratic Approximation: $\Delta R_{\sigma Q} = 1.9402 \times 10^{-11} \text{ m}$
3. FCW center: $\Delta R_{\sigma C FCW} = 1.963 \times 10^{-11} \text{ m}$
4. Exact value: $\Delta R_{\sigma E} = 2.000 \times 10^{-11} \text{ m}$
5. FCW high extremum: $\Delta R_\sigma = 2.045 \times 10^{-11} \text{ m}$
6. FCR high extremum = $\Delta R_{\sigma L}$ of the Linear approximation:
   $$\Delta R_{\sigma L} = 2.216 \times 10^{-11} \text{ m}$$

The width of the FCW is $1.65 \times 10^{-12} \text{ m}$ or 0.017 Å.
The width of the FCR is $3.36 \times 10^{-12} \text{ m}$ or 0.034 Å.
Figure 3.5 The Franck-Condon region (FCR) in Figure 3.2(c) on which are marked all values of $\Delta R_e$ that are relevant to the discussion. The gross intensity pattern defining the Franck-Condon window (FCW) is

$$S_{20''}^2 > S_{110''}^2 > S_{30''}^2 > S_{020''}^2 > S_{410''}^2$$

Its limits are determined by the circled crossings (see Legend at right):

- $2' \leftarrow 0''$ and $1' \leftarrow 0''$
- $0' \leftarrow 0''$ and $4' \leftarrow 0''$

The following values of $\Delta R_e$ are labeled:

1. FCR low extremum = FCW low extremum:
   $$\Delta R_e = 1.895 \times 10^{-11} \text{ m}$$

2. Quadratic Approximation: $\Delta R_e Q = 1.906 \times 10^{-11} \text{ m}$

3. Exact value: $\Delta R_e E = 2.000 \times 10^{-11} \text{ m}$

4. FCW center: $\Delta R_e C_{FCW} = 2.0375 \times 10^{-11} \text{ m}$

5. FCW high extremum: $\Delta R_e = 2.180 \times 10^{-11} \text{ m}$

6. FCR high extremum = $\Delta R_e$ of the Linear approximation:
   $$\Delta R_{eL} = 2.211 \times 10^{-11} \text{ m}$$

The width of the FCW is $2.85 \times 10^{-12} \text{ m}$ or $0.029 \text{ Å}$.
The width of the FCR is $3.16 \times 10^{-12} \text{ m}$ or $0.032 \text{ Å}$. 

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Figure 3.6  Theoretical vibronic spectra (unnormalized) extracted from Figure 3.1 for the cited values of $\Delta R_e$. 

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to $\Delta R_{E}$, in other words, to ascertain the degree of trust one can invest in the analytical apparatus.

The calculated values of $\Delta R_{e}$ that will be considered are:

1. $\Delta R_{e, \text{Best Fit}}$: This value is the test for fitness of Equation 2.10.
2. $\Delta R_{e, \text{AR}}$: The value calculated using the quadratic approximation of Equation 2.17.
3. $\Delta R_{e, \text{AR}}'$: The value calculated using the linear approximation of Equation 2.19.
4. $\Delta R_{e, \text{FCW}}$: The range of $\Delta R_{e}$ values, as calculated from the FCI intensity distribution that matches the gross intensity pattern for $\Delta R_{e, E}$. The value at the center of the FCW is denoted $\Delta R_{e, FCW}$.

Further discussion of item 4 above is required. It became evident during the course of these studies that very precise intensity distributions were not a prerequisite for the determination of good values of $\Delta R_{e}$. In fact, it was found that gross intensity patterns sufficed to calculate $\Delta R_{e}$ to within 0.01 Å in the great majority of instances. A "gross intensity pattern" is defined as a simple non-numerical statement about the relative intensities of the vibronic bands: for example, in the absorption transition set, $\nu' \leftarrow 0''$, where the intensity is given as $I_{\nu''}$, a gross intensity pattern might be

$$I_{3''''} > I_{2''''} > I_{1''''} > I_{0''''} > I_{1'''} > I_{0''} > I_{0''} > I_{1''} > I_{0''}$$

which happens to be the case for the FCI shown in Figure 3.6(a). This is an important observation (i) because it permits one to eschew lengthy fitting procedures and (ii) because it coheres with the fact that exact experimental vibronic intensity
distributions are not commonplace in the literature. Indeed, the older literature is largely based on the use of spectrographic instruments, and the quality of the photographic intensity data does not usually surpass that of the gross intensity pattern defined here. This has led us to define the concept of a Franck-Condon window, \( FCW \), namely the range of \( \Delta R_e \) that an FCIM associates with a specific gross-intensity pattern, say that of Equation 3.1.

The range of \( \Delta R_e \) encompassed by all of \( \Delta R_e L, \Delta R_e Q, \Delta R_e E \) and \( \Delta R_e FCW \) is referred to as the Franck-Condon region (FCR). Such regimes are illustrated in Figures 3.3, 3.4 and 3.5. The minimum width of the FCR is the width of the FCW.

Some other definitions are:

5. \( \Delta R_e C \) or \( \Delta R_e FCW \): The value of \( \Delta R_e \) at the midpoint of the Franck-Condon window. Thus, the FCW is more generally defined as

\[
\Delta R_e^c \geq \Delta R_e C \geq \Delta R_e^b
\]

where \( \Delta R_e C \) lies at the center of the FCW and \( \Delta R_e^c \) and \( \Delta R_e^b \) are the respective low extremal and high extremal values of \( \Delta R_e FCW \). The FCR is defined in a similar manner.

6. \( \Delta R_e R \): The value of \( \Delta R_e \) obtained by rotational analysis [19].

### 3.1 Objectives

The Franck-Condon integral, in the form of Equation 2.5, generates a map of the exact vibronic intensity distributions (e.g., Figure 3.1). In this chapter, we will compare this exact case with spectra pertinent to the FCW which includes the center of the FCW and the spectra closest to the literature rotational values, the "best fit", and spectra pertinent to the two approximations of Equations 2.17 and 2.19.
procedure will be described in Section 3.2. A fourth comparison, the most important one, is based on the juxtaposition of experiment and theory. This last comparison will be made in Chapter 6.

The procedures adopted here are:

1. In order to assess the validity of the various approximations, namely the degree to which they reproduce the exact vibronic intensity distributions, we must select spectra for specific values of $\Delta R_{\text{e}}$. Examples of such spectra for $\Delta R_{\text{e}} = 0.200 \text{ Å}$ are shown in Figure 3.6 (a, b & c).

2. In order to assess the accuracy of the various $\Delta R_{\text{e}}$ values, as calculated by the various approximation methods (Equation 2.17 for the quadratic approximation which yields $\Delta R_{\text{e}q}$ and Equation 2.19 for the linear approximation which yields $\Delta R_{\text{el}}$), the spectra for those values of $\Delta R_{\text{e}}$ are extracted and compared with that for $\Delta R_{\text{e}E}$. (The linear approximation regression analyses also provide computed values for $\Delta_{L}$; these will be compared with the actual input values of $\Delta_{E}$.)

3. The manner in which the above correlation procedures for $\Delta R_{\text{e}E}$, $\Delta R_{\text{el}}$ and $\Delta R_{\text{e}q}$ are carried out is prelude to a study of the "experimental" value of $\Delta R_{\text{e}}$, namely $\Delta R_{\text{e}\exp}$, to be described in Chapter 6.

4. A natural outcome of the correlation objective is the concept of the Franck-Condon window, $\text{FCW}$. That, in turn, induces another critical spectrum, that for $\Delta R_{\text{e}C}$, where $\Delta R_{\text{e}C}$ is the value of $\Delta R_{\text{e}}$ at the midpoint of the $\text{FCW}$. 

63
5. The error-handling and validity of all these procedures will be discussed in Chapter 4.

An analogous study, one based on this chapter, will also be concerned with theoretical intensity distributions; this study, elaborated in Chapter 5, will examine trends (broad, common occurrences in the exact intensity plots), patterns (systematic arrangements of the intensity distributions) and/or motifs (repeating, particular elements of regularity) that may be used to make broad qualitative statements about $\Delta R_e$ from direct visual inspection of vibronic intensity patterns. Chapter 5 will be concerned with the situation in which $\Delta R_eE$ is varied and $\Delta$ is constant, in contrast to the situation in this chapter in which $\Delta$ is varied and $\Delta R_eE$ is held constant.

3.2 The Model

The generation of the vibronic intensity distribution map requires (1) the specification of the two force constants $k'$ and $k''$ (or, equivalently, the vibrational frequencies and the reduced mass) and (2) the sets of vibrational quantum numbers $\{v'\}$ for the case of absorption or $\{v''\}$ for the case of emission. The force constants generate the $\sigma$ and $\Delta$ parameters that are used for the mapping and the approximation equations, respectively.

The operative Franck-Condon integral, Equation 2.5, is

$$S_{v'0''} = \frac{1}{2v'!} S_{00'}^2 \left| \sum_{n=0}^{\infty} (-1)^{n} \frac{v'_{n}}{m(v'_{n} - 2n)} (-\sigma + 2)v'_{n} - 2n (-\sigma + 1) n v'_{n} - 2n \right|^2 \tag{2.5}$$

This equation produces the intensity maps, FCIM's. The $\sigma$-parameter is the critical component of the exact mapping because it permits the summation representation of Equation 2.5. The replacement of $\sigma$ by $\Delta$ makes possible the approximations of Equations 2.13 and 2.14. Once the map of the exact vibronic intensity distributions is

64
generated, the emphasis is then shifted to $\Delta$ because of its more direct relation to the molecular characteristics, as provided by the quadratic approximation

$$y^4 - \frac{2y}{1-\Delta^2} \left[ \frac{S_{v'}^{2} g'}{S_{v'-1}^{2} g'} + \frac{(v'-1)}{v} \Delta + \frac{1}{2} \frac{(v'-1)}{v^2} \Delta^2 \right] y^2 - (v'-1)(v'-3) \Delta^2 = 0 \tag{2.17}$$

and the linear approximation

$$y^2 - 2y \left[ \frac{S_{v'}^{2} g'}{S_{v'-1}^{2} g'} + \frac{(v'-1)}{v} \Delta \right] = 0 \tag{2.19}$$

The values of $\Delta$ used in this work are

$$\Delta = 0.1, 0.2, 0.3, 0.4, 0.5 \text{ and } 0.6$$

This range covers the great majority of all situations of experimental interest, as will be seen in Table 6.1. This range of $\Delta$, via Equation 2.11, corresponds to the relative frequency range: $0.9v'' < v' < 0.4v''$. The value of the vibrational frequency $v''$ that we choose is $v'' = 6.00 \times 10^3$ s$^{-1}$, which corresponds to the wavenumber of 2000 cm$^{-1}$; this value lies within the normal range of molecular vibrational wavenumbers and is used here merely for illustrative purposes. All situations for which $\Delta < 0.1$ are similar in gross detail to the result for $\Delta = 0.1$. All cases for which $\Delta > 0.6$ will usually imply unstable excited states that are of no interest in this work. The range of $v'$ that is chosen is

$$v' = 0', 1', 2', 3', 4', 5', 6', 7' \text{ and } 8'$$

This range involves the first nine FCI equations from Appendix III for each value of $\Delta$. The confinement of the study to the lower energy levels is a modest attempt to restrict attention to the bottom of the potential well. It avoids the danger that, at higher levels, the anharmonic nature of real molecular potentials will be dominant.
The emission case, $0' \rightarrow v''$, serves just as well for purposes of illustration. The fundamental tenets of emission were discussed in Section 1.18. As regards the development of the FCI's for use in the emission analysis, one simply replaces the $v' \leftrightarrow 0''$ intensities with those for $0' \rightarrow v''$. However, when comparison of FCI's with the experimental emission spectrum is required, the experimental intensities must be remediated using the factor $\bar{v}^3$ (see Equations 1.35 and 1.36). The remediation procedure is:

1. Tabulate the raw emission data
2. Divide each individual band (i.e., datum) by $\bar{v}^3$
3. Normalize the corrected set of vibronic emission bands
4. Compare the normalized spectra to the FCI's and perform linear, quadratic, FC region and FC window analyses, as one would with the absorption spectra.

It is not required that one of the combining electronic states be a ground state. Transitions between two neutral excited states, two ionic states or even a neutral and ionic state all fall within the purview of our approach.

The conceptual diatomic is chosen such that $M_1 = 6 \text{ amu}$ and $M_2 = 7 \text{ amu}$, a situation for which $\mu = 3.231 \text{ amu}$. Any other value of $\mu$ may be used with impunity. Although one might wish to link the chosen masses to a real diatomic system, namely $^6\text{Li}^7\text{Be}$, it is well to emphasize that the arbitrariness of the remaining parameters, for example the frequencies of the transitions, do not necessarily imply any correspondence to real systems. It is advisable to view our model diatomic as a totally abstract case.

The next choice requires selection of a particular value of $\Delta R_\ast$ from the complete range, $-\infty < \Delta R_\ast < \infty$, for each chosen value of $\Delta$ (see Figure 3.1). We have
chosen $\Delta R_{E} = 2.000E-11 m$ for illustrative purposes, but it is well to emphasize that this is also a common experimental value.

In review, we investigate a total of six exact spectra for six different values of $\Delta$ and one specific $\Delta R_{E}$. The spectra for $\Delta R_{E}$ are then treated as if they were "experimental" in order to investigate the approximation procedures which attempt to replicate them.

3.3 Approximations

The test of whether the approximations can regenerate the $\Delta R_{E}$ spectra is begun here. Each of three of the exact (E) spectra, generated as described above, is treated as though it were an "experimental" spectrum, Figure 3.6 (a, b and c). That is, the theoretical quantities $\frac{s_{2p\alpha}^{2}}{s_{2p-11,0}^{2}}$ for $\Delta R_{E}$ are taken to be the equivalent of $\frac{I_{2p\alpha}}{I_{2p-11,0}}$, a ratio of "experimental" intensities, Equation 2.10. This ratio is then used in the quadratic and linear equations, Equations 2.17 and 2.19, to determine $\Delta R_{Q}$ for the case of the quadratic approximation, and $\Delta R_{L}$ and $\Delta_{L}$ for the case of the linear least squares approximation for each spectrum in Figure 3.6 (d, e, f, g, h, and i).

The linear least-squares analysis is performed using

$$\frac{I_{2p\alpha}}{I_{2p-11,0}} = \left[ (\Delta R_{E})^{2} \left( \frac{s_{2p}^{2}}{2} - \Delta_{L} \right) \right]^{\frac{1}{2}} - \Delta_{L}$$

where $I = \text{exact, computed intensity from Equation 2.5.}$ One then computes

$$\Delta R_{E} = \Delta R_{E} = ((m + \Delta_{L})^{2})^{\frac{1}{2}}$$

The result of the linear regression analyses are values of $\Delta R_{E}$ and $\Delta_{L}$ for each spectrum.

In the case of the quadratic approximation of Equation 2.17, the $a$, $b$, and $c$, terms are obtained using the quadratic formula (see Equation 2.18). An average of
several results for $\Delta R_{eQ}$ is obtained. In the test case, as many as seven values for $\Delta R_{eQ}$ were obtained for the smaller values of $\Delta$ and as few as three values for larger values of $\Delta$ for reasons to be discussed in Chapters 4 and 5.

3.4 The Franck-Condon Window/Region

A natural outcome of this work has been the development of a new perspective, one indicated by the ellipses placed on Figure 3.1 and shown in close-up in Figure 3.2. These elliptical areas on the FCI map denote the boundaries along the abscissae that enclose the values of $\Delta R_e$ for the exact spectrum, $\Delta R_{eE} = 0.200 \text{ Å}$, $\Delta R_{eL}$ for the linear regression analysis, $\Delta R_{eQ}$ for the quadratic processing, and the Franck-Condon Window, the FCW. This inclusive region is termed the Franck-Condon Region, the FCR. The significance of this region relative to experiment will be developed in Chapter 6. The boundaries and widths of the FCW's and FCR's are indicated in Figures 3.3, 3.4 and 3.5 and given in Tables 3.1 and 3.2, respectively.

3.5 Synopsis

The Franck-Condon regions, FCR's, inscribed by the ellipses, were a natural outcome of this work. The FCR and FCW are direct links between the linear approximation, the quadratic approximation, the exact theoretical spectrum and the specific experimental results (to be discussed in Chapter 6). The FCR encloses all spectra of interest, including those that may lie far outside the observed pattern of the spectrum for $\Delta R_{eE}$. The FCW is the range in which the gross non-numerical pattern based on $\Delta R_{eE}$ is replicated. The minimum range of FCR is the FCW. Generally, for small $\Delta$ and small $\Delta R_e$, the window and the region will approximate each other to second order, that is, to within $1E-13$ meters. Error analysis is discussed in Chapter 4.
Table 3.1 The Franck-Condon windows, FCW's, of the examples discussed in Chapter 3 and shown in Figures 3.3, 3.4 and 3.5.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta R_{e}^{A}$ x 10^{-10} m</th>
<th>$\Delta R_{e}^{A}_{FCW}$ x 10^{-10} m</th>
<th>$\Delta R_{e}^{B}_{FCW}$ x 10^{-10} m</th>
<th>$\Delta(\Delta R_{e}^{B}_{FCW})^{*}$ x 10^{-10} m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.2000</td>
<td>0.1948</td>
<td>0.2030</td>
<td>0.0082</td>
</tr>
<tr>
<td>0.4</td>
<td>0.2000</td>
<td>0.1880</td>
<td>0.2045</td>
<td>0.0165</td>
</tr>
<tr>
<td>0.6</td>
<td>0.2000</td>
<td>0.1895</td>
<td>0.2180</td>
<td>0.0285</td>
</tr>
</tbody>
</table>

* width of FCW

Table 3.2 The Franck-Condon regions, FCR's, of the examples discussed in Chapter 3 and shown in Figures 3.3, 3.4 and 3.5.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta R_{e}^{A}$ x 10^{-10} m</th>
<th>$\Delta R_{e}^{A}_{FCR}$ x 10^{-10} m</th>
<th>$\Delta R_{e}^{B}_{FCR}$ x 10^{-10} m</th>
<th>$\Delta(\Delta R_{e}^{B}_{FCR})^{**}$ x 10^{-10} m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.2000</td>
<td>0.1948</td>
<td>0.2108</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.4</td>
<td>0.2000</td>
<td>0.1880</td>
<td>0.2216</td>
<td>0.0336</td>
</tr>
<tr>
<td>0.6</td>
<td>0.2000</td>
<td>0.1895</td>
<td>0.2211</td>
<td>0.0316</td>
</tr>
</tbody>
</table>

** width of FCR

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CHAPTER 4
THE THEORETICAL SPECTRA: LIMITATIONS AND ACCURACY

The limitations, ranges of validity, and degrees of confidence implicit in the analysis that was outlined in Chapter 3 will be discussed here. Conclusions are also specified for both the exact and approximate analyses.

Four major types (or measures) of uncertainty occur:

(1) Each Franck-Condon window has a finite width. That width is considered to be the uncertainty associated with $\Delta R_{e,FCW}$.

(2) Unexpected ratios or outliers occur infrequently in the relative-intensity ratios. When these occur, they render the data sets containing them inappropriate for either the linear or quadratic analyses. Such data sets occur more frequently at higher values of $\Delta$ and small $\Delta R_e$. They are readily detected.

(3) Alternating intensities, obvious in the FCI plots but less so in the extracted spectra, also occur; these, clearly, are also inappropriate for either the linear or quadratic analyses.

(4) The Franck-Condon region also has a finite width. Since the FCR spans the $FCW, \Delta R_{e,R}, \Delta R_{e,L}$ and $\Delta R_{e,Q}$, it provides a good measure of the degree of concurrence of different evaluations of $\Delta R_e$.

4.1 Objectives

It is easier to proceed if we first present a brief synopsis of our conclusions and restrictions. These are:

• For any value of $\Delta$, application of the exact FCI is valid. We will discuss the region $0 \leq \Delta \leq 0.6$ because this range of $\Delta$ covers the full range of experiment.
• For $|\Delta| \leq 0.2$, both the linear and quadratic methods are applicable.

• For $|\Delta| \leq 0.4$, the quadratic method is applicable.

• The FCW approach, which is solely based on the pattern of intensities, is valid in the entire range of $\Delta$, $0 \leq \Delta \leq 0.6$.

The restrictions are:

• For $v'$ (vibrational quantum number) too large and/or $v'$ (vibrational frequency) too large, anharmonicity may come into play. Since our analysis is based on the harmonic oscillator, care must be exercised at large $v'$ and/or large $v'$.

• A minimum of 3 FCI ratios, $R_{v''}^{v'}$, or 4 individual band intensities, $I_{v''}^{v'}$, are required for the analysis that leads to $\Delta R_L$ and $\Delta L$.

• The minimum number of bands required for the quadratic analysis is somewhat arbitrary since one may extract a value of $\Delta R_{\text{FCW}}$ from just one intensity ratio. However, the validity of a single ratio must be questioned since it is chosen from a field of ratios many of which may be atypical. Confidence in the results of the quadratic method, therefore, requires that several values of $\Delta R_{\text{FCW}}$ be available and that these be subjected to error analysis.

4.2 The Franck-Condon Window (FCW)

The concept of the Franck-Condon window is totally vested in the gross pattern of intensities of the vibronic bands. It is essentially non-numerical insofar as the intensities are concerned. This concept was discussed extensively in Chapter 3 and will be explored further in Chapter 6, when the focus will be on experiment.

The results of an analysis of the situation $\Delta R_{E} = 0.2000 \times 10^{-10} m$ and $0.0 \leq \Delta \leq 0.6$ are shown in Table 4.1. The agreement of $\Delta R_{E}$ and $\Delta R_{\text{FCW}}$ is good to three significant figures (to thousandths of an Angstrom) in most cases and,
Table 4.1 Analysis of the FCW (Franck-Condon window).

<table>
<thead>
<tr>
<th>$\Delta$</th>
<th>$\Delta R_{FE}$ x $10^{-10}$ m</th>
<th>$\Delta R_{CFCW}$ x $10^{-10}$ m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.2000</td>
<td>0.1989±0.0041</td>
</tr>
<tr>
<td>0.4</td>
<td>0.2000</td>
<td>0.1963±0.0083</td>
</tr>
<tr>
<td>0.6</td>
<td>0.2000</td>
<td>0.2038±0.0143</td>
</tr>
</tbody>
</table>

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at worst, is off by $\sim 2\%$. This is an impressive result because it suggests that qualitatively correct experimental data should suffice for the determination of trustworthy values of $\Delta R_e$. The uncertainty associated with $\Delta R_{e,FCW}$, also shown in Table 4.1, indicates that in most cases it is in the range $10^{-3}$ Å and in the worst case 0.0143 Å. Again, this is an impressive result.

A plot of $\Delta R_{e,FCW}$ is shown in Figure 4.1, as well as the fitted upper and lower extrema in $\Delta R_e$ of the window itself. It seems clear that the FCW concept is an excellent approximation, essentially valid well within $\pm 0.01$ Angstroms. We take this to be one of the major findings of this work. It is particularly important because the primary data source for diatomic vibronic intensities lies in the older, pre-1930 literature, prior to the advent of precise spectrometric intensity measurements. Consequently, the FCW concept permits one to access those data in a meaningful and important way.

4.3 The Linear Approximation

We will now subject the relative intensity ratios to the linear analysis. We will consider the cases $\Delta R_e = 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6 Å and $\Delta = 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6. We will apply, as appropriate, the Q-test for deletion of untenable or outlier ratios. The objective is to determine the range of $\Delta R_e$ over which the linear approximation is trustworthy.

The study involves the same exact spectral sets for the transitions $0' \leftrightarrow 0'', 1' \leftrightarrow 0'', 2' \leftrightarrow 0'', ..., 8' \leftrightarrow 0''$ that were discussed in the previous chapter. Each exact set is based on one of the particular maps, FCIM, for $\Delta = 0.1, 0.2, 0.3, 0.4, 0.5$ or 0.6 that were shown in Figure 3.1. One then extracts spectra for the values $\Delta R_{e,E} = (0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6) $\times 10^{-10}$ m from each of these maps. The
Figure 4.1 Analysis of the FCW (Franck-Condon window). The legend is:

- center of the Franck-Condon window
- fitted high extremum of the Franck-Condon window
- fitted low extremum of the Franck-Condon window

The exact value is $\Delta R_{*E} = 0.2 \times 10^{-10}$ m.
analyses of three of these six sets of exact spectra, namely the cases $\Delta E = 0.2, 0.4,$ and $0.6$ for $\Delta R_{eE} = 0.2000 \times 10^{-10} \text{m}$, were broached in Chapter 3. However, in this chapter, the error analyses are given for all six cases, a total of 36 spectra. This analysis is given in Table 4.2 and Figures 4.2 and 4.3. The exact spectral sets were subjected to the linear analysis in order to determine the relevant values for $\Delta R_e$ and $\Delta$: These are denoted $\Delta R_{eL}$ and $\Delta_L$. The values for $\Delta$, $\Delta_L$, $\Delta R_{eE}$, and $\Delta R_{eL}$, are listed in Table 4.2. A comparison of the exact and calculated values of $\Delta R_e$ is given in Figure 4.2. A comparison of the exact and calculated values of $\Delta$ is given in Figure 4.3.

4.3.1 Analytical Details of the Linear Approximation

One requires a minimum of 3 sequential ratios for linear analysis. These ratios should exhibit smoothness to a reasonable statistical degree where $0.95 \leq R_{\text{stat}}^2 \leq 1.00$. The $R_{\text{stat}}^2$-statistical parameter (or correlation coefficient) is an indicator of fit of the intensity ratios to a linear least-squares line: it specifies the correlation of the dependent, $\Delta R_{eL}$ and independent $\Delta R_{eE}$ variables. The range of $R_{\text{stat}}^2$ is $0 \leq R_{\text{stat}}^2 \leq 1$. The range of acceptability used here is $0.95 \leq R_{\text{stat}}^2 \leq 1.00$.

An example of the application of the linear approximation method, using Equation 2.19 for the case $\Delta R_{eE} = 0.2000 \times 10^{-10} \text{m}$ and $\Delta = 0.2$, will now be detailed. The exact intensity ratios, as well as those calculated using the value $\Delta R_{eL}$ obtained from the linear least-squares analysis, are given in Table 4.3. The exact values of the intensity ratios are plotted versus $\frac{1}{\nu}$ in Figure 4.4 and the slope and intercept are extracted. These, in turn, are used to determine the values of $\Delta_L$ and $\Delta R_{eL}$, the latter of which is then used to extract a new set of vibronic intensities from.
Table 4.2 A comparison of the exact values of $\Delta$ and $\Delta R_e$ with the corresponding values extracted by the linear and quadratic approximations.

<table>
<thead>
<tr>
<th>$\Delta$</th>
<th>$\Delta_L$</th>
<th>$\Delta R_{eE}$</th>
<th>$\Delta R_{eL}$</th>
<th>$\Delta R_{eQ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1000</td>
<td>0.1181</td>
<td>0.1000</td>
<td>0.1118</td>
<td>0.1000</td>
</tr>
<tr>
<td>0.1058</td>
<td>0.1076</td>
<td>0.2000</td>
<td>0.2053</td>
<td>0.1999</td>
</tr>
<tr>
<td>0.1056</td>
<td>0.1062</td>
<td>0.3000</td>
<td>0.3033</td>
<td>0.2999</td>
</tr>
<tr>
<td>0.1055</td>
<td>0.1058</td>
<td>0.4000</td>
<td>0.4022</td>
<td>0.3999</td>
</tr>
<tr>
<td>0.1076</td>
<td>0.1062</td>
<td>0.5000</td>
<td>0.5015</td>
<td>0.4999</td>
</tr>
<tr>
<td>0.2000</td>
<td>0.2275</td>
<td>0.1000</td>
<td>0.1211</td>
<td>0.1002</td>
</tr>
<tr>
<td>0.2238</td>
<td>0.2288</td>
<td>0.2000</td>
<td>0.2108</td>
<td>0.1991</td>
</tr>
<tr>
<td>0.2247</td>
<td>0.2268</td>
<td>0.3000</td>
<td>0.3060</td>
<td>0.2994</td>
</tr>
<tr>
<td>0.2238</td>
<td>0.2268</td>
<td>0.4000</td>
<td>0.4034</td>
<td>0.3994</td>
</tr>
<tr>
<td>0.2233</td>
<td>0.2238</td>
<td>0.5000</td>
<td>0.5016</td>
<td>0.4993</td>
</tr>
<tr>
<td>0.3000</td>
<td>0.3186</td>
<td>0.1000</td>
<td>0.1278</td>
<td>0.1021</td>
</tr>
<tr>
<td>0.3557</td>
<td>0.3570</td>
<td>0.2000</td>
<td>0.2168</td>
<td>0.1985</td>
</tr>
<tr>
<td>0.4000</td>
<td>0.4271</td>
<td>0.3000</td>
<td>0.3080</td>
<td>0.2978</td>
</tr>
<tr>
<td>0.5142</td>
<td>0.5265</td>
<td>0.4000</td>
<td>0.4034</td>
<td>0.3977</td>
</tr>
<tr>
<td>0.5087</td>
<td>0.5142</td>
<td>0.5000</td>
<td>0.4950</td>
<td>0.4932</td>
</tr>
<tr>
<td>0.2233</td>
<td>0.5087</td>
<td>0.6000</td>
<td>0.6002</td>
<td>0.5922</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.4357</td>
<td>0.1000</td>
<td>0.1352</td>
<td>0.1058</td>
</tr>
<tr>
<td>0.6779</td>
<td>0.6835</td>
<td>0.2000</td>
<td>0.2228</td>
<td>0.1934</td>
</tr>
<tr>
<td>0.6835</td>
<td>0.6950</td>
<td>0.3000</td>
<td>0.3089</td>
<td>0.2865</td>
</tr>
<tr>
<td>0.6779</td>
<td>0.6835</td>
<td>0.4000</td>
<td>0.3980</td>
<td>0.3866</td>
</tr>
<tr>
<td>0.6000</td>
<td>0.1000</td>
<td>0.5000</td>
<td>0.4884</td>
<td>0.4848</td>
</tr>
<tr>
<td>0.6000</td>
<td>0.1000</td>
<td>0.6000</td>
<td>0.5781</td>
<td>0.5863</td>
</tr>
<tr>
<td>0.6891</td>
<td>0.8891</td>
<td>0.1000</td>
<td>0.2280</td>
<td>0.0968</td>
</tr>
<tr>
<td>0.8781</td>
<td>0.9128</td>
<td>0.2000</td>
<td>0.2211</td>
<td>0.1906</td>
</tr>
<tr>
<td>0.9383</td>
<td>0.9128</td>
<td>0.3000</td>
<td>0.3058</td>
<td>0.2751</td>
</tr>
<tr>
<td>0.9128</td>
<td>0.9383</td>
<td>0.4000</td>
<td>0.3872</td>
<td>0.3725</td>
</tr>
<tr>
<td>0.8891</td>
<td>0.9128</td>
<td>0.5000</td>
<td>0.4720</td>
<td>0.4693</td>
</tr>
<tr>
<td>0.8781</td>
<td>0.8891</td>
<td>0.6000</td>
<td>0.5588</td>
<td>0.5651</td>
</tr>
</tbody>
</table>
Figure 4.2 Graphs of $\Delta R_{e L}$ and $\Delta R_{e Q}$ versus $\Delta R_{e E}$. The cases represented are listed in Table 4.2. The values of $\Delta R_{e L}$, represented by a blue square, and $\Delta R_{e Q}$, represented by a red circle, are plotted along the vertical axis. The red line lies at 45° to the x-axis.
Figure 4.3 The plot of the $\Delta L$ versus $\Delta E$. The cases represented are given in Table 4.2. The center blue line lies at $45^\circ$ angle to the $\Delta$-axis. The symbols represent the following separations:

- $\Delta R_{eE} = 0.1\,\text{Å}$, yellow triangle
- $\Delta R_{eE} = 0.2\,\text{Å}$, red triangle
- $\Delta R_{eE} = 0.3\,\text{Å}$, blue diamond
- $\Delta R_{eE} = 0.4\,\text{Å}$, red star
- $\Delta R_{eE} = 0.5\,\text{Å}$, green square
- $\Delta R_{eE} = 0.6\,\text{Å}$, asterisk
Table 4.3  The exact set of intensity ratios, \( \frac{I_{v'}}{I_{v'-10^{\gamma}}},\text{Exact} \), calculated from Equation 2.5 using the exact parameters

\[
\Delta E = 0.2 \\
\Delta R_{eE} = 0.2 \times 10^{-10} \text{ m}
\]

for \( v' = 0, 1, 2, 3, 4, 5, 6, 7 \) and \( 8 \) are compared with those obtained using the value \( \Delta R_{eL} \), obtained by Equation 2.19 for the linear least squares (LLS) analysis. The LLS analysis, using Equations 2.20 and 2.21, yields

\[
\Delta L = 0.2341 \\
\Delta R_{eL} = 0.2108 \times 10^{-10} \text{ m}
\]

The \( \frac{1}{v} \) term is the required x-axis parameter and \( \frac{I_{v'}}{I_{v'-10^{\gamma}}},\text{Exact} \), is the required y-parameter for the LLS analysis of Equation 2.20.

<table>
<thead>
<tr>
<th>( \frac{1}{v} )</th>
<th>Ratio</th>
<th>( \frac{I_{v'}}{I_{v'-10^{\gamma}}},\text{Exact} )</th>
<th>( \frac{I_{v'}}{I_{v'-10^{\gamma}}},\text{LLS} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1</td>
<td>3.7857</td>
<td>3.7904</td>
<td></td>
</tr>
<tr>
<td>1/2</td>
<td>1.7834</td>
<td>1.7782</td>
<td></td>
</tr>
<tr>
<td>1/3</td>
<td>1.1139</td>
<td>1.1074</td>
<td></td>
</tr>
<tr>
<td>1/4</td>
<td>0.7773</td>
<td>0.7720</td>
<td></td>
</tr>
<tr>
<td>1/5</td>
<td>0.5737</td>
<td>0.5708</td>
<td></td>
</tr>
<tr>
<td>1/6</td>
<td>0.4361</td>
<td>0.4367</td>
<td></td>
</tr>
<tr>
<td>1/7</td>
<td>0.3382</td>
<td>0.3408</td>
<td></td>
</tr>
<tr>
<td>1/8</td>
<td>0.2569</td>
<td>0.2690</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.4. The LLS plot of $\frac{l_{oo'}}{l_{o'-o'}}$, Exact versus $\frac{1}{\sqrt{v'}}$ for the case listed in Table 4.3. The derived equation for the line, Equation 2.20, is

$$\frac{l_{oo'}}{l_{o'-o'}} = (4.0245 \pm 0.0088) \frac{1}{\sqrt{v'}} - (0.2341 \pm 0.0068)$$

for which the $R^2_{stat} = 1.0000$. The value for $\Delta R_{eL}$ is derived from the slope of this equation using Equation 2.21. The calculated value $\Delta_L = (0.2341 \pm 0.0068)$ is derived from the intercept.
the FCI map. This new set is compared with the exact set in Figure 4.5. The two sets are also compared numerically in Table 4.3. The results are impressive.

Similar processing to that illustrated above was carried out for all 36 combinations of the parameters $\Delta_E$ and $\Delta_L$ listed in Table 4.2. The results of that analysis are also listed in Table 4.2. These results led to the conclusions detailed in the previous section, Section 4.3.

It is appropriate to stress that, within the specified range of applicability of the linear approximation that we have adopted, namely, $0.00 \leq \Delta \leq 0.02$, no adjustment of any data set is required.

4.3.2 Results of the Linear Approximation

The results/conclusions are quite straightforward. If the required accuracy is $0.01 \text{Å}$ or less, Figure 4.2 suggests that the linear approximation remains more or less good up to and including $\Delta = 0.3$. However, as is shown in Figure 4.3, this accuracy for $\Delta = 0.3$ is obtained only as a result of compensation in the parameter $\Delta$. That is, the requirement for regeneration of values for $\Delta$, i.e., $\Delta_L$, indicates that deviation from $\Delta_E$ and $\Delta_L$ become unacceptable for $\Delta_E > 0.2$. If, as a result, we conclude that the range of validity of the linear approximation is $\Delta_E \leq 0.2$, we find with one exception that the approximation is good to within $5 \%$. That exception occurs when $\Delta = 0.2$ and $\Delta = 0.100 \text{Å}$, the error is $21 \%$. We conclude, therefore, that the linear approximation is excellent for $\Delta_E \leq 0.2$, but that caution should be exercised when the computed value of $\Delta$ lies near $0.100 \text{Å}$.

4.4 The Quadratic Approximation

This study involves the same 36 sets of $\{\Delta_E, \Delta_R\}$ values used for the LLS analysis. The results of the quadratic analysis are shown in the fifth column of Table
Figure 4.5 (a) The bar-plot of $\frac{I_{\Delta g^h}}{I_{\Delta g^l,0^r}}$, Exact for each ratio calculated for $\Delta_E = 0.2$ and $\Delta R_{e,E} = 0.2000 \times 10^{-10}$ m. The numerical values are listed in column 3 of Table 4.3. (b) The bar-plot of $\frac{I_{\Delta g^l}}{I_{\Delta g^l,0^r}}$, LLS for each ratio calculated for $\Delta_L = 0.2341$ and $\Delta R_{e,L} = 0.211 \times 10^{-10}$ m. The numerical values are listed in column 4 of Table 4.3.
4.2, under the heading $\Delta R_{*Q}$. The results show that the quadratic approximation yields results good to 0.01 $A$ for $\Delta \leq 0.4$, and good to 0.02 $A$ for $\Delta \leq 0.05$. Thus, the quadratic approximation is an excellent one.

Details of the analysis for $\Delta E = 0.2000$ and $\Delta R_{*E} = 0.2 \times 10^{-10} m$ are given in Table 4.4 and are illustrated by bar graphing in Figure 4.6. Details of the analysis for $\Delta E = 0.4$ and $\Delta R_{*E} = 0.2 \times 10^{-10} m$ are shown in Table 4.5 and are illustrated in Figure 4.7. This latter case is interesting because it represents a situation in which an outlier value of $\Delta R_{*Q}$ occurs. This value, shown in boldface in Table 4.5, occurs for the ratio $\frac{I_{r}^{\text{exp}}}{I_{r}^{\text{opt}}}$. Such outliers are readily detected and may be eliminated by inspection or, if one so prefers it, by statistical means. In any event, the value $\Delta R_{*Q} = 0.1940 \times 10^{-10} m$ was obtained by such an elimination; this value for $\Delta R_{*Q}$ is also the value listed in Table 4.2.

4.5 Conclusions

The primary conclusions are

1. The FCW approach provides precise and fast estimates of $\Delta R_{*}$ that are trustworthy for all values of $\Delta$ and $\Delta R_{*}$, that is for $\Delta \leq 0.6$ and $\Delta R_{*} \leq 6 \times 10^{-11} m$.

2. The linear approximation is excellent for $\Delta \leq 0.2$.

3. The quadratic approximation is excellent for $\Delta \leq 0.4$.

However, for larger values of $\Delta$ and $\nu^\prime$ some care must be exercised in detecting and eliminating outlier values of the intensity and the intensity ratios. Within the range of $\Delta \leq 0.4$, this is not a significant consideration. However, while infrequent, it can occur and for values of $\Delta > 0.4$, it can be of frequent occurrence. Consequently, it is well to devote a little time to it.
Table 4.4 The quadratic (Q) approximation, Equation 2.17, applied to the case \( \Delta E = 0.2000 \) and \( \Delta R_e = 0.2000 \times 10^{-10} \text{m} \). The values of \( \frac{I_d}{I_{d-10''}} \) Exact for this analysis are identical to those for the linear approximation, and are given in Table 4.3. The average value of \( \Delta R_e \) is

\[
\Delta R_e = 0.1991 \times 10^{-10} \text{ m}
\]

which is also the value listed in Table 4.2.

<table>
<thead>
<tr>
<th>( \frac{I_d}{I_{d-10''}} )</th>
<th>( \Delta R_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{I_{10''}}{I_{0''}} )</td>
<td>0.1998</td>
</tr>
<tr>
<td>( \frac{I_{20''}}{I_{10''}} )</td>
<td>0.1997</td>
</tr>
<tr>
<td>( \frac{I_{30''}}{I_{20''}} )</td>
<td>0.1997</td>
</tr>
<tr>
<td>( \frac{I_{40''}}{I_{30''}} )</td>
<td>0.1995</td>
</tr>
<tr>
<td>( \frac{I_{50''}}{I_{40''}} )</td>
<td>0.1993</td>
</tr>
<tr>
<td>( \frac{I_{60''}}{I_{50''}} )</td>
<td>0.1990</td>
</tr>
<tr>
<td>( \frac{I_{70''}}{I_{60''}} )</td>
<td>0.1988</td>
</tr>
<tr>
<td>( \frac{I_{80''}}{I_{70''}} )</td>
<td>0.1972</td>
</tr>
</tbody>
</table>
Figure 4.6 A plot of $\Delta R_{eq}$ from Table 4.4 for $\Delta = 0.2000$ and $\Delta R_{eq} = 0.2000 \times 10^{-10} m$ in the quadratic approximation, Equation 2.17. The graph shows the complete $\Delta R_{eq}$ set used in the averaging to obtain $\Delta R_{eq} = 0.1991 \times 10^{-10} m$. The numerical subscript is $\Delta R_{eq}$, namely $\nu'$, corresponds to $\nu'$ in the numerator of $\frac{L_{\nu'}^{\nu}}{T_{\nu' - 10^5}}$. 

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Table 4.5 The quadratic (Q) approximation for the case $\Delta = 0.4000$ and $
abla \Delta R_a = 0.2000 \times 10^{-10}$ m. The values of $\frac{l_v''}{l_v'-10''}$, Exact, for use in Equation 2.17, are identical to those given in Table 4.3. The analysis yields an average

$$\Delta R_{aQ} = 0.1940 \times 10^{-10} \text{ m}$$

One outlier, shown in boldface, occurs in this case. This value was eliminated and was not part of the averaging process.

<table>
<thead>
<tr>
<th>$\frac{l_v''}{l_v'-10''}$</th>
<th>$\Delta R_{aQ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{l_{i0''}}{l_{i00''}}$</td>
<td>0.1976</td>
</tr>
<tr>
<td>$\frac{l_{i0''}}{l_{i10''}}$</td>
<td>0.1973</td>
</tr>
<tr>
<td>$\frac{l_{i0''}}{l_{i20''}}$</td>
<td>0.1967</td>
</tr>
<tr>
<td>$\frac{l_{i0''}}{l_{i30''}}$</td>
<td>0.1955</td>
</tr>
<tr>
<td>$\frac{l_{i0''}}{l_{i40''}}$</td>
<td>0.1933</td>
</tr>
<tr>
<td>$\frac{l_{i0''}}{l_{i50''}}$</td>
<td>0.1892</td>
</tr>
<tr>
<td>$\frac{l_{i0''}}{l_{i60''}}$</td>
<td>0.1885</td>
</tr>
<tr>
<td>$\frac{l_{i0''}}{l_{i70''}}$</td>
<td>0.4928</td>
</tr>
</tbody>
</table>
Figure 4.7 A plot of $\Delta R_{e0}$ from Table 4.5 for $\Delta = 0.4000$ and $\Delta R_{eE} = 0.2000 \times 10^{-10} m$ in the quadratic approximation, Equation 2.17. The graph shows the $\Delta R_{e0}$ set used in the averaging to obtain $\Delta R_{e0} = 0.1940 \times 10^{-10} m$. The numerical subscript in $\Delta R_{e0} \nu'$, namely $\nu'$, corresponds to $\nu'$ in the numerator of $\frac{I_{\nu'}}{I_{\nu'-1\nu'}}$. 

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The case $\Delta E = 0.6$ and $\Delta R_{eE} = 0.2 \, \text{Å}$ is shown in Table 4.6. Considerable intensity alternation is evident in the last four rows of this table and these are even more strikingly depicted in Figure 4.8. Such a situation, obviously, is not amenable to the analysis by either the linear or quadratic approximations. It is, however, totally amenable to analysis by either the FCW approach or by the exact FCI analysis. This latter statement is a simple consequence of the fact that the alternation of intensities is quite a predictable phenomenon. It is also convenient that such alternations are generally expected to occur in situations that are not usually expected to be experimentally accessible. This phenomenon will be discussed in the next chapter, Chapter 5, which is concerned with intensity patterns.
Table 4.6 The case $\Delta = 0.6000$ and $\Delta R_e = 0.2000 \times 10^{-10}$ m. Note the alternation of intensity ratios in the last four rows of this table.

<table>
<thead>
<tr>
<th>$\frac{1}{v}$</th>
<th>$\frac{I_{v/10''}}{I_{v/0''}}$</th>
<th>$\frac{I_{v/10''}}{I_{v/10''}}$ Exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1</td>
<td>$l_{v/10''}/l_{v/0''}$</td>
<td>3.1290</td>
</tr>
<tr>
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<td>$l_{v/20''}/l_{v/10''}$</td>
<td>1.1653</td>
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<tr>
<td>1/3</td>
<td>$l_{v/30''}/l_{v/20''}$</td>
<td>0.4860</td>
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<tr>
<td>1/4</td>
<td>$l_{v/40''}/l_{v/30''}$</td>
<td>0.1239</td>
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<tr>
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<td>$l_{v/50''}/l_{v/40''}$</td>
<td>0.0887</td>
</tr>
<tr>
<td>1/6</td>
<td>$l_{v/60''}/l_{v/50''}$</td>
<td>4.1443</td>
</tr>
<tr>
<td>1/7</td>
<td>$l_{v/70''}/l_{v/60''}$</td>
<td>0.0265</td>
</tr>
<tr>
<td>1/8</td>
<td>$l_{v/80''}/l_{v/70''}$</td>
<td>0.4135</td>
</tr>
</tbody>
</table>

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Figure 4.8 The bar-plot of $\frac{I_{\Delta g}^\alpha}{I_{\Delta g}^\beta}$, exact for $\Delta = 0.6$ and $\Delta R_{\theta E} = 0.2 \times 10^{-10}m$. 

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The emphasis of the previous chapter concerned the expansion parameter $\Delta$ particularly the ranges of $\Delta$ within which one or the other of the two approximations, linear and quadratic, retained validity. Having established these ranges, we now focus on $|\Delta R_0|$. In specific, we wish to investigate the vibronic patterns that characterize different $|\Delta R_0|$ ranges, and query the possibility that a simple visual inspection of the pattern might permit one to make a reasonable guess about the magnitude of $|\Delta R_0|$. We will show that such is indeed the case. However, prior to engaging this question, we intend to spend a little time on the subject of emission versus absorption patterns, and the advantages that accrue to use of the former.

5.1 Emission versus Absorption

This topic was discussed in Chapter 2 and will not be elaborated here, except for the following. The two FCI's are expected to be different, illustrated in Figures 5.1 and 5.2. The origin of this difference lies in the factors:

1. The vibrational frequencies in the ground state are different from those in the excited state, the former being usually larger.
2. The value of $\beta$ for emission is the inverse of that for absorption.
3. The emission starts with the $0' \rightarrow 0''$ event and extends to lower energy. The absorption also begins with the equienergetic, but converse $0' \leftarrow 0''$ event and extends from there to higher energy. Thus, emission occurs at lower
\[ \beta = 1.2, \Delta = -0.2 \]

**ABSORPTION**

\[ \beta = 0.83, \Delta = 0.17 \]

**EMISSION**

\[ \beta = 0.8, \Delta = 0.2 \]

**ABSORPTION**

\[ \beta = 1.25, \Delta = -0.25 \]

**EMISSION**

Figure 5.1 Schematic Franck-Condon intensities illustrating differences between converse processes and inverse \( \beta \)-parameters.

Upper two spectra: Left, absorption: \( \beta = 1.2, \Delta = -0.2 \); Right, emission: \( \beta = 0.83, \Delta = 0.17 \);

Lower two spectra: Left, absorption: \( \beta = 0.8, \Delta = 0.2 \); Right, emission: \( \beta = 1.25, \Delta = -0.25 \)

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Figure 5.2 Schematic Franck-Condon intensities illustrating differences between converse processes and inverse $\beta$-parameters

Upper two spectra: Left, absorption: $\beta = 1.6$, $\Delta = -0.6$;
Right, emission: $\beta = 0.625$, $\Delta = 0.375$;

Lower two spectra: Left, absorption: $\beta = 0.4$, $\Delta = 0.6$,
Right, emission: $\beta = 2.5$, $\Delta = -1.5$
energies than absorption. In view of the fact that emission is a spontaneous event whereas absorption is stimulated, and that the relative probability of the two processes is energy dependent, this will also lead to a difference of vibronic patterns moderated by Equation 1.35.

The differences, illustrated in Figures 5.1 and 5.2, are obvious and we must underscore that these differences demonstrate the necessity of using equations specific to the individual processes.

Finally, the use of emission, from an experimental standpoint, is preferable. The reason for this lies in the density of states which is always higher at larger energies. Thus, as one traverses the excited state vibrational manifold, \( \nu' \), the chances of near-degeneracy with some other near-lying state is much larger than similar encounters that might occur as one traverses the set of ground state vibrational frequencies, \( \nu'' \). In other words, unexpected perturbations and interferences are more likely in absorption then emission; that is, emission is expected to be cleaner. An example of such an interference, one that occurs in the Schumann-Runge bands of oxygen, will be discussed in Chapter 6.

5.2 Patterns

Four major vibronic pattern sets occur for any value of \( \Delta \). These patterns may be defined by specifying the \( \Delta R_e \) intervals within which they occur. This specification is given in Figure 5.3 and is defined as follows:

Pattern 1: Occurs for \( |\Delta R_e| = 0 \)

Pattern 2: Occurs for \( 0 \leq |\Delta R_e| \leq 1 \times 10^{-11} m \)

Pattern 3: Occurs for \( 1 \times 10^{-11} \leq |\Delta R_e| \leq 3 \times 10^{-11} m \)

Pattern 4: Occurs for \( |\Delta R_e| \geq 3 \times 10^{-11} m \)
Figure 5.3 A specification of the ranges of $|\Delta R_0|$ for $\Delta = 0.3$ within which different pattern sets of vibronic intensities occur. These ranges remain essentially unchanged for all values of $\Delta$ in the range $0 \leq \Delta \leq 0.6$. 

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Some uncertainty is associated with the various limits because some slight variation does occur for different values of $A$. Thus, while operating well inside the limits specified above is rather precise with respect to pattern type, care should be exercised when working at or near the limits.

The vibronic patterns for the entire range of $A$ are shown across the tops of Figures 5.4 to 5.9. The specific spectrum for the $|\Delta R_e|$ values of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 are illustrated in these figures only for 9 vibronic bands because the provision of details for $\nu' > 8$ would yield no great amount of new information. We now proceed to discuss the individual patterns.

Pattern 1: This pattern for $A = 0$, $|\Delta R_e| = 0$ is shown in Figure 5.10. It consists of only one line, the $0' \leftrightarrow 0''$ or origin band. The reason for this is that the two sets of vibrational wavefunctions $\psi'$ and $\psi''$ are identical and, as a result, $\int \psi_i \psi_j^* d\tau = \delta_{ij}$. Thus, all $S_{ij}^2$ except $S_{00}^2$ are zero.

As one changes $A$ but maintains $|\Delta R_e| = 0$, as is shown in Figures 5.4 to 5.9, the origin band remains dominant over the whole range of $A$, so much so, in fact, that overtones may well not be experimentally detectable. In any event, an alternation phenomenon is evident, particularly at large $A$: only the even overtones exhibit any intensity and the odd overtones are completely absent. Again, the reason for this is entirely vested in the symmetry of the problem. The vibrational wavefunctions for both states may be classified as symmetric/antisymmetric with respect to the inversion in $\Delta R_e = 0$. Thus, all integrals

\[ \int \psi_0'' \psi_j^* d\tau \neq 0, \quad j = 0, 2, 4, ... \]

\[ \int \psi_0'' \psi_j^* d\tau = 0, \quad j = 1, 3, 5, ... \]
Figure 5.4  Theoretical FCI intensities from Figure 3.1(a) for \( \Delta = 0.1 \), configured for pattern recognition.

(a) A selection of spectra extracted at intervals of \( |\Delta R_e| = 0.1 \AA \).

(b) A close-up of Figure 3.1(a) in the region of small \( |\Delta R_e| \).

(c) Close-up of the lower part of the spectrum at \( |\Delta R_e| = 0 \AA \) in (a) above. The \( S_{Q_D}^2 \) (red bar) extends all the way up to \( \sim 1 \).
Figure 5.5 Theoretical FCI intensities from Figure 3.1(b) for $\Delta = 0.2$, configured for pattern recognition.

(a) A selection of spectra extracted at intervals of $|\Delta R_e| = 0.1 \text{Å}$.
(b) A close-up of Figure 3.1(b) in the region of small $|\Delta R_e|$.
(c) Close-up of the lower part of the spectrum at $|\Delta R_e| = 0 \text{Å}$ in (a) above. The $S_{00}$ (red bar) extends all the way up to $\sim 1$. 

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Figure 5.6 Theoretical FCI intensities from Figure 3.1(c) for $\Delta = 0.3$ A configured for pattern recognition.
(a) A selection of spectra extracted at intervals of $|\Delta R_e| = 0.1 \, \text{Å}$.
(b) A close-up of Figure 3.1(c) in the region of small $|\Delta R_e|$.
(c) Close-up of the lower part of the spectrum at $|\Delta R_e| = 0 \, \text{Å}$ in (a) above. The $S_{0,0r}^2$ (red bar) extends all the way up to $\sim 1$. 

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Figure 5.7  Theoretical FCI intensities from Figure 3.1(d) for $\Delta = 0.4$, configured for pattern recognition.

(a) A selection of spectra extracted at intervals of $|\Delta R_e| = 0.1 \text{Å}$.  
(b) A close-up of Figure 3.1(d) in the region of small $|\Delta R_e|$.  
(c) Close-up of the lower part of the spectrum at $|\Delta R_e| = 0 \text{Å}$ in (a) above.  The $S_{00}'$ (red bar) extends all the way up to $\sim 1$.  

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Figure 5.8 Theoretical FCI intensities from Figure 3.1(e) for Δ = 0.5, configured for pattern recognition.

(a) A selection of spectra extracted at intervals of |ΔR*| = 0.1 Å.
(b) A close-up of Figure 3.1(e) in the region of small |ΔR*|.
(c) Close-up of the lower part of the spectrum at |ΔR*| = 0.1 Å in (a) above. The S110 (red bar) extends all the way up to ~0.5.
Figure 5.9 Theoretical FCI intensities from Figure 3.1(f) for $\Delta = 0.6$, configured for pattern recognition.
(a) A selection of spectra extracted at intervals of $|\Delta R_e| = 0.1 \times 10^{-10} \text{Å}$.
(b) A close-up of Figure 3.1(f) in the region of small $|\Delta R_e|$.
(c) Close-up of the lower part of the spectrum at $|\Delta R_e| = 0$, 0.1 and 0.2 Å in (a) above. The $S^2_{\text{for}}$ (red bar) extends up to $\sim 0.9, 0.53$ and 0.10, respectively.
Figure 5.10 The theoretical spectrum for $\Delta = 0$ and $\Delta R_0 = 0 \text{ m}$, Pattern 1. This is the only case where the intensity is totally resident in the $0' \leftrightarrow 0''$ band. The intensity is exactly one: $I_{0'0''} = 1$. No alternation exists in this case.
Changes of $|ΔR_o|$ destroy the common inversion characteristic: both $y''$ and $y'$ no longer possess the inversion characteristic in $R''_o$; only $y''$ does. Consequently, the orthonormality arguments outlined above no longer hold. Thus, as $|ΔR_o|$ is varied above zero, the consequences of near-orthogonality may induce weak alternation characteristics. These rapidly merge into Pattern 2.

- **Pattern 2:** Typical pattern 2 vibronic spectra may be seen in Figures 5.4 to 5.9 (see the spectra at $ΔR_o = 0.1 \times 10^{-11}$ m). A typical spectrum in the middle of the $|ΔR_o|$ range for Pattern 2 is extracted in Figure 5.11. The intensity distribution is characteristically "right-triangle like", the origin band being the most intense.

- **Pattern 3:** Typical Pattern 3 vibronic spectra may be seen in Figures 5.4 to 5.9 (see the spectra at $|ΔR_o| = 0.2$ and $0.3 \times 10^{-11}$ m). Some typical Pattern 3 spectra are extracted in Figure 5.12. The intensity distribution is somewhat bell-shaped but quite irregular, in the sense that the origin band is somewhat intense at the lower $|ΔR_o|$ limit but very weak, almost absent, at the upper $|ΔR_o|$ limit. At the same time as the intensity of the origin band decreases, the maximum intensity also diminishes and the spectrum broadens out to cover a larger range of $v'$.

Pattern 3 is the most common pattern in the experimental spectra.

- **Pattern 4:** Typical Pattern 4 vibronic spectra may be seen in Figures 5.4 to 5.9 (see the spectra at $|ΔR_o| = 0.4, 0.5$ and $0.6 \times 10^{-11}$ m. These spectra are identical to Pattern 3 in all but two regards:

  1. The intensity at low values of $v'$ is either zero or close to zero. For example, for $Δ = 0.6$, $|ΔR_o| = 0.6 \times 10^{-11}$ m the intensity of even the $0'' \rightarrow 8'$ vibronic transition is more or less zero (see Figure 5.13.)
Figure 5.11 Typical Pattern 2 spectrum. This particular example has the parameters of $\Delta = 0.1$ and $\Delta R_e = 5.1 \times 10^{-11}$ m. There is no discernible alternation in this region.
Figure 5.12 Typical Pattern 3 spectra. The x-axes are labeled with each $|\Delta R_{el}|$ value. As $|\Delta R_{el}|$ increases, the intensity in the lower energy vibronic bands diminishes, that in the higher energy vibronic bands increases, the spectrum flattens out, and the overall width increases. This widening is not noticeable here because we extend our considerations only as far as $l_{ggy}$. 

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Figure 5.13 Typical Pattern 4 vibronic spectra for $\Delta = 0.3$. The first spectrum on the left illustrates the diminishing intensity of the $0'0''$ and $1'0''$ transitions.

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2. The intensity maximum is much lower
and the intensity is distributed over a very
much broader range of \( \nu' \).

5.3 Intensity Alternation

Alternation occurs when \( |\Delta R_e| \) is small, close to zero, and is essentially
caused by the near-maintenance of a common inversion characteristic by both sets of
wavefunctions, \( \psi' \) and \( \psi'' \). Examples of this alternation are shown in the lower right
corners of Figures 5.4 to 5.9. The effects are generally small and outside
measurement capabilities. However, as \( \Delta \) becomes large, as shown in Figures 5.8
and 5.9, alternation becomes more severe, extends to larger values of \( |\Delta R_e| \), and
moves into the photometric measurements range.

It is well to emphasize that alternation is an expected phenomenon: there is
no reason to expect that the overlaps of two sets of discrete wavefunctions should not
oscillate with \( \nu' \) (i.e., exhibit resonances). While we have shown that alternation is
uncommon within the ranges of \( \Delta \) and \( |\Delta R_e| \) that are of normal occurrence, we must
emphasize that we have restricted our discussion to low values of \( \nu \), the vibrational
quantum number. For larger values of either \( \nu' \) or \( \nu'' \), alternation can be more the
rule than the exception. An example follows:

\textit{Alternation in the System} \( l_2: B^3\Pi_o^\ddagger \rightarrow X^1\Sigma_g^+\)

Researchers, Steinfeld et al. [20], have observed multiple
 alternation cycles in the \( B^3\Pi_o^\ddagger \rightarrow X^1\Sigma_g^+ \) emission spectrum
of \( l_2 \), the emitting vibronic level being \( \nu' = 27 \), and the
terminal levels of the ground state traversing the range
\( \nu'' = 37 \) to 0. Other researchers, Stwalley et al. [21], have
invoked computational simulations of such alternations to
explain vibronic radiationless energy transfer between highly excited vibronic levels of two different electronic states of \( \text{Na}_2 \). A situation of "seemingly random Franck-Condon factors", ones showing "no comprehensible patterns" is also discussed by Struve [22]. Struve mentions the use of Delandres analysis as a method of assigning the high temperature spectra of the \( \text{Na}_2 \) system, \( X^1\Sigma^+_g \rightarrow A^1\Sigma^+_u \).

5.4 Conclusions

A summary of the various patterns that can occur and the approximate values of \( |\Delta R_e| \) that determine them is shown schematically in Figure 5.14. The various caveats with which this schematization must be accompanied are detailed in the text.
Figure 5.14 Schematic Overview of Patterns.

(FCIM Model from Table 6.1: SnO, Δ = −0.4)
CHAPTER 6

THE EXPERIMENTAL SPECTRA: RESULTS

We will now present our analysis of the experimental vibronic spectra. We will apply all the techniques of the previous chapters (i.e., the linear, quadratic, FCW and “best fit” procedures) to these spectra in order to extract bond lengths, $R'$, of the relevant excited electronic states. We consider only diatomics but, among these, there will be neutral, radical and ionic molecules. That is, our considerations will cover the entire gamut of diatomic types.

The decision to restrict the study to diatomics is based on the following three facts:

1. There is a great variety of vibrationally resolved electronic spectra available for diatomics. This is not to say that such spectra are not available for polyatomics because, in fact, they are. However, the quality, diversity and numbers of such spectra for the polyatomics is very much less than for diatomics.

2. A diatomic has only one normal vibrational coordinate and the algebraic expression for it is very simple. Any rather common polyatomic possesses many such coordinates and the corresponding vibrational modes may all appear in the vibronic spectrum. Chlorine dioxide, for example, has three normal vibrational modes and, since all of these can appear in any vibronic spectrum, that spectrum can be complex, difficult to analyze and often intractable insofar as the extraction of individual vibronic intensities is concerned. Thus, it seems wise to limit oneself, at least initially, to the diatomics.
3. The test of the various techniques that we will apply is the degree to which they reproduce experiment. Experimental values of $R'_e$ (called $r_e$ by Herzberg [19]) are generally available only for the diatomics and very rarely for the polyatomics. These "experimental values" are obtained from a rotational analysis of rovibronic spectra and their determination implies the availability of very highly resolved spectra, a correct analysis of these spectra and highly accurate wavelength measurements. A great variety of such good "experimental values" is available for the diatomics, and it is this rich source that permits us to test the validity of our vibrational techniques. However, it is well to remember that these "experimental values" of $R'_e$ can also be erroneous. Nonetheless, this is all that is available for test purposes. These experimental values are referred to as $R'_e R$, since they come from "rotational" spectra.

The types of vibronic spectra to be considered are also diverse. In effect, in order to test the nondiscriminatory aspects of the vibronic analysis, we will apply it to photon absorption spectra, photon emission spectra, photoelectron spectra, and electron energy loss spectra. While it is known that the intensities of the spectra in the latter two cases are functions of incident photon and/or electron energies, it is thought that the vibrational intensity distributions in the spectra remain relatively constant. This work make no pretense to investigate such variations and, instead, merely assumes that the vibrational intensity distribution does remain unaffected.

This work will exhibit very little concern with error limits. Indeed, it may well be criticized for a cavalier attitude about experimental uncertainties. However, we believe we have no choice because we are, after all, dealing with the data of other people who, for the most part, provide no information about the uncertainties of their numbers. In fact, since much of the data is of spectrographic origin, it is subject to the non-linearities of photographic detection and, in our opinion, is often wrong.
Consequently, whenever we suspect that such data suffers from plate overexposure, we feel free to eliminate the suspect information. In circumstances such as this, a preoccupation with the error limits of an individual datum seems misplaced. The stress, in this work, is placed on the entire collection of $R'_e$ values.

6.1 Objectives

The first objective is the determination of the "experimental value" of $R'_e$, namely $R'_e R$. As stated, this is obtained from the available rotational parameters which eventually, lead to

$$R''_e - R'_e = \Delta R_e R$$

where $R''_e$ is the rotational ground state intermolecular distance, and $R'_e$ is the rotational excited state intermolecular distance; these are variously labeled $R_g$ and $R_e$, respectively, in the literature. Since our concern is the equilibrium separation, we have adopted the labeling $R''_e$ and $R'_e$ as a compromise, using the prime notation to differentiate states and their levels (e.g., $v'' = 0''$ or $v' = 0'$). Table 6.1, 7th and 8th columns, contains these parameter values. The difference between them gives $\Delta R_e R$, the rotational value of $\Delta R_e$, which is an "experimental value." The values of $\Delta R_e R$ are the set of numbers to which we will make correspondence of the values derived from vibrational considerations.

The second objective is determination of the vibrational values for linear, $\Delta R_e L$, quadratic, $\Delta R_e Q$, center of Franck-Condon window, $\Delta R_e CF CW$ and best fit with experiment, $\Delta R_e Best Fit$. These were determined by methods identical to those of Chapters 2-4, except that experimental vibronic spectrum was used instead of those of a computed theoretical spectrum. When approximations were determined we used
Table 6.1 Diatomic Parameters [19,23,24] and $\Delta R_e$ Results.

Absorption (→)

| Plot | Molecule | Band | $\mu$ | $\nu'$ | $\nu''$ | $R_e'$ | $R_e''$ | $\Delta$ | $\Delta R_e^R$ | $\Delta R_e^L$ | $\Delta R_e^O$ | $\Delta R_e^{PCW}$ | $\Delta R_e^{BP_{exp}}$ |
|------|----------|------|------|--------|--------|--------|--------|------|-----------|-----------|-------------|---------------|----------------|-----------------|
| Index | Levels Ref. | System | $\times 10^{-5}$ | cm$^{-1}$ | cm$^{-1}$ | x $10^{-3}$ m | x $10^{-3}$ m | | x $10^{-3}$ m | x $10^{-3}$ m | x $10^{-3}$ m | x $10^{-3}$ m | x $10^{-3}$ m |
| 1 | BaO | $A^1 \Sigma$ | 406.8 | 2.134 | -0.34 | 0.194 | 0.210 | 0.189 | 0.190 | 0.190 | +/- 0.002 |
| 2 | Ar | $A \rightarrow X$ | 1786.22 | 1.268 | 0.082 | 0.046 | 0.107 | 0.034 | 0.088 | 0.080 | +/- 0.002 |
| 3 | C$^{12}$O | $X^1 \Sigma^+$ | 1739.25 | 1.2093 | -0.248 | 0.081 | 0.109 | 0.083 | 0.092 | 0.096 | +/- 0.005 |
| 4 | Ar | $A \rightarrow X$ | 1515.81 | 1.2351 | -0.248 | 0.081 | 0.087 | 0.109 | 0.089 | 0.091 | 0.087 | +/- 0.005 |
| 5 | Ar | $A \rightarrow X$ | 1515.81 | 1.2351 | 0.302 | 0.107 | 0.081 | 0.076 | 0.100 | 0.098 | 0.103 | +/- 0.010 |


Herzberg, G., Ibid., p. 520.


Herzberg, G., Ibid., p. 513.
Table 6.1/2

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7: Rathbone, J. & Potasoff, E., personal communication, Fall 2000. Fluorescence, \( hν = (20-165 \text{ eV}) \).

Herzberg, G., ibid., p. 522.

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The data in Lee and Rabelais is close to that of Turner, D. W. & May, D. P., J. Chem. Phys., 45 No. 2, 473, (1966); \( hν = (21.21 \text{ eV}) \), He resonance; Franck-Condon calculation and experimental finds 2D⁺ maximum at 15.98 eV.


Herzberg, G., ibid., p. 522.

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<th>v'' (cm⁻¹)</th>
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<th>R'_e (10⁻² m)</th>
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<th>ΔR_e L (10⁻³ m)</th>
<th>ΔR_e Q (10⁻⁴ m)</th>
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Myer, J. A. & Samson, J. A. R., ibid., 269. The authors cite their result for the \( v' = 2880 \text{ cm}⁻¹ \) which is used in this work.

Herzberg, G., ibid., p. 534.

The value for \( ΔR_e \) cited here was taken from the "best fit" of experiment to the FCI Map; no literature value of \( R_e \) was available.
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12: Piper, L. G., J. Chem. Phys., Vol. 99, No. 5, 3175, September 1, 1993. $\Delta R_e^a$ was not calculated because only two relative intensity ratios were available (at least three are required). Emission.


14: Schoen, L. J., & Rebbert, R. E., J. Mol. Spec. 3, 421 (1959). 4.2 K in argon matrix. The calculations were carried out on two data sets, one obtained in nitrogen matrix and another in argon matrix. It is obvious that the nitrogen matrix data is inappropriate for these calculations. The authors, Schoen and Rebbert, point out that there is a marked increase of sharpness and a wavelength contraction in the Ar matrix relative to the N$_2$ matrix. The extreme coupling between the quadrupolar nucleus of the matrix N$_2$ and the target N$_2$ molecules seems to affect critical distances. The effect is greatly diminished in the rare gas atomic system. Emission.


Herzberg, G., ibid., p. 553.

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<table>
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Herzberg, G., ibid., p. 554.

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Table 6.1/3
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<th>( \nu'' )</th>
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<th>( R''_e \times 10^{-2} \text{ m} )</th>
<th>( \Delta )</th>
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<th>( \Delta R''_e \text{PDIW} \times 10^{-2} \text{ m} )</th>
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<tr>
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Table 6.1/4
| Plot | Molecule | Band | System, Ref. | \( \mu \) | \( \bar{\nu}' \) | \( \bar{\nu}'' \) | \( R'_0 \) | \( R''_0 \) | \( \Delta \) | \( \Delta R_{eR} \) | \( \Delta R_{eL} \) | \( \Delta R_{eQ} \) | \( \Delta R_{eFCW CF} \) | \( \Delta R_{e B exp} \) |
|------|----------|------|-------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| a | \( ^2 \Pi \) | OH | 0.15745 | 3737.761 | 1.029 | | | | | | | | | |
| b | \( ^3 \Sigma^- \) | 3113.37 | 1.025 | | | | | | | | | | | |
| c | \( ^1 \Delta \) | 2980 | 1.025 | | | | | | | | | | | |
| d | \( ^1 \Sigma^+ \) | 2980 | 1.035 | | | | | | | | | | | |
| e | \( ^3 \Pi \) | 2981 | 1.032 | | | | | | | | | | | |
| f | \( ^5 \Pi \) | 2133.65 | 1.1354 | | | | | | | | | | | |
| g | \( ^5 \Pi \) | 1980 | 1.135 | | | | | | | | | | | |
| 28 | \( ^3 \Sigma^- \rightarrow ^2 \Pi \) | | 0.167 | 0.059 | 0.063 | 0.062 | 0.057 | 0.057 +/- 0.014 | | | | | | |
| 29 | \( ^3 \Sigma^- \rightarrow ^2 \Pi \) | | 0.203 | 0.055 | 0.063 | 0.097 | 0.055 | 0.055 +/- 0.015 | | | | | | |
| 30 | \( ^1 \Delta \rightarrow ^2 \Pi \) | | 0.208 | 0.055 | 0.061 | 0.067 | 0.055 | 0.055 +/- 0.011 | | | | | | |
| 31 | \( ^1 \Sigma^+ \rightarrow ^2 \Pi \) | | 0.202 | 0.062 | 0.061 | 0.060 | 0.061 | 0.061 +/- 0.010 | | | | | | |
| 32 | \( ^3 \Pi \rightarrow ^2 \Pi \) | | 0.429 | 0.166 | 0.142 | 0.164 | 0.166 | 0.166 +/- 0.020 | | | | | | |
| 33 | \( ^5 \Pi \rightarrow ^2 \Pi \) | | 0.475 | 0.166 | 0.142 | 0.166 | 0.164 | 0.164 +/- 0.009 | | | | | | |

28: Photon Absorption (1)
29: PES (1)
30: PES (2)
31: PES (3)
32: Photon Absorption (2)
33: PES (4)

Table 6.1/5
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<th>( \nu'' ) cm(^{-1} )</th>
<th>( R_e \times 10^8 ) m</th>
<th>( R_a \times 10^8 ) m</th>
<th>( \Delta \times 10^8 ) m</th>
<th>( \Delta R_e R \times 10^8 ) m</th>
<th>( \Delta R_e L \times 10^8 ) m</th>
<th>( \Delta R_e Q \times 10^8 ) m</th>
<th>( \Delta R_e FCW Cy \times 10^8 ) m</th>
<th>( \Delta R_e \text{ sf} \text{ exp} \times 10^8 ) m</th>
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</table>
the real molecular parameters [19,23,24]. We illustrate the results using the experimental emission spectrum for barium oxide, \( \text{BaO} \), [Table 6.1, 1], Figures 6.1-6.

The third objective is to plot each of the \( \Delta R_{eL}, \Delta R_{eQ}, \Delta R_{eCFCW}, \) and \( \Delta R_{eBestF} \) versus the experimental value \( \Delta R_{eR} \) and to assess the degree to which correspondence is obtained between the different sets. This is done in Figures 6.7, 6.8, 6.9 and 6.10.

6.2 The Data Set

The data set is given in Table 6.1. Every entry on Figures 6.7, 6.8, 6.9 and 6.10 is identified by an arabic numeral. This same numeral occurs in Table 6.1 where it identifies both the molecule and the electronic transition (band system) of that molecule. The reduced mass of the molecule, and the vibrational frequencies in the various electronic states as well as the values of \( R_e \) for these same states are also listed and referenced in Table 6.1. The values of \( \Delta \) and those for \( \Delta R_e \) obtained here from vibrational intensity considerations constitute the rightmost listings in Table 6.1; it is these values that are plotted along the ordinates of Figures 6.7, 6.8, 6.9, and 6.10. The literature references in Table 6.1 are indexed according to the same arabic numeral used in Figures 6.7, 6.8, 6.9, and 6.10; this literature reference may also be accompanied by some other information about the data set that is deemed to be important.

It was thought that some comments on the individual electronic transitions analyzed in this work would provide the reader some insights into the nature of the data sets with which the author had to work. Consequently, what follows is an eclectic mix of transitions, some of which exhibit good, well-resolved spectra and some bad, questionable spectra, some of which we have had to reassign and some of which suffered from multiple assignments. This list is not meant to be complete; it is
Figure 6.1 The spectrum computed for $\Delta R_{e R} = 1.940E-11 m$.

Figure 6.2 (a) The experimental spectrum, emission.

Figure 6.2 (b) The spectrum of 2 (a) divided by $v^3$.

Figure 6.3 The spectrum computed for $\Delta R_{e L} = 2.101E-11 m$.

Figure 6.4 The spectrum computed for $\Delta R_{e Q} = 1.892E-11 m$.

Figure 6.5 The spectrum computed for $\Delta R_{e CF} = 1.895E-11 m$.

Figure 6.6 The spectrum computed for $\Delta R_{e Best FR} = 1.890E-11 m$. 

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Figure 6.7 $\Delta R_\text{e BestFit, A}$ versus $\Delta R_\text{e R, A}$. 

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Figure 6.8 $\Delta R_e L, \AA$ versus $\Delta R_e R, \AA$. 

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Figure 6.9 $\Delta R_{eQ}$, Å versus $\Delta R_{eR}$, Å.
Figure 6.10 \( \Delta R_\theta C_{FCW} \) vs. \( \Delta R_\theta R, A \)
merely illustrative. The bracketed number again serves as the same index used in Figures 6.7, 6.8, 6.9, and 6.10 and Table 6.1.

(1.) The $X \rightarrow A$ System of $\text{BaO}$

The vibrational ground state frequency of the chemiluminescent system (670.3 cm$^{-1}$) is identical to the gas phase infrared value (669.8 cm$^{-1}$). The spectrum is very clean and sharp with a minimal baseline noise component. Enhancement techniques were used to observe the lowest vibronic levels of this system [Table 6.1, 1]. These spectra were of optimal quality, and the analysis was both facile and accurate.

(2.) The $A \rightarrow X$ System of $^{12}\text{C}_2$

The Swan system [Table 6.1, 2] exemplifies an excited state of shorter bond length than the ground state (c.f., compare the columns for $R''_e$ and $R'_e$). This situation occurs because the excitation $A \rightarrow X$ promotes an electron out of an antibonding orbital. The vibronic techniques of this work cannot distinguish positive or negative values of $\Delta R_e$; in fact, they only generate $|\Delta R_e|^2$. Consequently, some other facet of the spectrum, usually the vibrational frequency in the excited state, must be used to make a decision about the sign of $\Delta R_e$.

The spectrum was probably obtained by a photographic plate method and the intensities read "by eye". This method of reading plates is very limited and difficulties are expected. At very small $\Delta$, which is the situation for this transition, we expect both the linear and quadratic approximations to yield reasonable $\Delta R_e$’s. The results do not meet this expectation.

The cited intensity numbers may well be good to +/- 10%. This is a very large range and it yields unacceptable variances in the intensity ratios. Given these criticisms, it is not surprising that the methods used here fail. Nonetheless, it is concluded that the bond length change will be small, in full accord with experiment.
This case, however, does not constitute a worst case scenario. This particular case has to do with "eye-ball error." There are many examples of plate overexposure errors in the literature, in which case several intensity maxima may occur serially. We have chosen to interpret such cases as plate-saturation events, and to excise all but one maximum, usually the one of lowest energy, from the intensity data set.

(5, 6.) The A ← X System of CO

The spectrum for the 4th positive system of carbon monoxide yields extremely good results in the Ajello case [Table 6.1, 5], and ones that are slightly less so in the Myer and Samson case [Table 6.1, 6]. The value of Δ is a borderline case between the linear and quadratic approximations. The linear approximation is not really expected to yield viable results, but in this case even it lies within acceptable limits.

(10.) The X ← X PES Spectra of \(^1\)H_2^+

The spectral assignments of Lee and Rabalais [Table 6.1, 10] differ from those of Åsbrink [16]. In effect, the two assignment differ by transposition of one vibrational quantum: that which Rabalais assigns as \(v' \leftarrow 0''\), Åsbrink assigns as \((v + 1)' \leftarrow 0''\) [16]. The analysis given here selects the Rabalais assignment as the correct designation.

(27.) The a ← X System of O_2

This system is an excellent example of alternation (See Section 4.4) As pointed out, this phenomenon is most prominent for very small distances, ones of the order of \(\Delta R_a = 5 \times 10^{-12}\) or smaller. The investigators [Table 6.1, 27] found that the 0' ← 0'' band was 50 times more intense than the 1' ← 0'' band. Unfortunately, I conclude that their assignment was wrong: the 1' ← 0'' band is actually the 2' ← 0'' band and the 1' ← 0'' is missing. Thus, the intensities, as interpreted here, are

127
\[ 0' \rightarrow 0''(50), \ 1' \rightarrow 0''(0), \ 2' \rightarrow 0''(1). \] Given these numbers and assignments, very precise agreement with experiment occurs.

(20,21.) The \( B \rightarrow X \) System of \( O_2 \)

Several examples of spectra encountered in this work were problematic for one reason or another, photographic saturation being one such example. Another situation, one in which two close-lying electronic excited states cause an overlapping of absorption bands, is exemplified by the Schumann-Runge bands of \( O_2 \); one transition is so close to the other that it is not possible to obtain a clean spectrum for either transition. The Schumann-Runge bands are shown in Figure 6.11, as are also our efforts to extrapolate the higher energy absorption band to lower energy and, in this way, to subtract this residual intensity from the Schumann-Runge intensities. Unfortunately, these efforts are only partially successful.

6.3 CONCLUSIONS

The conclusions of this chapter follow directly from Figures 6.7, 6.8, 6.9, and 6.10. They are:

1. The FCW best-fit schema works exceedingly well. In fact, it works so well that those transitions which exhibit discrepancy are probably ones for which the spectroscopic data are suspect. These spectra should be reinvestigated.

2. The FCW center schema is as accurate as the FCW best fit. Thus, while highly accurate data are certainly desirable, an accurate gross-intensity pattern is really all that is needed insofar as \( \Delta R \) considerations are concerned.

3. The quadratic approximation is surprisingly good. Major failures occur with transitions 18, 20 and 23. Of these, 18 and 23 appear to point up deficiencies in the quadratic approximation.
Figure 6.11 The Schumann-Runge (S-R) Bands of Oxygen, $B^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ [26].

(a) The experimental absorption spectrum is the upper spectrum, and is labeled by $v'$ from the designation $v' \leftarrow 0''$. The smooth curve represents an attempt to extrapolate the absorption intensity of the higher energy electronic transition to lower energies. The lower spectrum is obtained by subtracting the extrapolated intensity from the upper spectrum; this spectrum is thought to be the "isolated" S-R absorption spectrum of $O_2$.

(b) The experimental intensities for the "isolated" S-R bands in bar-graph form; taken from (a) above.

(c) The graph of ratio of experimental intensities for $O_2 : B^3\Sigma_u^+, v' \leftarrow X^3\Sigma_g^-, 0''$ from integrated areas under the spectrum for the individual transitions.

This spectrum is unusable for either linear or quadratic processing. Whether this is due to an improper subtraction procedure or to spectroscopic perturbation by other electronic states is unknown at this time.
4. The linear approximation provides mixed results, so much so that we hesitate, at this point, to recommend its use.

5. Outlier points that appear as such in all four plots, probably represent situations caused by errors either in $R_s^l$ or in the recorded spectrum, or by intrusion of spectroscopic interferences or gross anharmonicity.

6. Outlier points that occur in Figures 6.7 and 6.8, but not in Figures 6.9 and 6.10, probably represent cases in which the linear and/or the quadratic approximations fail.
CHAPTER 7
RESULTS OF THIS WORK

An exact, formal, power series expression has been obtained for the Franck-Condon integral, FCI, in the harmonic approximation. It is distinguished by the fact that it is a function of a parameter \( \Delta \), where \( \Delta \) was chosen in such a way that \( \Delta \approx 0 \) for most vibronic spectra. Consequently, certain functions of the FCI’s which may be expressed as power series in \( \Delta \) may well be truncated by neglect of the higher powers of \( \Delta \), namely \( \Delta^m \) where \( m > 1 \).

The power series expression was obtained by the elementary use of algebra and calculus, often called the “brute force” method: The lowest 9 FCI’s were solved analytically in power series form, and compact expressions were sought, and found, for the series coefficients.

Other exact expressions for FCI’s do exist. These are discussed in Appendix V. However, we have verified that the numerical values for the FCI’s obtained by the use of our expression are identical to iterative computation (e.g., Mathematica [14]).

The function of the FCI’s that we have chosen to use in order to make correspondence with experiment is the ratio of adjacent FCI’s, namely \( \frac{S_{\nu \rightarrow \nu + 1}}{S_{\nu \rightarrow \nu - 1}} \). This ratio yields a power series in \( \Delta \) which may be truncated, depending on the value of \( \Delta \), at \( \Delta \), \( \Delta^2 \), \( \Delta^4 \), .... We have performed truncation at \( \Delta \) and \( \Delta^2 \) and obtained tractable linear and quadratic expressions in \( \Delta \).

The linear and quadratic approximations were tested on exact, computed vibronic spectra that cover the entire, experimentally-reasonable ranges of both \( \Delta \) and
\( \Delta R_e \), where \( \Delta R_e \) is the equilibrium separation of the minima of the two states between which an electronic transition is taking place. It was found that the linear approximation is good for \( \Delta \leq 0.2 \) and that the quadratic approximation is good for \( \Delta \leq 0.4 \).

Plots of the FCI's, \( S_0^{2\nu''} \), from Equation 2.5, for a specific value of \( \Delta \) over the entire range of \( \Delta R_e \) for

- **Emission:** \( S_0^{2\nu''} \), where \( \nu'' = 0'', 1'', 2'', ..., \) and
- **Absorption:** \( S_0^{2\nu''} \), where \( \nu' = 0', 1', 2', ... \)

gives rise to the Franck-Condon integral maps, FCIM's. The FCIM was found to be useful in developing the concepts of the Franck-Condon window, FCW, and Franck-Condon region, FCR.

It was observed that precise values of the ratios \( \frac{S_0^{2\nu''}}{S_0^{2\nu'\nu''}} \) were not required in order to extract good values of \( \Delta R_e \). Correspondence with the FCW suggests that values of \( \Delta R_e \) good to 0.01\( \text{Å} \) can be obtained from the gross intensity pattern of spectra. A "gross intensity pattern" is defined as a correct but non-numeric enumeration of the relative vibronic intensities.

The relative intensities of vibronic bands obtained from FCI maps are found to be extremely sensitive functions of \( \Delta R_e \) and somewhat insensitive functions of \( \Delta \). As a result, one can specify intensity patterns that characterize different ranges of \( \Delta R_e \); and use these, without recourse to any computation or any map, to estimate \( \Delta R_e \) to within 0.025\( \text{Å} \).

The Franck-Condon considerations outlined above were applied to experiment. The vibronic intensities \( \frac{S_0^{2\nu''}}{S_0^{2\nu'\nu''}} \) were set equal to \( \frac{S_0^{2\nu''}}{S_0^{2\nu'\nu''}} \). These

132

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intensities were then subjected to analysis by the linear approximation, the quadratic approximation, the gross intensity pattern and the exact relative intensities. The results were compared to values of $\Delta R_e$ that were available from rotational analysis. It was found, as expected, that Franck-Condon analyses of precise intensity data were generally good. It was found that the analysis based on gross intensity patterns was of comparable quality to those based on numerical intensity data. The quadratic approximation was effective over the range $0 \leq \Delta R_e \leq 0.4 \text{ Å}$. The linear approximation gave mixed results.

Our calculations for the emission spectra included the consideration that $A_{\nu'-\nu}$ is proportional to $v_{\nu'}^2 B_{\nu'-\nu}$. Differences between the experimental data and the adjusted data were significant in a few cases but, overall, the difference was so small that both patterns had either the same or nearly the same gross intensity distributions.

Approximately, 60 electronic transitions were subjected to the above comparative study. Some 20 of these had to be rejected because of lack of confidence in the data. Of the 40 that passed muster for inclusion in the comparative analysis, we had to reassign one because the literature assignment was wrong, we had to choose between two different assignments that existed in the literature for another transition, and we had to neglect certain individual band measurements because of defects associated with obvious detector overload. This list could continue... the point being that the available experimental data left much to be desired in many instances. Consequently, many of the inconsistencies in Figures 6.7, 6.8, 6.9, and 6.10 may well be associated with the experimental data bases and not with the approaches developed here.
REFERENCES AND BIBLIOGRAPHY


15. Margenau, H., & Murphy, G. M., *The Mathematics of Physics and Chemistry*, Van Nostrand, New York, 1943, Sec. 3.10. (b) Antosiewicz, H. A., *Bessel Functions of Fractional Order*, in *Handbook of Mathematical Functions*, Eds. M. Abramowitz & I. A. Stegun, Dover, 1965, p. 437. This latter article gave clues for solving the knotty problem of the coefficient of Eq. 2.5: the numbers that needed to be generated, namely the coefficients of Equation A11.1, are \{1, -56, +840, -3360, +1680\}. These display some relation to the Hermite polynomials in that they are either a transform and/or transpose of the coefficients of the originating integrated, overlapped Hermite polynomials. The Antosiewicz article listed various generating functions that, when rearranged, yielded the generator to fit those sought-after sequences.


Evidence of alternation in A-X systems of LiH, and Na₂.


The general Franck-Condon integral (FCI) is usually written as

$$ S_{v''}^2(\Delta \zeta, v', v'') = \left| \left\langle \chi_{v'}(\zeta + \Delta \zeta, v') | \chi_{v''}(\zeta, v'') \right\rangle \right|^2 \quad \text{(Al.1, 2.3)} $$

We will usually be engrossed with the parametric values $v'' = 0''$ and $v' = 0, 1, 2, ...$. The variable $\Delta \zeta$ is equivalent to $\Delta R_e$. Other definitions will be introduced as needed.

The FCI of concern is given by

$$ \left| \left\langle \chi_{v'}(\zeta) | \chi_{v''}(\zeta) \right\rangle \right|^2 = $$

$$ \left| \left\langle \sqrt{\frac{\alpha'}{\pi}} \frac{1}{2^{v'}!} \phi_{v'} \left( \sqrt{\frac{\alpha'}{\pi}} \zeta \right) \right| e^{-\frac{\Delta E}{kT}} \phi_v \left( \sqrt{\frac{\alpha''}{\pi}} \zeta \right) \right|^2 $$

where $\sqrt{\frac{\alpha'}{\pi}} \frac{1}{2^{v'}!} \phi_{v'} \left( \sqrt{\frac{\alpha'}{\pi}} \zeta \right) \right| e^{-\frac{\Delta E}{kT}} \phi_v \left( \sqrt{\frac{\alpha''}{\pi}} \zeta \right)$ are pertinent harmonic oscillator wave functions; $\chi$, the nuclear part of the wave function exclusive of rotation and translation, is a function of $\zeta$; where $\zeta$ is a symmetry-adapted vibrational coordinate, one for each of the 3N-6 (or 3N-5 for diatomics) internal molecular coordinates; $\Delta \zeta (= \Delta R_e)$ is the difference $R_e - R''_e$ at the minima of the two harmonic potential curves; $\alpha' = \frac{\mu \omega'}{\hbar} = \sqrt{\frac{\mu k}{\hbar^2}}$ and $\alpha'' = \frac{\mu \omega''}{\hbar} = \sqrt{\frac{\mu k''}{\hbar^2}}$, where $\mu$ is the effective (or reduced) mass appropriate to the normal coordinate in question; $\omega'$ and $\omega''$ are the angular vibrational frequencies of the excited, $v'$, and ground states, $v''$, respectively.
respectively; \( k' \) and \( k'' \) are the corresponding molecular harmonic oscillator spring constants; \( H_\nu \) and \( H_{\sigma'} \) are Hermite polynomials; and \( \hbar, \nu \) and \( \nu' \) have the usual meanings [4].

When all the obvious constants are factored out and because \( H_{\sigma'}(\sqrt{\alpha''} \xi) = 1 \) and \( \frac{1}{2\sigma'^2} = 1 \), we find

\[
|\langle \chi_{\nu'}(\xi + \Delta \xi, \nu')|\chi_{\sigma'}(\xi, \nu'')\rangle|^2 =
\]

\[
\left( \left( \frac{\xi}{\sqrt{2}} \right)^{\frac{1}{2}} \left( \frac{\xi + \Delta \xi}{2\nu'!} \right)^{\frac{1}{2}} \left( \frac{1}{2\nu'!} \right)^{\frac{1}{2}} \langle \exp(-\frac{a''\xi^2}{2}) H_{\nu'}(\sqrt{\alpha'(\xi + \Delta \xi)}) | \exp(-\frac{a''\xi^2}{2}) \rangle \right)^2
\]

\[
= \frac{\sqrt{2}}{\sqrt{\pi}} \frac{\sqrt{\pi}}{2\nu!} \left| \int \exp(-\frac{a''\xi^2}{2}) e^{\frac{a'^2}{2}\xi^2} H_{\nu'}(\sqrt{\alpha'(\xi + \Delta \xi)}) \, d\xi \right|^2
\]

The first exponential, expanded, yields

\[
\frac{a'}{2}(\xi + \Delta \xi)^2 = \frac{a'}{2}\xi^2 + \frac{a'}{2}2\xi(\Delta \xi) + \frac{a'}{2}(\Delta \xi)^2
\]

which, when consolidated with the second exponential, gives

\[
\exp \left( \frac{a'}{2}\xi^2 + \frac{a'}{2}2\xi(\Delta \xi) + \frac{a'}{2}(\Delta \xi)^2 \right) \exp \left( \frac{a''\xi^2}{2} \right) = \exp \left( \frac{a' + a''}{2}\xi^2 - a'\xi(\Delta \xi) - \frac{a'}{2}(\Delta \xi)^2 \right)
\]

\[
= \exp \left( \frac{a' + a''}{2}\xi^2 - a'\xi(\Delta \xi) - \frac{a'}{2}(\Delta \xi)^2 \right)
\]

The expanded exponential expression is then introduced into Eq. A1.3, to yield

\[
S_{\nu'\nu''}^2 = \frac{\sqrt{2}}{\sqrt{\pi}} \frac{\sqrt{\pi}}{2\nu!} \left| \left( \exp \left( \frac{a' + a''}{2}\xi^2 - a'\xi(\Delta \xi) - \frac{a'}{2}(\Delta \xi)^2 \right) H_{\nu'}(\sqrt{\alpha'(\xi + \Delta \xi)}) \right) \right|^2
\]

We now introduce the following simplifications and consolidations:
These, when substituted into Eq. A1.6, give

\[ S_{\nu_0} = c \cdot \frac{1}{2 \nu_1} \mid \int \exp(-a\xi^2 - b\xi - c_2)H_\nu(\sqrt{a'}(\xi + \Delta\xi)) \, d\xi \mid^2 \]

\[ = c \cdot \frac{1}{2 \nu_1} \mid \int \exp(-a\xi^2 - b\xi - c)H_\nu(\sqrt{a'}(\xi + \gamma)) \, d\xi \mid^2 \]  

(A1.12)

Since the exponential involving \( c_2 \) is itself a constant, it may be removed from the integral, and one finds

\[ S_{\nu_0}^2 = c \mid \exp(-c_2) \mid^2 \frac{1}{2 \nu_1} \mid \int_{-\infty}^{\infty} \exp(-a\xi^2 - b\xi)H_\nu(\sqrt{a'}(\xi + \gamma)) \, d\xi \mid^2 \]  

(A1.13)

The introduction of one final consolidation

\[ C_3 = c \mid \exp(-c_2) \mid^2 \]  

(A1.14)

generates the equation that provides the framework for the exact integrals:

\[ S_{\nu_0}^2 = C_3 \frac{1}{2 \nu_1} \mid \int_{-\infty}^{\infty} \exp(-a\xi^2 - b\xi)H_\nu(\sqrt{a'}(\xi + \gamma)) \, d\xi \mid^2 \]  

139
The exact Franck-Condon integral(s) (FCI) for $v' \leftarrow v'' = 0' \leftarrow 0''$ is as follows:

Beginning with Equations A1.15 or 2.4, we find for $v' = 0$

$$H_{v'}(\sqrt{\alpha'}(\xi + \Delta \zeta)) = H_{v'}(\sqrt{\alpha'}(\xi + \gamma)) = 1$$

$$\frac{1}{2^{v'v''}} = \frac{1}{2^{00}} = 1$$ (AII.1)

$$S^2_{v'v''} = C_3 \langle \exp(-a\zeta^2 - b\zeta) d\zeta \rangle^2$$ (AII.2)

The solution of this integral is the common statistical expression [6,14,15]:

$$\int_{-\infty}^{\infty} d\zeta e^{-a\zeta^2} e^{-b\zeta} = \frac{\sqrt{\pi} e^{b^2/4a}}{\sqrt{a}}$$ (AII.3)

which corresponds, upon resubstitution of constants from Equations A1.8 and A1.9, to

$$\frac{\sqrt{\pi} e^{b^2/4a}}{\sqrt{a}} = \frac{\sqrt{\pi}}{\sqrt{a'}} \exp\left[\frac{a^2(\Delta \zeta)^2}{4 \frac{a'}{a''}}\right]$$

The Franck-Condon integral (FCI) can now be written in terms of the constants given in Appendix I:

$$S^2_{v'v''} = \frac{\sqrt{\alpha'}}{\pi} \left| \exp\left[-\frac{a'}{2}(\Delta \zeta)^2\right] \right|^2 \frac{\sqrt{\pi}}{\sqrt{a'} + a} \exp\left[\frac{a^2(\Delta \zeta)^2}{4 \frac{a'}{a''}}\right]^2$$

$$= \frac{2\sqrt{\alpha'} a''}{a' + a''} \left| \exp[-a'(\Delta \zeta)^2] \exp\left[\frac{a^2(\Delta \zeta)^2}{(a' + a'')}\right]\right|$$

$$= \frac{2\sqrt{\alpha'} a''}{a' + a''} \exp\left[-\frac{a'a''}{a' + a''}(\Delta \zeta)^2\right]$$

and then simplified:
It can be shown that the set of constants which comprises the FCI, $S_{0'0''}^2$, for the
$0' \leftarrow 0''$ transition, Equation AII.4, becomes factored as the leading term of successive
equations for $v' \leftarrow v'' = v' \leftarrow 0''$ where $v' = 1, 2, 3, \ldots$, exemplified by the
complete solutions illustrated in Appendix IV. The only other entity that varies for
each value of $v'$ is $\frac{1}{2v'v'}$ (see Appendix III).
APPENDIX III
FRANCK-CONDON INTEGRAL RESULTS

The result of Appendix II, Equation A11.4

\[ S_{0'0''}^2 = \frac{2^{\frac{1}{2}}}{\beta + 1} \exp\left[ -\frac{1}{\beta + 1} \gamma^2 \right] \]

is a factor in each of the FCI given below in the expansions of Equation 2.5 for the next eight transitions. The use of the matrix notation is not meant to imply a determinant relation; at this point in the work, it is meant only for ease in reading.

\[
S_{0'0''}^2 = \frac{1}{2^{8/2}} S_{0''0'}^2
\]

\[
\begin{array}{cccc}
(-1)^0 & \frac{8!}{3!(8'-2*0)} & (-\sigma+2)^8 & (-\sigma+1)^0 \gamma^6 \\
(-1)^1 & \frac{8!}{1!(8'-2*1)} & (-\sigma+2)^6 & (-\sigma+1)^1 \gamma^6 \\
(-1)^2 & \frac{8!}{2!(8'-2*2)} & (-\sigma+2)^4 & (-\sigma+1)^2 \gamma^4 \\
(-1)^3 & \frac{8!}{3!(8'-2*3)} & (-\sigma+2)^2 & (-\sigma+1)^3 \gamma^2 \\
(-1)^4 & \frac{8!}{4!(8'-2*4)} & (-\sigma+2)^0 & (-\sigma+1)^4 \gamma^0 \\
\end{array}
\]

\[
= \frac{1}{2^{8/2}} S_{0''0'}^2
\]

\[
\begin{array}{cccc}
(-\sigma+2)^8 & (-\sigma+1)^0 \gamma^6 \\
-56 & (-\sigma+2)^6 & (-\sigma+1)^1 \gamma^6 \\
+840 & (-\sigma+2)^4 & (-\sigma+1)^2 \gamma^4 \\
-3360 & (-\sigma+2)^2 & (-\sigma+1)^3 \gamma^2 \\
-1680 & (-\sigma+2)^0 & (-\sigma+1)^4 \gamma^0 \\
\end{array}
\]

(AIII.1)

\[
S_{7'0''}^2 = \frac{1}{2^7} S_{0''0'}^2
\]

\[
\begin{array}{cccc}
(-\sigma+2)^7 & \gamma^7 \\
-42 & (-\sigma+2)^5 & (-\sigma+1) \gamma^5 \\
+420 & (-\sigma+2)^3 & (-\sigma+1)^2 \gamma^3 \\
-840 & (-\sigma+2) & (-\sigma+1)^3 \gamma \\
\end{array}
\]

(AIII.2)
\[ S^2_{\theta'\phi'} = \frac{1}{2\pi^2} S^2_{\theta'\phi'} \begin{vmatrix} (-\sigma + 2)^6 \gamma^6 \\ -30(-\sigma + 2)^4(-\sigma + 1)\gamma^4 \\ +180(-\sigma + 2)^2(-\sigma + 1)^2\gamma^2 \\ -120(-\sigma + 1)^3 \end{vmatrix}^2 \quad (\text{III.3}) \]

\[ S^2_{\theta'\phi'} = \frac{1}{2\pi^2} S^2_{\theta'\phi'} \begin{vmatrix} (-\sigma + 2)^5 \gamma^5 \\ -20(-\sigma + 2)^3(-\sigma + 1)\gamma^3 \\ +60(-\sigma + 2)(-\sigma + 1)^2\gamma \end{vmatrix}^2 \quad (\text{III.4}) \]

\[ S^2_{\phi'\phi'} = \frac{1}{2\pi^2} S^2_{\phi'\phi'} \begin{vmatrix} (-\sigma + 2)^4 \gamma^4 \\ +12(-\sigma + 2)^2(-\sigma + 1)\gamma^2 \\ +12(-\sigma + 1)^2 \end{vmatrix}^2 \quad (\text{III.5}) \]

\[ S^2_{\phi'\phi'} = \frac{1}{2\pi^2} S^2_{\phi'\phi'} \begin{vmatrix} \sigma + 2)^3 \gamma^3 - 6(-\sigma + 2)(-\sigma + 1)\gamma \end{vmatrix}^2 \quad (\text{III.6}) \]

\[ S^2_{\theta'\phi'} = \frac{1}{2\pi} S^2_{\phi'\phi'} \begin{vmatrix} (-\sigma + 2)^2 \gamma^2 - 2(-\sigma + 1) \end{vmatrix}^2 \quad (\text{III.7}) \]

\[ S^2_{\phi'\phi'} = \frac{1}{2\pi} S^2_{\phi'\phi'} \begin{vmatrix} \sigma + 2) \gamma \end{vmatrix}^2 \quad (\text{III.8}) \]

The full solutions for \( S^2_{\theta'\phi'} \) and \( S^2_{\phi'\phi'} \) are shown in the Appendix IV.
The full solutions for $S^{2}_{\nu'\nu}$ and $S^{3}_{\nu'\nu}$ are shown in this section so that the reader may have the opportunity to clarify the source of, and to verify the series notation of Equation 2.5. The full expression of the first FCI, given in Appendix II, is

$$S^{2}_{\nu'\nu} = C_{3} \int \exp(-a\xi^{2} - b\xi) \, d\xi \right|^{2}$$

$$= C_{3} \frac{\sqrt{\pi}}{\sqrt{a}} e^{\frac{a^{2}}{4a}}$$

We now show this expression is a factor in all higher level solutions.

Now, the derivation of the Franck-Condon integral for $\nu' \leftarrow \nu'' = 3' \leftarrow 0''$ proceeds as follows:

First, from the framework for the exact integrals, we find

$$S^{2}_{\nu'\nu} = C_{3} \frac{1}{2\nu''} \left| \int_{0}^{\infty} \exp(-a\xi^{2} - b\xi) H_{\nu''}(\sqrt{a^{2}} \xi + \gamma) \, d\xi \right|^{2}$$

Specifically for $\nu' = 3$, we have

$$S^{2}_{30} = \frac{\sqrt{\pi}}{\sqrt{2}} \frac{1}{2\nu''} \left| \int_{0}^{\infty} e^{\frac{-a\xi^{2}}{2}} e^{-\xi^{2}/2} e^{-\xi \xi} e^{-\xi \xi} e^{-\xi \xi} H_{3}(\sqrt{a^{2}} \xi + \gamma) \, d\xi \right|^{2}$$
where \( H_3(\sqrt{a^T}\xi + \gamma) = 8(\sqrt{a^T}\xi + \gamma)^3 - 12(\sqrt{a^T}\xi + \gamma) \). Consequently, \( S_{3y'}^2 \) becomes

\[
S_{3y'}^2 = \frac{1}{2a} \left| \int_0^\infty \exp(-a\xi^2 - b\xi - c_3) \left[ 8(\sqrt{a^T}\xi + \gamma)^3 - 12(\sqrt{a^T}\xi + \gamma) \right] d\xi \right|^2
\]

Removing the exponential involving \(-c_2\) from the integrand, gives \( C_3 = c\exp(-c_2) \)

and the result:

\[
S_{3y'}^2 = \frac{1}{2a} C_3 \left| \int_0^\infty \exp(-a\xi^2 - b\xi) \left[ 8(\sqrt{a^T}\xi + \gamma)^3 - 12(\sqrt{a^T}\xi + \gamma) \right] d\xi \right|^2
\]

Expanding the inner cubed terms yields

\[
(\sqrt{a^T}\xi + \gamma)^3 = (\sqrt{a^T}\xi + \gamma)(\sqrt{a^T}\xi)^2 + 2\gamma(\sqrt{a^T}\xi) + \gamma^2
\]

\[
= (\sqrt{a^T}\xi)^3 + 3\gamma(\sqrt{a^T}\xi)^2 + 3\gamma^2(\sqrt{a^T}\xi) + \gamma^3
\]

Replacement and distribution produces

\[
S_{3y'}^2 = \frac{1}{2a} C_3 \left| \int_0^\infty \exp(-a\xi^2 - b\xi) \left[ 8\left((\sqrt{a^T}\xi)^3 + 3\gamma(\sqrt{a^T}\xi)^2 + 3\gamma^2(\sqrt{a^T}\xi) + \gamma^3\right) - 12(\sqrt{a^T}\xi + \gamma) \right] d\xi \right|^2
\]

Distribution of the integrand sum yields

\[
S_{3y'}^2 = \frac{1}{2a} C_3 \left| \left[ 8(\sqrt{a^T}\xi)^3 \int_0^\infty \xi^3 \exp(-a\xi^2 - b\xi) d\xi \\
+ 24\gamma(\sqrt{a^T}\xi)^2 \int_0^\infty \xi^2 \exp(-a\xi^2 - b\xi) d\xi \\
+ 24\gamma^2(\sqrt{a^T}\xi) \int_0^\infty \xi \exp(-a\xi^2 - b\xi) d\xi \\
+ 8\gamma^3 \int_0^\infty \exp(-a\xi^2 - b\xi) d\xi \right]
\]

\[
+ 12(\sqrt{a^T}\xi) \int_0^\infty \xi \exp(-a\xi^2 - b\xi) d\xi \\
+ 12\gamma \int_0^\infty \exp(-a\xi^2 - b\xi) d\xi \right] \right| \right|^2
\]
The following substitutions are performed [8,14]:

The solution for the integral with the $\xi^0$ term is

$$\int_{-\infty}^{\infty} e^{-a\xi^2 - b\xi} d\xi = \frac{\sqrt{\pi} e^{-\frac{b^2}{4a}}}{\sqrt{a}}$$ (All.3)

The solution for the integral with the $\xi^1$ term is

$$\int_{-\infty}^{\infty} \xi e^{-a\xi^2 - b\xi} d\xi = \frac{\sqrt{\pi} \exp\left(\frac{b^2}{4a}\right) (-\frac{b}{2a})}{\sqrt{a}}b$$

The solution for the integral with the $\xi^2$ term is

$$\int_{-\infty}^{\infty} \xi^2 e^{-a\xi^2 - b\xi} d\xi = \frac{\sqrt{\pi} \exp\left(\frac{b^2}{4a}\right) (b^2 + 2a)}{\sqrt{a}}$$

$$= \frac{\sqrt{\pi} \exp\left(\frac{b^2}{4a}\right) (b^2 + 2a)}{\sqrt{a}}$$

The solution for the integral with the $\xi^3$ term

$$\int_{-\infty}^{\infty} \xi^3 e^{-a\xi^2 - b\xi} d\xi = \frac{\sqrt{\pi} \exp\left(\frac{b^2}{4a}\right) (b^3 + 6ab)}{\sqrt{a}}$$

$$= \frac{\sqrt{\pi} \exp\left(\frac{b^2}{4a}\right) (b^3 + 6ab)}{\sqrt{a}}$$

The above entries are included in the following equation. Their leading terms, factoring out Eq. All.4, yields

$$S_{300}^2 = \frac{1}{48} C_3 \frac{\sqrt{\pi} e^{-\frac{b^2}{4a}}}{\sqrt{a}}$$

$$\left[ \begin{array}{c} 8\left(\frac{\sqrt{a}}{a}\right)^3 (-\frac{b}{2a})^3 (b^3 + 6ab) \\
+24\sqrt{\pi} \left(\frac{\sqrt{a}}{a}\right)^2 (\frac{b}{2a})^2 (b^2 + 2a) \\
+24\sqrt{\pi} \left(\frac{\sqrt{a}}{a}\right) \left(\frac{b}{2a}\right) b \\
+8\sqrt{\pi} b \\
+12\sqrt{\pi} \left(\frac{b}{2a}\right) b \\
-12\sqrt{\pi} \end{array} \right]$$

Substituting $S_{300}^2$ yields...
Redistributing parameters for possible cancellation and consolidation yields:

\[
S_{30^\prime}^2 = \frac{1}{4\delta} S_{30^\prime}'^2
\]

\[
= \frac{1}{4\delta} \left( \begin{array}{c}
8\left(\sqrt{\delta}\right)^3\left(-\frac{1}{\delta}\right)^3b^3 \\
+6\left(\sqrt{\delta}\right)^3\left(-\frac{1}{\delta}\right)^2ab \\
+24\left(\sqrt{\delta}\right)^2\left(\frac{1}{\delta^2}\right)^2b^2 \\
+24\sqrt{\delta}\left(\frac{1}{\delta^2}\right)^22a \\
+8\sqrt{\delta} \\
+\left(-12\sqrt{\delta}\left(\frac{1}{\delta^2}\right)b \\
-12\sqrt{\delta} \end{array} \right) \right)^2
\]

Substitution of \( b = \sqrt{\delta} \gamma \) gives

\[
S_{30^\prime}^2 = \frac{1}{4\delta} S_{30^\prime}'^2
\]

\[
= \frac{1}{4\delta} \left( \begin{array}{c}
\left(-1\right)^3\left(\sqrt{\delta}\gamma\right)^3b^3 \\
+6\left(-1\right)^3\left(\sqrt{\delta}\gamma\right)^2ab \\
+6\left(-1\right)^2\left(\sqrt{\delta}\gamma\right)^2b^2 \gamma \\
+12\left(-1\right)^2\left(\sqrt{\delta}\gamma\right)^22a \gamma \\
+8\gamma^3 \\
-6\left(-1\right)\left(\sqrt{\delta}\gamma\right)b \\
-12\sqrt{\delta} \end{array} \right) \right)^2
\]
Consolidating like terms

\[
S^2_{30r} = \frac{1}{64} S^2_{50r}
\]

\[
\begin{bmatrix}
(-1)^3 \left(\frac{\alpha}{a}\right)^3 \left(\sqrt{a^2}\right)^3 y^3 \\
+6(-1)^3 \left(\frac{\alpha}{a}\right)^3 a \left(\sqrt{a^2}\right) y \\
+6(-1)^2 \left(\frac{\alpha}{a}\right)^2 \left(\sqrt{a^2}\right)^2 y^3 \\
+12(-1)^2 \left(\frac{\alpha}{a}\right)^2 a y \\
+12(-1)(\frac{\alpha}{a})(\sqrt{a^2}) y^3 \\
+8y^3 \\
-6(-1)(\frac{\alpha}{a})(\sqrt{a^2}) y \\
-12y
\end{bmatrix}
\begin{bmatrix}
-\left(\frac{y}{a}\right)^3 \\
+8\left(\frac{y}{a}\right)^2 y \\
-12\left(\frac{y}{a}\right) + 8
\end{bmatrix}
\begin{bmatrix}
-\left(\frac{y}{a}\right)^3 \\
+8\left(\frac{y}{a}\right)^2 y \\
-12\left(\frac{y}{a}\right) + 8
\end{bmatrix}
= \frac{1}{64} S^2_{50r}
\]

\[
S^2_{30r} = \frac{1}{64} S^2_{50r} \left[ (-1)^3 \left(\frac{\alpha}{a}\right)^3 y^3 + (-6 \left(\frac{\alpha}{a}\right)^3 + 18 \left(\frac{y}{a}\right) - 12) y \right]^2
\]

\[
= \frac{1}{64} S^2_{50r} \left[ (-1)^3 \left(\frac{\alpha}{a}\right)^3 y^3 + (-6 \left[ \left(\frac{y}{a}\right)^2 - 3 \left(\frac{y}{a}\right) + 2 \right] y \right]^2
\]

\[
S^2_{30r} = \frac{1}{64} S^2_{50r} \left[ (-1)^3 \left(\frac{\alpha}{a}\right)^3 y^3 - 6 \left(\frac{y}{a}\right) - 2 \left(\frac{y}{a}\right) - 1 \right]^2
\]

If we let \( \frac{y}{a} = \sigma \), we find

\[
S^2_{30r} = \frac{1}{64} S^2_{50r} \left[ (-y + 2)^3 y^3 - 6 (-y + 2)(-y + 1) \right]^2
\]

(AIII.6)

The derivation of the Franck-Condon integral for \( \nu' - \nu'' = 4' - 0'' \) proceeds in a similar way.

For \( \nu' = 4 \), we have

\[
S^2_{40r} = \left[ \frac{\sqrt{\alpha}}{a} \right]^2 \left[ \frac{1}{24i} \int_0^1 e^{-\frac{a}{\alpha} \xi^2} e^{-(\xi + \Delta \xi)} e^{-\frac{1}{4}(\xi + \Delta \xi)^2} H_\nu(\sqrt{a} (\xi + \Delta \xi)) d\xi \right]^2
\]

where

\[
H_\nu(\sqrt{\alpha} (\xi + \Delta \xi)) = 16(\sqrt{\alpha} (\xi + \Delta \xi))^4 - 48(\sqrt{\alpha} (\xi + \Delta \xi))^2 + 12.
\]

148
Consequently, \( S_{4v^0} \) becomes

\[
S_{4v^0}^2 = \frac{1}{24a} C_2 \int_0^\infty \exp(-a\xi^2 - b\xi - c_2) \left[ 16(\sqrt{a^2} + \gamma)^4 - 48(\sqrt{a^2} + \gamma)^2 + 12 \right] d\xi
\]

Again, removing the exponential involving \(-c_2\) from the integral to form the constant \( C_3 = c|\exp(-c_2)|^2 \) yields

\[
S_{4v^0}^2 = \frac{1}{32a} C_3 \int_0^\infty \exp(-a\xi^2 - b\xi) \left[ 16(\sqrt{a^2} + \gamma)^4 - 48(\sqrt{a^2} + \gamma)^2 + 12 \right] d\xi
\]

Expanding inner squared term leads to

\[
(\sqrt{a^2} + \gamma)^2 = (\sqrt{a^2} + \gamma)((\sqrt{a^2} + \gamma)^2 + 2\gamma(\sqrt{a^2} + \gamma) + \gamma^2)
\]

\[
= (\sqrt{a^2} + \gamma)^3 + 3\gamma(\sqrt{a^2} + \gamma)^2 + 3\gamma^2(\sqrt{a^2} + \gamma) + \gamma^3
\]

\[
(\sqrt{a^2} + \gamma)^4 = (\sqrt{a^2} + \gamma)((\sqrt{a^2} + \gamma)^3 + 3\gamma(\sqrt{a^2} + \gamma)^2 + 3\gamma^2(\sqrt{a^2} + \gamma) + \gamma^3)
\]

\[
= (\sqrt{a^2} + \gamma)^4 + 4\gamma(\sqrt{a^2} + \gamma)^3 + 6\gamma^2(\sqrt{a^2} + \gamma)^2 + 4\gamma^3(\sqrt{a^2} + \gamma) + \gamma^4
\]

whence

\[
S_{4v^0}^2 = \frac{1}{32a} C_3 \int_0^\infty d\xi \exp(-a\xi^2 - b\xi) \exp\left[ 16((\sqrt{a^2} + \gamma)^4 + 4\gamma(\sqrt{a^2} + \gamma)^3 + 6\gamma^2(\sqrt{a^2} + \gamma)^2 + 4\gamma^3(\sqrt{a^2} + \gamma) + \gamma^4) - 48((\sqrt{a^2} + \gamma)^2 + 2\gamma(\sqrt{a^2} + \gamma) + \gamma^2) + 12 \right]
\]

Distributing the integrand sum yields
The solution for the integral with the $\xi^4$ term is

$$\int_0^\infty \xi^4 e^{-a\xi^2} e^{-\beta \xi} d\xi = \frac{\sqrt{\pi}}{16a^3} \exp\left(\frac{b^2}{a^2}\right) (12a^2 + 12ab^2 + b^4)$$

$$= \frac{\sqrt{\pi}}{a^\frac{3}{2}} \exp\left(\frac{b^2}{a^2}\right) (-\frac{1}{2a})^4 (12a^2 + 12ab^2 + b^4)$$

Solutions for the other component integrals are the same as those found in the solution for $v' = 3'$.

For the transition $v' \to v'' = 4' \to 0''$ the integral, including the factor $\frac{\sqrt{\pi} \exp\left(\frac{b^2}{a^2}\right)}{a^\frac{3}{2}}$, can now be written as

$$S_{40''} = \frac{1}{384} C_3 \left[ \frac{\sqrt{\pi} \exp\left(\frac{b^2}{a^2}\right)}{\frac{3}{8}} \right]^2$$

$$\begin{bmatrix}
16(\sqrt{a'} \xi)^4 \exp(-a\xi^2 - b\xi) \\
+84\gamma(\sqrt{a'} \xi)^3 \exp(-a\xi^2 - b\xi) \\
+96\gamma^2(\sqrt{a'} \xi)^2 \exp(-a\xi^2 - b\xi) \\
+84\gamma^3(\sqrt{a'} \xi) \exp(-a\xi^2 - b\xi) \\
+16\gamma^4 \exp(-a\xi^2 - b\xi)
\end{bmatrix}^2$$

$$\begin{bmatrix}
-48(\sqrt{a'} \xi)^2 \exp(-a\xi^2 - b\xi) \\
-96\gamma(\sqrt{a'} \xi) \exp(-a\xi^2 - b\xi) \\
-48\gamma^2 \exp(-a\xi^2 - b\xi) \\
+12 \exp(-a\xi^2 - b\xi)
\end{bmatrix}$$
We continue to consolidate and simplify, to find

\[
S_{\text{A0r}}^2 = \frac{1}{364} S_{\text{vo}}^2
\]

\[
16 \left( (-\frac{1}{2a})^4 \left( \sqrt{a'} \right)^4 \left( \sqrt{a'} \gamma \right)^4 + (-\frac{1}{2a})^4 \left( \sqrt{a'} \right)^4 12\alpha \left( \sqrt{a'} \gamma \right)^2 + (-\frac{1}{2a})^4 \left( \sqrt{a'} \right)^4 12\alpha^2 + 4(-\frac{1}{2a})^3 \left( \sqrt{a'} \right)^3 \left( \sqrt{a'} \gamma \right)^3 \gamma + 4(-\frac{1}{2a})^3 \left( \sqrt{a'} \right)^3 6\alpha \left( \sqrt{a'} \gamma \right)^\gamma + 6(\frac{1}{2a})^3 \left( \sqrt{a'} \right)^3 \left( \sqrt{a'} \gamma \right)^2 \gamma^2 - 6(\frac{1}{2a})^2 \left( \sqrt{a'} \right)^2 \left( \sqrt{a'} \gamma \right)^2 \gamma^2 + 4(\frac{1}{2a}) \left( \sqrt{a'} \right) \left( \sqrt{a'} \gamma \right)^3 \gamma^4 - 48 \right) \]

Consecutive consolidation and/or rearrangement of the parameters within each large bracket inside the integral (without further comment) yields

\[
S_{\text{A0r}}^2 = \frac{1}{364} S_{\text{vo}}^2
\]

\[
16 \left( (-\frac{1}{2a})^4 \left( \sqrt{a'} \right)^4 \left( \sqrt{a'} \gamma \right)^4 + (-\frac{1}{2a})^4 \left( \sqrt{a'} \right)^4 12\alpha \left( \sqrt{a'} \gamma \right)^2 + (-\frac{1}{2a})^4 \left( \sqrt{a'} \right)^4 12\alpha^2 + 4(-\frac{1}{2a})^3 \left( \sqrt{a'} \right)^3 \left( \sqrt{a'} \gamma \right)^3 \gamma + 4(-\frac{1}{2a})^3 \left( \sqrt{a'} \right)^3 6\alpha \left( \sqrt{a'} \gamma \right)^\gamma + 6(\frac{1}{2a})^3 \left( \sqrt{a'} \right)^3 \left( \sqrt{a'} \gamma \right)^2 \gamma^2 + 6(\frac{1}{2a})^2 \left( \sqrt{a'} \right)^2 \left( \sqrt{a'} \gamma \right)^2 \gamma^2 + 4(\frac{1}{2a}) \left( \sqrt{a'} \right) \left( \sqrt{a'} \gamma \right)^3 \gamma^4 - 48 \right) \]

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\[
\begin{align*}
\frac{1}{384} S^2_{000} &= \left[ (-1)^4 \frac{1}{16} \left( \frac{3}{4} \right)^4 \gamma^4 
+ (-1)^4 \frac{3}{16} \left( \frac{3}{4} \right)^3 \gamma^2 
+ (-1)^4 \frac{1}{16} \left( \frac{3}{4} \right)^2 \gamma^2 
+ (-1)^4 \frac{3}{16} \left( \frac{3}{4} \right)^2 \gamma^2 
+ (-1)^4 \frac{1}{16} \left( \frac{3}{4} \right)^2 \gamma^2 
\right] \cdot 16 \\
&= -48 \\
&+ 12 \end{align*}
\]
\[
S_{4\text{vo}}^2 = \frac{1}{384} S_{4\text{vo}}^2 \cdot \left(\begin{array}{c}
(\frac{1}{4})^4 \gamma^4 \\
-8(\frac{1}{4})^3 \gamma^4 \\
+24(\frac{1}{4})^2 \gamma^4 \\
-32(\frac{1}{4}) \gamma^4 \\
+12(\frac{1}{4})^3 \gamma^2 \\
-48(\frac{1}{4})^2 \gamma^2 \\
+48(\frac{1}{4}) \gamma^2 \\
+12(\frac{1}{4})^2 \gamma \\
-24(\frac{1}{4}) \\
+12 \\
\end{array}\right)\]

\[
S_{4\text{vo}}^2 = \frac{1}{384} S_{4\text{vo}}^2 \cdot \left[\begin{array}{c}
(\frac{1}{4})^4 - 8(\frac{1}{4})^3 + 24(\frac{1}{4})^2 - 32(\frac{1}{4}) + 1 \\
-32(\frac{1}{4})^4 \\
+12(\frac{1}{4})^3 - 48(\frac{1}{4})^2 - 12(\frac{1}{4})^2 \\
+48(\frac{1}{4}) - 48 \\
+12(\frac{1}{4})^2 - 24(\frac{1}{4}) + 12 \\
\end{array}\right] \gamma^4
\]

The solutions shown above, along with the other six exact solutions were juxtaposed as in Appendix III, whence it was determined by trial and error that they constituted members of the general series of Eq. 2.5.
APPENDIX V

COMPARATIVE FRANCK-CONDON INTEGRALS

Carl J. Ballhausen, CJB, [4], for instance, has obtained an analytic expression for the Franck-Condon overlap integral of interest in this work. Beginning with the harmonic oscillator wave function

$$\chi_f = \sqrt{\left(\frac{\pi}{2a}\right)^{1/2}} \exp\left(-\frac{1}{2} a \zeta^2\right) H_j\left(\sqrt{a} \zeta\right)$$  \hspace{1cm} (AI.2)

Ballhausen's overlap integral equation is

$$\langle \chi_f | \chi_{f'} \rangle = \left(\frac{\pi}{2a}\right)^{1/2} \left(\frac{a}{a'}\right)^{1/2} H_j\left[\frac{a}{a'} \sqrt{\frac{a}{a'}} \Delta \zeta\right]$$ \hspace{1cm} (CJB: 4.108)

where

$$\langle \chi_f | \chi_{f'} \rangle = \exp\left[-\frac{a a'}{2(a^2 + a'^2)}(\Delta \zeta)^2\right] \sqrt{\frac{a a'}{1(a^2 + a'^2)}}$$ \hspace{1cm} (CJB: 4.107)

and the notation is identical to that which is used in Chapter 2. If we now make the following definitions

$$\frac{s}{a} = s$$

$$a^2(\Delta \zeta)^2/2 = a^2$$

and take the absolute value of Equation (CJB: 4.108), we find the Wolfgang P. Schleich, WPS, [17] equation:

$$W_m = \frac{2^{s/2}}{(2m+1)} \left(2^{m+1}\right)^{1/2} \exp\left[-\frac{2s+1}{2s+1} a^2 \right]$$ \hspace{1cm} (WPS: 6)

Thus, the Ballhausen and Schleich equations are identical.

If we now make the substitutions

$$-\sigma + 2 = \frac{2s}{s+1}$$

$$-\sigma + 1 = \frac{s-1}{s+1}$$

$$\gamma^2 = 2a^2$$

154
and identify $m$ as $v'$, we generate, for $m = 0, 1, 2, 3, 4, ... , 8$ the equations labeled as Equations All.I.1 through All.I.8 of Appendix III.

Thus, these equations, as also the Schleich equation, are consistent with the Ballhausen equation. We learned of the Schleich works, thanks to Professor Robert O'Connell of the Physics Department at LSU, after we had completed the theoretical portion of our research and a major portion of our experimental research. With earlier discovery of these equations and the positions introduced by their authors, more progress with the approximations' objectives of the thesis could have been made.

The work of Von Max Wagner, VMW, [18] is also pertinent to our study. Wagner obtained an exact solution to the $\langle x_{\nu} | x_{\rho} \rangle$ integral but was unable to formulate this solution in terms of a single, known polynomial. Wagner's expression is

$$\langle \varphi_n | \varphi_m \rangle = K \left( \sqrt{2k} \sum_{\mu} \frac{m^{m+n}}{\mu^{m+n}} \He_{m+n} \left( \sqrt{\frac{m+n}{2k}} \right) \right) \left( \sqrt{\frac{m-n}{2k}} \right) \left( \sqrt{\frac{m-n}{2k}} \right) \He_{m-n} \left( \sqrt{\frac{m+n}{2k}} \right)$$

(VMW: 49)

This equation appears to have common components with the equations studied, Ballhausen and Schleich, and to our general equation, Equation 2.5. Unfortunately, time being a critical factor, we were unable to delve into its intricacies and had to postpone its study to a later time.
VITA

Dorothy Marie Wood was born to Anne Gertrude Rodrigue Wood and James Joseph Wood on June 20, 1943, in the parish of St. James, Louisiana, USA. Their land on the banks of the Mississippi was named "Point Brilliant", probably by Native Americans. Her father, as a consequence of being the sole survivor of his family in World War II, remained home to run the family businesses which included a very large country store with a roll-top desk; sugarcane planting was added after the war. The store and farm were Dorothy's first experiences with mathematics and meticulous record-keeping by her parents. Nearby, her paternal grandfather, John Trimble Wood, had obtained Sally Plantation, a 100-acre farm for his wife, Leah Alexander and their family. Dorothy's family lived there following a complete destruction by fire of her parents' original home. Several miles from Sally, her maternal grandfather, Maxime Rodrigue, had built a machine shop business where she observed what seemed to be the operation of giant lathes, the sparks of the welding machines and other technical work his employees performed in order to repair river barges and build sport yachts. Dorothy observed the activity from the sunroom of his neighboring house where his wife, Ludivine Torres Rodrigue, Dorothy's grandmother, explained as best she could to her curious grandchildren, the high tech goings-on in the shop. Dorothy attended St. James High School, the same school attended by her parents. Her children, Joey, Kermit Joseph Babin, Jr., of Clinton, Louisiana, and Dee Dee, Jean Monique Babin-Gibson, of Austin, Texas are graduates of Lee High School in Baton Rouge and Louisiana State University, engineering and economics, respectively. Jean Monique is also a master's graduate of Florida State University.
Candidate: Dorothy Marie Wood

Major Field: Chemistry

Title of Dissertation: The Geometry of Electronically-Excited States: Vibronic Intensity Distributions and Bond Length Changes

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Dean of the Graduate School

EXAMINING COMMITTEE:

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Date of Examination: February 6, 2001