Rydberg States of Polyatomic Molecules: Multichannel Approaches for the Simple Halides.

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RYDBERG STATES OF POLYATOMIC MOLECULES: MULTICHANNEL APPROACHES FOR THE SIMPLE HALIDES

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RYDBERG STATES OF POLYATOMIC MOLECULES:
MULTICHANNEL APPROACHES FOR THE
SIMPLE HALIDES

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in
The Department of Chemistry

by
John A. Dagata
B.A., Rhode Island College, 1979
December 1983
To my wife and parents
ACKNOWLEDGEMENTS

I wish to sincerely thank my advisor, Professor S. P. McGlynn, for providing guidance and support during the course of this investigation. I would like to express my gratitude to Professor A. R. P. Rau for the interest he has shown in this work and for many discussions over the past year. These exchanges were always helpful and enjoyable to me. I would also like to express appreciation for the suggestions and hospitality of Dr. K. T. Lu during my visit to Argonne. Many key aspects of the present work appear as a direct result of our conversations.

In addition, I acknowledge the benefit I have derived from many discussions of spectroscopy I have had with Professor G. L. Findley and Dr. W. S. Felps. A special thanks is due to Professor C. J. Marzzacco for his encouragement.

Research was supported by the United States Department of Energy. Financial assistance for the preparation of this dissertation was provided from the "Dr. Charles E. Coates Memorial Fund of Louisiana State University Foundation" donated by George H. Coates.

Finally, I wish to thank Ms. Sue Scott and Ms. Donann Lee for the efficient wordprocessing of this manuscript.

John A. Dagata
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ABSTRACT:

A major portion of the high resolution photoabsorption spectrum of methyl iodide in the region between 49000 and 77000 cm$^{-1}$ has been analyzed by methods based on multichannel quantum defect theory (MQDT.) Nearly all bands in this energy region can be assigned as members of molecular rydberg series which converge to the two lowest ionization limits of the molecule.

However, it is also found that the Born-Oppenheimer separability of the totality of electronic surfaces is not nearly as complete as might be implied by the above results. Specifically, a nonrydberg, valence electronic state is shown to interact with the rydberg progressions and to produce anomalous intensity and position variations of the series members. Evidence is presented which indicates that this state, which is also observed in other alkyl halides, is related to the charge-transfer complex CH$_3$I$^-$. 

Thus, the role of rydberg series as probes of the subtle dynamics of electrons in atoms is transferable to molecules, namely, to the simple halides, and these series constitute an important device with which to gauge the complicated dynamics of highly excited molecules. Further experimental and theoretical work which could extend our comprehension of these processes is discussed.
INTRODUCTION:

Recent advances in molecular spectroscopic and beam techniques permit the production and resolution of highly excited transitions lying in spectral regions where the density of states is very high. Techniques which can photoselect an individual vibronic level from those nearby are commonplace. On the other hand, standard perturbative methods for handling state interactions prove to be inadequate in such regions. The problem, in part, lies in the limited ability of all current models to delineate those rules which govern the relative probabilities of molecular energy acquisition by optical or collisional excitation, the partitioning of this energy among various directly coupled states and the subsequent deexcitation or fragmentation to other energetically accessible sets of states not initially connected to the ground state. Indeed, it is generally impossible to "hold a sufficient number of variables fixed" in a polyatomic molecule, even under very precise experimental situations, or to elicit much about the exact details of energy transfer among many possible relaxation modes. Complementary experimental observations in this spectral region must be related through a framework capable of unifying molecular processes that have traditionally appeared quite unrelated.

Insight into the nature of many of these processes is available from the spectroscopy of the hydrogen and n-alkyl halides (which we
collectively denote the "simple halides"). The detailed analysis of the electronic states of these molecules and their interactions is relatively straightforward since the electronic surfaces of these excited states are predominantly rydberglike (see below), and the inherent regularity of rydberg series over a substantial energy range allows them to act as a sensitive probe of both rydberg-rydberg and rydberg-valence interactions. Until recently, it has not been possible to observe these series at a resolution sufficient to exploit this ability to probe interactions, though the analytical part had been articulated in the linear correlation approach of Wang.¹ Later, we will appeal to this latter empirical result which states that the same rydberg transition in two different, but related, molecules can be understood by partitioning the system into chromophoric and substituent functionalities. The halogen atom for the simple halides can be identified as the chromophore. The alkyl group, possessing only sigma-type orbitals, has electronically excited states considerably higher in energy than the nonbonding p-electrons of the halogen. It is optically transparent for our purposes and therefore constitutes the substituent. The band shifts produced by alkyl replacement are generally small and predictable. These molecules have been the subject of considerable photoabsorption, photoionization and photoelectron studies as well as experiments that have probed photodissociation from the lowest-energy repulsive states. Extensive work has been done on the positive ion and the
spectroscopy of some of the radical fragments is also known. The electronic potential surfaces of these molecules have been considered to be rydberglike but this is only partially correct since predissociation is evident at nearly all energies for the alkyl halides though to a lesser degree, apparently, in the hydrogen halides.

It is important that this class of molecules, the simple halides, be well understood because it lends itself to a very detailed, systematic analysis of the entire set of excited electronic states generated by one-electron valence-shell transitions. Implicit in this supposition is the sense that the change from atom to molecule can be visualized as an essentially smooth, predictable redistribution of electronic charge density in both the ground and excited state. One is led to consider the following examples of operations of this type:

i) the breaking of spherical symmetry into the finite point group of the nuclear geometry of the molecule;

ii) variations of the nuclear geometry about the relative equilibrium positions of the nuclei (Born-Oppenheimer Approximation);

iii) substitution of one element of the chromophoric part of a molecule by another from the same column of the periodic table, or, more generally, an appropriate substitution by a related functional group; and
iv) substitution of the "optically transparent" part of
the molecule by other transparent atoms or functional
groups.

It is evident that structural stability under i) is a fundamental
requisite of molecular functionality, reactivity and absorptivity.
Furthermore, it can be appreciated that the validity of the supposed
smooth changes conditioned by iii) and iv) depends strongly on both
i) and ii).

By implementing a form of Seaton's multichannel quantum defect
theory\(^2\) (MQDT) that was developed by Lu\(^3\) for the analysis of
atomic photoabsorption and photoionization data and by applying it
to the recently available high resolution photoabsorption spectrum
of methyl iodide, a relatively simple interpretation of the
electronic state structure of this molecule has emerged. This same
interpretation should apply equally well to all simple halides.
Specifically, it is possible to assign all highly excited levels to
a weakly-coupled complex of the ground electronic state of the
molecular ion core (CH\(_3\)I\(^+\)) plus a rydberg electron with
orbitals labeled \((n;\ell_e;j_e)\) where \(n\) is a principal quantum number and
\(\ell_e\) and \(j_e\) are the orbital and total electronic angular momentum
quantum numbers, respectively.

This labeling scheme is correct, of course, only for high \(n\)
rydberg states and for cases where the spin-orbit interaction is
large enough so that this limit is rapidly approached with increasing n. It must be mentioned, however, that as yet no satisfactory labeling scheme offers a similar simplification for classifying the lower series members. This limitation should not detract from the main result of this dissertation in which virtually every observed transition in the energy range 72000 to 82000 cm$^{-1}$ of the methyl iodide photoabsorption spectrum has been assigned as a member of one of fourteen rydberg series converging on the ground state molecular ion core limit.

Each of these rydberg series, together with its adjoined continuum, constitutes a channel. A set of optimized parameters, which will be described in the next chapter, is obtained by fitting theoretical curves to the experimental energy positions of the series members. Because these parameters yield information on the rydberg orbital-core overlap and the mutual interactions of all coupled series, the changes in parameter values can be used to quantify the effects of substitutions on the local environment of the optical electron as the chromophore or substituent is varied.

The spectrum of the methyl iodide molecule does not fully yield to such a simple scheme because interactions with a valence state alter positions and intensities of particular series members. These perturbations are identifiable in the vicinity of the dissociation limit of the ion-pair complex ($\text{CH}_3^+\text{I}^-$) and appear to exert the largest effects on levels that have been assigned the
quantum numbers \((n; l_e = s, p; j_e = 1/2)\). This observation is consistent with the expected effects of core penetration by electron orbitals of low orbital angular momentum and with the implication that the stability of the ion-pair complex is primarily associable with the filled 5p subshell of the iodine negative ion, \((\text{i.e., } I^- (5p^6))\). The term symbol of this valence state in the spectroscopic notation of linear molecules is \('\Sigma^+\) and we are lead to the expectation that spin-dependent interactions may be an important factor. This will be so because the valence state is more appropriately represented by the \((\Lambda, S)\) coupling scheme even though it occurs energetically in a region where nearby rydberg levels are best represented in \((j_e, n)\) coupling. The presence of this alternate channel causes rapid oscillations in the radial wavefunction of the rydberg electron inside the molecular core where electron-electron exchange terms are important. These additional oscillations introduce effects that cannot be accounted for in the original form of MQDT which solely treated the coupling of rydberg series. Here we are describing the mixing of rydberg and valence states. Inasmuch as rydberg-rydberg interactions are completely described by MQDT and, recalling the fact that these states are clearly well-defined within the Born-Oppenheimer Approximation, it is therefore permissible to equate Born-Oppenheimer breakdown with interactions of this kind. (For simplicity we have considered only a single valence channel. See Chapter Two for further details.) One of the goals of this dissertation is to demonstrate that this
rydberg-valence interaction is observed in other alkyl iodide spectra as well. The transferability of electronic state structure that had been shown by Wang to apply to rydberg series of a set of related molecules is extended in this work to include valence states for which such a comparison is also meaningful.

This dissertation is divided into the following chapters:

----- the origin and role of QDT are developed in Chapter One. The viewpoint that this theory is a useful spectroscopic tool is developed. Criteria for rydberg states in atomic and molecular systems that have been put forward previously by others are briefly reviewed.

----- the Second Chapter begins with the interpretation of the high resolution photoabsorption spectrum of methyl iodide. This is followed by more general considerations concerning the systematics of the ordering of relative orbital energies in the simple halides. This data, together with what is presently known about the dynamics of fragmentation in these systems, is then used to infer the general nature of the rydberg-valence interactions responsible for deviations from the expected pattern were the Born Oppenheimer Approximation valid at all energies.

----- in the Third and final Chapter, the experimental data and theoretical apparatus necessary to bring about a global description
of the excited state manifold of the simple halides are described and enumerated.
REFERENCES:

CHAPTER ONE.

ATOMIC AND MOLECULAR RYDBERG STATES.
INTRODUCTION.

It is not possible to discuss highly-excited molecular electronic states without 1) the consideration of rydberg orbitals and, hence, conditions for the observation of rydberg series in photoabsorption/photoemission spectra; 2) the criteria for the existence of these orbitals; 3) the relation between the molecular orbitals and the atomic orbitals which serve as their precursors; 4) the geometry of the rydberg states relative to the ground state; and 5) the nature of the interaction of rydberg states with valence states. All of these, of course, are phenomenologically-inspired questions posed by Robin in his two volumes on the electronic vacuum ultraviolet spectra of polyatomic molecules. The key attitudes pertinent to a theoretical basis for all of these queries had been discussed previously by Mulliken as elaborations from his studies of the special case of \( \text{H}_2 \)-like diatomics. Nevertheless, these questions have largely gone unanswered except in a few particular cases.

Meanwhile, atomic spectroscopy and theory have become subjects of renewed interest, in part due to technological advances (the synchrotron and laser, for example) but also because the accuracy of numerical calculations is on a par with the very best that high-resolution experimental studies can provide. This has resulted in successful efforts to rid the theoretical framework of
inefficient methodologies -- the multichannel quantum defect theory of Seaton\textsuperscript{3} being one such example. Another example that we only mention here is the recent development of methods of treating electron-electron correlation in doubly-excited states of atoms\textsuperscript{4}.

The spectroscopic analysis of polyatomic molecules in the vacuum ultraviolet (VUV) region, uses, of necessity, indirect means of identification of band systems. Where applicable, atomic, diatomic or functional group similarities can be exploited and justified after extensive, systematic comparisons of the behavior of a large number of related chromophores are made. The linear correlation approach of Wang has demonstrated the utility of this last approach for the case of molecular rydberg states.

Molecular rydberg states, however, are not line spectra. Partially resolved rotational bands and overlapping levels broaden the spectrum and these effects are complicated further by predissociation and autoionization phenomena. The present work, then, derives from the application of MQDT to spectra which are adequately well-resolved so that the rotational envelope approximates a purely electronic transition.

It is the aim of the first section of this chapter to review briefly the concepts of atomic and molecular rydberg series and the ways in which they are related. The second section will present the theoretical basis of quantum defect methods and their application.
I. BACKGROUND.

A. THE BOHR-SOMMERFELD ATOM.

Bohr's theory of the hydrogen atom is, of course, well-known. Before the old quantum theory was abandoned with the advent of Quantum Mechanics many attempts had been made to apply it to more complex atoms. Bohr's success was a result of the fact that the hydrogen atom energy levels form a simple convergent series, discovered empirically by Balmer and later generalized as the Rydberg-Ritz combination principle:

\[ E = R \left( \frac{1}{m^2} - \frac{1}{n^2} \right) \]  

where \( m \) and \( n \) are integers and \( R \) is the rydberg constant. The integers in the terms were considered, in the old quantum theory, to arise from the pure coulomb potential and the quantization of the action integrals:

\[ J_i = \oint p_i dq_i = n_i \hbar \]  

The above equation, of course, is the Bohr-Sommerfeld quantization condition for periodic motion in separable systems. Sommerfeld\(^5\), in his attempts to obtain a theoretical explanation for Rydberg's empirical term equation for series of lines in the spectra of the alkali atoms, which is,

\[ \frac{R}{(n-\mu)^2} \]
where \( \mu \) is a quantum defect, struck upon the underlying principle of all quantum defect methods. Sommerfeld reasoned that for a system consisting of a single, highly-excited electron whose orbit lies primarily outside a core region containing the atomic nucleus of charge \( Z \) and the remaining \( Z-1 \) other electrons, the true potential can be approximated by an expansion in powers of \( r^{-1} \), \( r \) being the radial distance of the electron from the core, so that evidently \( \mu \) is a measure of the effect of all terms other than \( r^{-1} \), the leading coulombic term.

The constancy of \( \mu \) for a given series reflects the similarities of the Bohr orbits for all members of the series whereas the magnitude of the quantum defect reflects the degree of core penetration by the rydberg electron. Attempts to extend this model to atoms other than the alkali metals were unsatisfactory because open-shell configurations produce ground states which cannot be associated with a single configuration and which, in turn, lead to low-lying, doubly-excited states and multiple ionization limits that severely complicate absorption and emission spectra. It should be noted that a complete theory of multiply-excited states has not yet been formulated. (See, however, Reference 4.)

B. THE QUANTUM MECHANICAL ATOM.

To the extent that rydberg series are the predominant type of transition observed in the excitation or emission spectra of atoms,
it may be said that quantum defect theory (QDT) and its many-channel analog, MQDT, represent a satisfactory theory of the atomic valence shell. Much of the emphasis of QDT centers on the threshold behavior, a result that could be expected from the relationship between the ionization potential and the limiting term value. As such, highly excited bound orbitals and low-lying continuum states are sufficiently extended outside the atomic core so that

i) relative to analytically-known coulomb wavefunctions, the actual wavefunctions, those that reflect the additional short-range interactions, can be easily constructed for asymptotically large values of the electron-core radial distance by using the quantum defect $\mu$ (for $\epsilon<0$) or a scattering phase shift $\delta$ (for $\epsilon>0$). The symbol $\epsilon$ denotes energy scaled relative to the ionization threshold; it is negative for bound states and positive in the continuum;

ii) across threshold, a smooth extrapolation connects $\mu$ and $\delta$; furthermore, these parameters are amenable to calculation or can be obtained from experimental data; and,

iii) the boundary conditions on the radial wavefunctions, at infinity (i.e., that the wavefunctions must vanish
(\varepsilon<0) or remain finite (\varepsilon>0)) are imposed only as a final step. In this view, the rydberg series and the (smoothly) adjoined continuum can be referred to, and treated as, a rydberg channel. The advantage in this approach is that the more general methods of scattering theory \textsuperscript{6} may also be applied to bound states. As a result, even in the presence of extensive rydberg series mixing, one can avoid the difficulty of summing perturbation expansions of infinite orders. The treatment of the rare gas xenon will be used to exemplify these methods.

C. THE RYDBERG STATES OF MOLECULES.

Rydberg series have been observed in many types of diatomic and polyatomic molecules but except for a small number of light diatomics (e.g., H\textsubscript{2}, He\textsubscript{2}, N\textsubscript{2}, and NO which have held a prominent place in theoretical and experimental spectroscopy) few others have unambiguously assigned rydberg progressions. Indeed, even among the light diatomics, the analyses are usually confined to the first few members. The reason is fairly obvious: for large values of the effective quantum number, the energy separation between electronic origins becomes comparable to rotational spacings. Thus, in general, diatomics may not be the most appropriate molecules to analyze for rydberg structure. Since the
regularity of rydberg series offers an important, detailed profile of internal structure, this is unfortunate because the angular coupling problem for diatomics, which is a generalization of the Hund's coupling cases, has been worked out by Chang and Fano\textsuperscript{7} and Fano and Dill\textsuperscript{8} in the frame transformation theory. Recall that orthogonal sets of wavefunctions, appropriate for the laboratory and molecular reference frames, can be rigorously labeled by component angular momentum quantum numbers. A single radial variable, the internuclear distance, remains after separating and integrating out these variables. The transformation that expresses the recoupling of these angular variables subject to total angular momentum conservation is represented by a matrix $U_{\alpha \beta}$, where the row index $i$ and the column index $\alpha$ refer to complete, conserved sets of angular quantum numbers which are appropriate to laboratory and molecular frames, respectively. The frame transformation is an integral part of multichannel methods because it allows one to express a total bound or continuum wavefunction as a linear combination of products of a radial scattering wavefunction and a residual part. (Actually, there is no need to restrict this argument to lab frame/body frame transformations. Any short-range interaction operator that causes a complete set of scattering state to mix at small values of a radial coordinate can be put into this form. See Section II.C of this chapter.) In summary then, while rydberg series in diatomics admit known solutions, only the absorption/emission spectra of a few prototypical molecules
(e.g., those listed above) are sufficiently well-characterized to allow the rigorous application of these theories.

In polyatomic molecules, on the other hand, one often has suppressed rotational structure (i.e., the rotational constants can be considered vanishingly small). In this situation, the complete description of angular momentum coupling is not possible. This is not due to a lack of a frame transformation theory for polyatomics but, rather, because a rotational analysis is necessary to extract conserved angular momentum quantum numbers and, hence, obtain state labels. The electronic origin of a photoabsorption band in a polyatomic molecule becomes the locus for the entire oscillator strength of (unresolved) rotational levels. This is the primary reason that rydberg levels are observed even at high principal quantum numbers in polyatomics. Therefore, the problem of the analysis of these highly-excited states of polyatomic molecules, even fairly simple ones, depends on reliable spectral data for a related class of molecules where the emphasis lies in tracing similarities in band shapes, positions, and intensities.

D. THE LINEAR CORRELATION OF WANG.

The linear correlation method of Wang attempts to utilize regularity of rydberg series in order to generate a smooth extrapolation of term values from atoms to molecules as well as
within groups of related molecules. Since relatedness in the above sense refers to small changes in the local ground and excited state environments of the optical electron caused by changes in the average charge distribution, systematic shifts in the magnitude of the quantum defect are expected to vary in predictable ways. On a coarse scale of energy data, this scheme works quite well. However, term values of penetrating orbitals can be subject to large deviations from expected values when the collection of potential curves which generate the rydberg series under consideration becomes interspersed with other potential curves of the same symmetry, leading to Born-Oppenheimer breakdown if the perturbers are valence states, or series coupling, if the perturbing states belong to other rydberg series.

E. THE PRESENT APPROACH

The main appeal of MQDT is that channel coupling is not restricted to electronic transitions nor indeed to channels that are only of a specific type. Whether reference is made to ionization or dissociation, which latter also requires a specification of electronic or molecular fragment states, the formalism is completely general.

The main goal of this dissertation is to indicate how multichannel methods, in conjunction with the Wang correlation approach can extend a detailed analysis of state interactions to
molecular absorption spectra which contain many perturbed, though relatively well-defined, transitions. In particular, we enquire into what can be determined about the meaningfulness of quantum numbers and symmetry relations that exist in polyatomic situations. We will show that, at least for the simple halides, an MQDT-based interpretation will sort out the rydberg electronic states of the molecules and their mutual interactions. However, it must be emphasized that, as an assignment device, MQDT does not determine state labels but merely coupling and phase shift parameters. Other spectroscopic methods must be used to obtain the appropriate symmetry labels of these states.
II. QUANTUM DEFECT THEORY.

The quantum defect theory of Seaton\textsuperscript{2,10} established the connection between the behavior of an electron in the coulomb field of a positive ion below and above the ionization potential. It did so by relating the analytically known solutions of the hydrogen atom to those for more complex atoms by showing that the quantum defect, the originally empirical spectroscopic parameter $\mu$, was simply related to the phase shift, $\delta$, of collision theory. In collision theory, it is standard practice to use analytically known comparison radial wavefunctions which are eigenfunctions of an approximate hamiltonian that obtains when the collision partners are well-separated. After scattering, the actual functions are modified by the neglected terms in the potential. By comparing the actual and approximate wavefunctions one identifies shifts in the nodes of the approximate set. The channel concept so familiar in collision theory can then be carried over, as a natural generalization of the Fano-Cooper discussion of photoionization\textsuperscript{12}, to include the description of discrete rydberg levels. The relationship of $\mu$ and $\delta$ follows ultimately from the fact that each is a gauge of the short-range electron-electron interactions (i.e., $J$ and $K$ integrals) and the rydberg electron's interaction with the unscreened nuclear core.
A. THE FUNDAMENTAL ASPECTS OF QUANTUM DEFECT THEORY.

The starting point of the quantum defect method is to begin with a Z-electron neutral atom and to focus on the analytical properties of solutions to the one-electron radial equation (in atomic units):

\[
(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} + V(r) - \varepsilon)F(\varepsilon, \ell, r) = 0
\]  

(4)

The central potential, \( V(r) \), has the asymptotic forms

\[
-\frac{Ze^2}{r} , r \to 0
\]

\[
-\frac{e^2}{r} , r \to \infty
\]

(5)

and \( \varepsilon = E - E_{\text{res}} \), where \( E_{\text{res}} \) is the residual energy of the \((Z-1)\) electron core and \( E \) is the total energy of the system.

The significance of partitioning the atomic system in this way is readily visualized for the situation of an "optical" electron that is well-separated from an ionic core. (The optical electron may be, depending on \( E \), in a bound (rydberg) or continuum (ionized) state.) In this case, the central field can be expressed as

\[
V(r) = -\frac{e^2}{r} + V_s(r)
\]

(6)

where the short-range potential \( V_s(r) \) contains terms that approach zero with increasing \( r \) more rapidly than does the coulombic term. A radius \( r_0 \), beyond which these terms are neglectable, can then be chosen.

An eigenstate of the total system can be written
\[ \psi_i = \{ \phi_i(r^{z-1}) F_i(r) \} \]  \hspace{1cm} (7)

where \( \phi(r^{z-1}) \) represents the ion core state wavefunction and implicitly includes spin and angular variables of the optical electron and the core as well. The index \( i \) collects the relevant state labels and the braces refer to antisymmetrization. Of particular interest is the wavefunction appropriate for \( r>r_0 \), where \( V(r) \) reduces to the coulomb term. Outside the core region, the eigenstates can be expressed as

\[ \psi_i = \Phi_i \left[ f(\nu_i, r) \ c - g(\nu_i, r) \right] \]  \hspace{1cm} (8)

where \( f \) and \( g \) are the regular and irregular coulomb functions which differ in phase by 90°. Also, \( \nu_i \) is the effective quantum number and \( c \) and \( d \) are coefficients by which the boundary conditions at infinity are applied and which can be shown to be of form

\[ c = \cos \pi \mu \] \hspace{1cm} \text{and} \hspace{1cm} \[ d = \sin \pi \mu \]  \hspace{1cm} (9)

Here, \( \mu \) is the quantum defect and represents the net accumulation of phase by the irregular solution, \( g \). (See below). For the case when \( V_s(r) = 0 \), that is, for the pure coulomb potential of the hydrogen atom, \( \mu = 0 \).

The boundary condition for discrete states (when \( \varepsilon<0 \)) is that the wavefunction vanish at infinity; it can be shown to be satisfied when

\[ \sin \pi (\nu+\mu)=0 \]

or, equivalently, when

\[ \nu = n - \mu \]  \hspace{1cm} (10)
which leads directly to the Rydberg formula, equation 3. Continuum states are given by the following relations:

\[ \epsilon > 0 \]
\[ \nu \to i/k \]
\[ \mu \to \delta/\pi \]  

(11)

where \( k \) is the wavenumber of the unbound electron and \( \delta \) is a scattering phase shift. Actually, equation 11 gives the main result of QDT which is to connect the quantum defect, defined for \( \epsilon < 0 \), to the phase shift, defined for \( \epsilon > 0 \). This allows the quantum defect to be identified with the mixing of \( f \) and \( g \) by \( V_s(r) \).

To recapitulate, the key elements are:

--- a one-electron radial equation can be defined;
--- the configuration space of the radial coordinate separates into small \( r \) and large \( r \) regions, defined by the potential, equation 6;
--- bound and continuum solutions can be represented at \( r > r_0 \) by a linear combination of regular and irregular Coulomb solutions where the irregular solution is mixed with the regular solution solely by short-range forces; and,
--- the coefficients that represent this mixing are simple functions of the quantum defect/phase shift.

B. MULTICHANNEL QUANTUM DEFECT THEORY.

The multichannel QDT, as formulated by Seaton\(^2,12\) and applied by Lu\(^,13\) Fano\(^4,15\) and others, exploits the lack of
distinction between discrete and continuum wave functions near threshold, enforcing the boundary conditions only at the end of the procedure. Moreover, channel mixing and the imposition of boundary conditions reduce the problem to one of solving a single highly nonlinear matrix equation for the coefficients of the eigenfunctions. In this work, we will demonstrate that MQDT, which was initially concerned solely with the radial behavior of a highly excited electron, is both a natural and, in fact, almost necessary procedure for sorting out the very complicated spectra of molecules. Indeed, MQDT is extremely useful for systematic studies of the relative strengths of interactions responsible for the complications of molecular spectra.

This empirical approach uses three sets of parameters. These parameters, in principle calculable ab initio, appear in any general description of the photoabsorption/photoionization process: first, the aforementioned quantum defects, \( \eta \), associated with short-range, noncoulombic interactions within a given eigenchannel are labeled with a subscript \( \alpha \) to distinguish the quantum numbers of these channels; second, the transformation matrix, \( U_{ij} \), which, in atomic problems, represents the recoupling of angular momentum vectors between the two alternative descriptions of the electron-target complex, the one appropriate for small distances, the \( \alpha \) eigenchannels, and the other, appropriate for large distance, the \( i \)-labeled collision channels; and third, the dipole matrix elements, \( D_{\alpha i} \), which connect the ground state to the \( \alpha \) eigenchannel states by photoabsorption.
An earlier paper discussed the possibility of extending Lu's analysis of Xe to the newly-available synchrotron data for CH₃I. This paper is included as Appendix I. This latter work focused on broad similarities and did not seek to unravel the intense mixings characteristic of the full set of rydberg series that can arise in molecular photoabsorption; indeed, these other series remained largely unassigned.

Before discussing the molecular theory, we will provide a brief description of channel coupling in the rare gas problem. The ground state of Xe has the configuration \textit{...5p}^6 \textit{^1S}_0 which, upon photoionization, yields the following coupled set of five final states which correspond to a continuum electron and an ion core in jj-coupling and so are denoted by roman letters:

\begin{align*}
\text{i} &= 1 & 2 & 3 & 4 & 5 \\
(2p_{1/2})d_{3/2} & (2p_{3/2})d_{5/2} & (2p_{3/2})d_{3/2} & (2p_{3/2})s_{1/2} & (2p_{1/2})s_{1/2}
\end{align*}

For this atom, spin-orbit coupling splits the core states by roughly 10500 cm⁻¹. The five final states, being of total angular momentum \textit{J}=1 and odd-parity, are mixed and the actual wavefunction is represented as some linear combination of all of them. At small \textit{r}, the wavefunction of the complex consisting of core plus
electron is more appropriately described by a superposition of
LS-coupled channels which are denoted by greek letters:

\[ \alpha = 1 \quad 2 \quad 3 \quad 4 \quad 5 \]

\[ p^5d^3p_1 \quad p^5d^3D_1 \quad p^5d^1p_1 \quad p^5s^3p_1 \quad p^5s^1p_1 \]

Thus, there arise three channels of predominantly d character and
two channels of predominantly s character. The initial
approximation made by Lu\textsuperscript{13} and Lee and Lu\textsuperscript{17} for argon was to
neglect s-d interactions. In this case, the interaction matrix
simply represents the spin-orbit coupling operator which implies
that the coupling matrix is diagonal in $l_e$, the orbital angular
momentum quantum number of the escaping electron. This is a
reasonable starting point because the electron wavefunction
penetration into the core region is much greater for s-waves than
for d-waves. The overlap of these wavefunctions at small $r$, where
mixing can occur, is consequently small. Transformation
coefficients, $U_{i\alpha}$ in this case, are given in a first
approximation by the recoupling coefficients for the (LS/jj)
transformation. The actual situation of small $r$ coupling includes
additional electrostatic and exchange terms, the consequence of
which is the appearance of nondiagonal matrix elements between s and
d channels. The graphical approach to MQDT can determine the actual
values of the matrix elements by treating them as parameters. It is
therefore important to have reasonable initial values since fitting must be done by trial and error.

The graphical procedure of Lu and Fano\textsuperscript{14} displays the experimental energy levels and links a visual representation of the perturbed spectra to the extraction of mixing coefficients and quantum defects. The functions used in this method are defined and discussed now.

Briefly, the radial eigenfunctions for small $r$ are matched at $r_0$ to the scattering form of the regular and irregular coulomb functions ($f$ and $g$, respectively) which are appropriate for large $r$, and a linear algebraic equation for the coefficients is solved. This may be stated as follows: A general solution for the electron plus core wavefunction is given by

$$\psi = \sum_{\alpha} \psi_{A_{\alpha}}$$

However, an expansion in the $i$-labeled collision channels gives for $r>r_0$

$$\psi = \sum_{i} \phi_i \{ f_i U_1 \cos \pi_{\alpha_{1\alpha}} A_{\alpha_{1\alpha}} - g_i U_1 \sin \pi_{\alpha_{1\alpha}} A_{\alpha_{1\alpha}} \}$$

where $\phi$ denotes the wavefunction of the residual ion core, the spins, and all angular parts of the total system, and the coefficients

$$\sum_{\alpha_1\alpha} U_1 \cos \pi_{\alpha_{1\alpha}} A_{\alpha_{1\alpha}} \quad \text{and} \quad \sum_{\alpha_1\alpha} U_1 \sin \pi_{\alpha_{1\alpha}} A_{\alpha_{1\alpha}}$$
appear as generalizations of the boundary conditions for the single channel case. Note that all quantum numbers are collected in the \( i \)-label.

Now, the boundary condition for discrete states is that the wavefunction must vanish as \( r \) approaches infinity. By substituting the asymptotic forms of \( f \) and \( g \) into equation 13, the boundary condition can be expressed more compactly:

\[
\Sigma_{\alpha} F_{i\alpha} A_{\alpha} = 0
\]  

(14)

where \( F_{i\alpha} = U_{i\alpha} \sin \pi(\nu_{1} + \mu_{\alpha}) \) and \( \nu_{1} \) is an effective quantum number.

This homogeneous linear equation for the coefficients \( A_{\alpha} \) has solutions only if the determinental equation vanishes

\[
F = \det |F_{i\alpha}| = 0
\]  

(15)

For a two-limit problem, the solution \( F = 0 \) is an analytic function of the effective quantum numbers \( \nu_{1} \) and \( \nu_{2} \). Additionally, the rydberg eigenenergy must be considered a continuous function of the effective quantum numbers:

\[
E = I_{1} - R/\nu_{1}^{2} = I_{2} - R/\nu_{2}^{2}
\]  

(16)

or,

\[
\nu_{1} = \nu_{2}[1-R^{-1}(I_{2}-I_{1})\nu_{2}]^{-\frac{1}{2}}
\]  

(17)
On a graph of $\nu_1$ vs. $\nu_2$, all physically significant rydberg levels simultaneously satisfy (i.e., lie at intersections of) equations 15 and 17. This is explained more fully in Appendix I, section II.C.

A many-channel, two-limit problem generalizes to include additional roots to the solution of the determinental equation which, for an n channel case, means varying the parameters of an nxn matrix. It is furthermore, highly nonlinear in these parameters. A judicious factorization of this matrix is helpful and the frame transformation theory is an essential element at this stage because it specifies the symmetry characteristics and magnitudes of the nondiagonal matrix elements. For the molecular problems with which we are concerned, no rigorously correct frame transformation exists. In fact, it is primarily in order to characterize the nature of the dominant interactions that we appeal to the MQDT technique.

C. GENERALIZED QUANTUM DEFECT THEORY.

1. THE NEED FOR GENERAL METHODS.

As noted in the Introduction, the present approach was developed when it was realized that the observed coupling among the seven series that converge on the first ionization limit of CH$_3$I required quite a different interpretation than was suggested by a straightforward relaxation of the atomic selection rules. Symmetry-breaking, leading to additional p-wave interactions with s
and d channels and the possibility of alternate, non-rydberg molecular electronic states, forced a reevaluation of the assumption made in Appendix I that major channel interactions in the molecule should follow in detail the situation as it appears in the rare gas atom.

The comparison of the s and d channel coupling problem in Appendix I and in the work of Lu indicated that there are major similarities in the coupling of these channels and that this simple 5-channel problem provides a fair representation of their interactions (see Figure 1 of Appendix I). However, when the full set of experimental points are plotted, it becomes imperative to look at the molecular problem differently. It appears that a spin dependence arises in the molecular case due to the rydberg state mixing associated with interactions involving, a different, excited core state. Such rydberg-valence interactions occur in a limited region of configuration space (which will be referred to as the "reaction zone") and presumably, it will be those states of low orbital angular momentum (i.e., greater core penetrability) that will be affected.

We have consistently classified the CH$_3$I molecule in the $C_{\infty v}$ point group and have assumed that ro-vibronic effects are minimal over the entire energy range of interest. These approximations have been of great assistance in articulating the concept of molecular rydberg channels but further insight and progress requires inclusion of alternative molecular processes.
Restricting our consideration to a single radial nuclear coordinate, it will be appreciated that motion in this dimension, coupled to the radial motion of a single highly excited electron, can be expressed in the language of rearrangement collisions. A rearrangement collision is defined as one in which the identities of molecules before and after the collision are no longer the same (e.g., A+B → C+D, a bimolecular gas-phase reaction). Present formulations of MQDT are incapable of treating so-called break-up reactions when the final state is composed of three (or more) independent particles.

In the theory of inelastic collisions, where only the internal states are changed (e.g., A(m) + B(n) → A(m') + B(n')), approximate solutions of the full hamiltonian are often known analytically at infinite separations of the fragments. Actual wavefunctions differ at small distances because interaction matrix elements do not conserve the identities of the fragment state quantum numbers. In rearrangement collisions, however, the approximate hamiltonian for dissociated atoms, A + B for example, is obviously different from that for a molecular ion core plus an electron at infinity, AB⁺⁺e⁻. Coupling between these channels occurs only in a restricted part of the configuration space consisting of the internuclear and electron-core distances which are denoted R and r, respectively. It is in this region that electronic and nuclear motions can be exchanged between Born-Oppenheimer states. We give in the second part of this section a brief, qualitative discussion of recent generalizations of QDT to this problem.
2. GUISTI'S APPROACH TO RYDBERG-VALENCE MIXING.

Photoabsorption spectra of highly-excited electronic states of molecules inevitably show features that are attributable to dissociation, predissociation and vibronic interactions. The well-characterized regularities of rydberg series provide a sensitive empirical gauge for the energies, intensities and symmetries of a whole manifold of states if these rydberg series are observed and properly assigned. A useful formulation of the rydberg-valence mixing problem, it is believed, can be used to further extract a small, but relevant, set of parameters which relates to these interactions as well. We will summarize here only the most important elements that are pertinent to our current and future applications. The basic extension of quantum defect methods to arbitrary potentials has been discussed in papers by Greene, Fano and Strinati\textsuperscript{19} and Greene, Rau and Fano\textsuperscript{20}. The following ideas that are fundamental to a study of rydberg-valence mixing are based on recent work by Jungen and Guisti\textsuperscript{21} and mainly explored in Guisti\textsuperscript{22}. This work focuses on computational aspects and, as such, it is complementary to our own empirical approach. It does, however, allow us to introduce additional phaseshifts associable with rydberg-valence coupling into the empirical approach that we have adopted.

---First, the set of electronic wavefunctions necessary to calculate all potential curves is supposed to be at hand. The assumption
of the BOA, or quasiadiabaticity, must be invoked at this point implying that rydberg and valence excited state potential energy curves can freely cross. The essence of the problem, then, is to investigate the actual coupling, the breakdown of the BOA. The rydberg state potential curve can be approximated as

\[ U_i(R) = U_i^+(R) - \text{Ry}/\nu_i(R)^2 \]  

where the rydberg constant is now written \( \text{Ry} \), the internuclear distance is \( R \), \( U_i^+(R) \) is the molecular ion potential curve and \( \nu_i(R) \) is the effective quantum number. This, of course, is reasonable because at large distances, the rydberg electron affects the core electron configuration minimally. The minimum of the rydberg potential curve is therefore generated by the \( R \)-dependent effective quantum number at \( R_0 \), the equilibrium internuclear distance. Upon dissociation, atomic or ionic fragments are produced, states that contribute to these processes must be determined and potential energy curves estimated.

Second, the rydberg-valence interaction is given by

\[ V(R) = \langle \psi_R(R) | H_{\text{el}} | \psi_V(R) \rangle \]  

where the subscripts \( R_y \) and \( V \) refer to rydberg and valence channel wavefunctions, respectively, and \( H_{\text{el}} \) is the electronic hamiltonian.
The "reaction zone" referred to earlier is bounded by those values of \( R \) beyond which \( V(R) \) vanishes as well as by those values of the electronic coordinate beyond which the screened electron-electron interactions become negligible. Consequently, outside this region of configuration space, the channel-type of the system is fully determined.

--- Third, outside the reaction zone, the effect of the interaction modifies the set of final state wavefunctions \( \psi_i \) by adding in a conjugated set \( \overline{\psi}_i \). (These sets are just BOA wavefunctions that serve as a generalization of the phase relation between regular and irregular coulomb functions in the standard QDT.) Therefore, the general wavefunction of a molecular system scattered into channel \( i \) is given by

\[
\psi = \psi_i + \sum_{j} K_{ij} \overline{\psi}_j
\]

(20)

where it is evident that the K-matrix alters the unscattered form of the channel functions, \( \psi_i \), to take account of the interactions when both \( R \) and \( r \) are small. Note that the sets \( \psi_i \) and \( \overline{\psi}_i \) are defined to include products of an electronic and vibrational part (i.e., the Born-Oppenheimer approximation is initially assumed). Corresponding to the appropriate channel-type, the electronic (or vibrational) wavefunction is matched to the standard scattering form for wavefunctions at large \( r \) (or \( R \)). The alternate set appropriate for the reaction zone, \( \psi_\alpha \), is defined as that basis
in which \( K_{ij} \) is diagonal. The phase shifts, \( \eta_\alpha \), associated with the interaction \( V(R) \), are determined by solving the eigenvalue equation:

\[
\Sigma_j K_{ij} U_j = -\tan \eta U_i \alpha
\]

(21)

where the transformation coefficients, \( U_i \alpha \) appear as eigenvectors of the interaction matrix. It is expected that \( \eta_\alpha \) and \( U_i \alpha \) can be obtained by fitting the distribution of oscillator strength density of an experimental spectrum in its perturbed regions.

---

Fourth, the coefficients of the expansion

\[
\psi = \Sigma \psi \alpha A \alpha
\]

(22)

are determined by imposing the boundary conditions applicable outside the reaction zone (i.e., for \( r>r_0 \) and \( R>R_0 \)). For rydberg channel functions, this leads to an additional short-range phaseshift. Effective quantum numbers are now given by

\[
\nu_\lambda = n-\mu_\alpha (R) + \eta_\lambda
\]

(23)

The influence of \( \eta_\alpha \) on the magnitude of the effective quantum number is expected to be more strongly energy-dependent than the influence of the quantum defect functions, \( \mu_\alpha \). This expectation follows from the localization of rydberg-valence interactions to a fairly narrow range of energies where their potential curves cross, thus fixing the energy. In the next chapter, we tentatively
identify such a region in the photoabsorption spectrum of CH₃I and discuss the probable nature of the valence state perturber.
REFERENCES:


CHAPTER TWO.

THE STRUCTURE OF THE ELECTRONIC STATES OF THE SIMPLE HALIDES.
INTRODUCTION:

This chapter outlines the results of an analysis of the molecular rydberg states of the simple halides and the questions arising from that analysis. In particular, emphasis is placed on the application of multichannel quantum defect theory\(^1\) (MQDT), the intention being to exploit similarities between the photoabsorption spectra of the alkyl halides and the closed-shell rare gases, and so generalize the many channel, two-limit formulation of Fano and Lu\(^2,3\) to these systems. That similarities ought to exist between the class of molecules consisting of a halogen atom bounded to an optically-transparent substituent was first discussed by Mulliken and Teller\(^4\) in terms of the predominantly atomic character of the resulting \(\pi\) molecular valence orbitals. Mulliken did not intend that such similarities should extend to multichromophore systems: ICN, for example, would be excluded.

However, it might be expected that the alkyl halides represent a simple nearly-atomic group of molecules and, consequently, that their common spectral characteristics could be clearly elucidated and understood.

Such is not the case. The reason seems to reside in the ill-definition of the concept of a molecular rydberg state. Historically, assignments were made in the following way: One or more rydberg series were observed to converge on, or to appear to converge on an ionization limit and, based on an assumed constant
value of a quantum defect, these series were then assigned as s, p or
d types. However, a fundamental problem appears when series members
are extrapolated backwards to the lowest energy members, many if not
all of which are more appropriately described in an LS-type rather
than a jj-type coupling scheme. This difficulty is compounded for
deeply penetrating orbitals for which the conservation of even a
principal quantum number no longer holds.

Furthermore, any breakdown of the Born-Oppenheimer
approximation or, equivalently, the coupling of rydberg and valence
states, means that the standard formulation of MQDT must be modified
even when it offers a useful lower-order approximation to the
treatment of rydberg-rydberg interactions. As stated in the
Introduction, we have taken the Born-Oppenheimer Approximation and
the adiabatic approximation to have the same meaning as
rydberg-valence coupling, it being implicit that transformations
which diagonalize rydberg-rydberg and valence-valence interaction
matrices have been determined prior to consideration of the more
localized rydberg-valence perturbations.
I. HOW QUANTUM DEFECT METHODS CAN BE APPLIED TO POLYATOMICS.

This manner of treating perturbative effects constitutes the most important aspect of MQDT, namely, that it is made up of stepwise procedures by which rydberg-rydberg interactions can be treated first, followed by rydberg-valence mixing, as has been stressed by Jungen and Guisti. We will adopt this same approach. Recent MQDT-based analyses of molecular predissociation and dissociative recombination in diatomics follow the theoretical work of Greene, Fano and Strinati and Greene, Rau and Fano, which we refer to as generalized QDT (GQDT) and which is no longer restricted to coulomb potentials. These latter papers obtain explicit formulas for quantities appropriate to the physically significant long-range potentials \( r^n \), where \( n = 0, -1, -2 \). It is the aim of this paper to show how these techniques can be used to "dissect" the strongly-coupled electronic and nuclear motions of a polyatomic molecule.

It is well to emphasize that the present attitude grew out of our prior attempts to ascertain the limits of applicability of the Lu-Fano graphical procedure with regards to high resolution photoabsorption spectra of polyatomic molecules. (See Appendix I.) In particular, while certain aspects of the \( \text{CH}_3\text{I} \) rydberg channel coupling were quite similar to results obtained by Lu for the rare gas Xe, the simplicity of the s-wave and d-wave channel structure did not extend in any reasonable interpretation of various
FIGURE 1. Lu-Fano plots for the discrete states of Xe and CH₃I.
This figure is reproduced from Appendix I. \( \nu_1 \) and \( \nu_2 \) are effective quantum numbers (modulo 1) defined with respect to the first and second ionization potentials, \( I_1 \) and \( I_2 \), respectively. The solid diagonal line is given by \( \nu_1 = -\nu_2 \), the solid curve is the locus of \( F(\nu_1, \nu_2) = 0 \), and the dashed curve is the function \( \nu_1(\nu_2) \). These functions are defined in Appendix I. Notation for the data points is as follows: \( d = d_5/2(I_1), \bar{d} = d_3/2(I_1), s = s_l/2(I_1), \)
\( s' = s_l/2(I_2), d' = d_3/2(I_2) \).
FIGURE 2. Assignments of the rydberg states of methyl iodide.
The coordinates are the effective quantum numbers $v_1$ and $v_2$. The integer portion of $v_1$ can be read by following the dashed curve through the numbers above the graph. Line segments connect members of series which converge on the first ionization potential ($v_2 = 4.66$). Tentative quantum number labels for the electron angular momentum are listed at the right hand side of the graph. Below $v_2 = 3.0$ significant core penetration is evident, as discussed in the text. For $3.5 < v_2 < 4.1$, the region marked by the dashed horizontal bar at the bottom of the figure, large variations in the quantum defects ($\mu = -v_1 \pmod{1}$) are observed. This is due to the presence of perturbing levels (those levels marked with primes that converge on the second ionization potential) and, as discussed in text, the presence of a nonrydberg (valence) state in the vicinity. It should be stressed that this graph is not a Lu-Fano plot though it presents the experimental data in a similar format.

Notation is as follows:

$s = s_{1/2}(I_1)$, $s' = p_{1/2}(I_2)$

$p = p_{3/2}(I_1)$, $p' = p_{1/2}(I_2)$

$\bar{p} = p_{1/2}(I_1)$, $\bar{p}' = p_{3/2}(I_2)$

$d = d_{3/2}(I_1)$, $d' = d_{3/2}(I_2)$
\[ \bar{d} = d_5/2(I_1), \quad \bar{d}' = d_5/2(I_2) \]
\[ f = f_5/2(I_1), \quad f' = f_5/2(I_2) \]
\[ \bar{f} = f_7/2(I_1), \quad \bar{f}' = f_7/2(I_2) \]

$I_1$ and $I_2$ refer to the first and second ionization potentials, respectively. Data points for $3.65 < \nu_2 < 4.55$ represent every line recorded at high resolution using a synchrotron light source (Reference 23).
other observed, but unassigned channels, presumably ones of p and f types. (Compare Figures 1 and 2.)

Progress was made when it was realized that the simple partial wave description broke down in the molecule because the actual vibronic states arising from rydberg-valence mixing introduce an additional spin dependence into the full description of the channel interactions. These interactions are particularly relevant to any consideration of the anomalous intensities of rydberg levels. It was found however that qualitatively correct results could be obtained without resorting to explicit inclusion of the valence channels for CH₃I. Therefore, we conclude that the rydberg coupling problem is solved for this molecule except perhaps for the frame transformation which allows extrapolation to the lowest series members.

The rydberg-valence problem is of paramount importance and it will remain so until methods of treating it become more straightforward. It is our contention that the simple halides constitute a system in which many aspects of this problem may be studied profitably.

A general scheme which will serve to introduce the important components of such a method is given in Fig. 3. The stepwise procedure by which a physical process can be simplified by quantum defect methods will become apparent. Not all processes are amenable to these methods, however. The fundamental condition is expressed at the top of the figure by the way in which a general polyatomic
FIGURE 3. Organization chart for the stepwise application of quantum defect methods to molecular problems. First, the molecular orbitals (MOs) of the diatomiclike molecule AB are designated as being primarily of rydberg or valence type. For motion along the A-B bond, the excited state potential curves belonging to states of different type are considered to cross freely, in accord with the Born-Oppenheimer Approximation (quasiadiabaticity). Second, the rydberg channel coupling problem is solved by Lu-Fano methods and a parametric R-dependence is introduced as necessary (R is the A-B internuclear coordinate). The frame transformation and the meaning of $r_0$ are explained in the text. Third, the valence states are characterized with respect to dissociation along the A-B bond. Though not explicitly shown in the figure, dissociation into ionic, as well as neutral, fragments is included in this step. Finally, the K-matrix formulation of Guisti in generalized QDT may be used to define additional phaseshifts which represent the rydberg-valence mixing. These phaseshifts can be extracted by fitting intensity data in the perturbed regions of Figure 2.
MANY-ELECTRON
MOLECULE, AB

M.O. SEPARABILITY
(quasiadiabaticity)

RYDBERG STATES

VALENCE STATES

MQDT

K-matrix, GQDT

small r  large r
frame transformations

small R  large R
vibration  dissociation

many-body
transformations  coulomb
interactions  potential

AB^+ + e^-

A + B

r_0

parametric R-dependence
molecule is represented (i.e., as being diatomiclike with respect to
dissociation). Molecules with significant photofragmentation yields
in channels that represent breakup or rearrangement collisions are
thereby excluded. The Born-Oppenheimer approximation (or
quasiadiabaticity) in the sense of our previous discussions allows
us to distinguish transitions between molecular orbitals that are,
in a first approximation, semi-localized: in other words, orbitals
primarily centered on the chromophore weakly interact with those
bonding orbitals adjacent to them and not all with orbitals purely
associated with the substituent. We refer to this as molecular
orbital (MO) separability. Thus, except for "local" perturbations,
which can in principle, be treated either perturbatively or by
K-matrix techniques⁷, coupled rydberg series in molecules can be
orthogonalized in full analogy to the atomic case. The set of
rydberg channel parameters obtained in this part of the procedure
give explicit form to the electronic wavefunctions which enter the
calculation of matrix elements of the rydberg-valence coupling if it
is assumed that the form of the wavefunctions for the valence states
are known. This is not, however, a trivial computational effort.
At the present time, the GQDT, which allows the coupling of
seemingly very different channels, has been applied only to limited
examples. The eigenvalues of the K-matrix are interpreted in the
theory as additional short range phaseshifts of the problem. It is
our intention to obtain these phaseshifts by fitting to experimental
spectra, calculated oscillator strengths: the Lu-Fano graphical
analysis sorts out the global (rydberg) parameters and rydberg-valence mixing contributions account for broadening, band shifts and intensity changes. It is anticipated that much of the understanding in the field of energy transfer and relaxation phenomena of excited states will turn out to be useful especially when the density of states is high even for small polyatomic molecules at high excitation energies in the vacuum ultraviolet.
II. INTERPRETATION OF THE ELECTRONIC STATES OF METHYL IODIDE.

We begin by referring to the characteristic features of the photoabsorption and photoelectron spectra of CH$_3$I. These represent the raw input data for an empirical MQDT approach similar to one of Lu and Fano. The spectra of HI and other alkyl iodides may be discussed simultaneously where the underlying assumption is that all these molecules exhibit the same rydberg transitions differing only by systematic shifts of band positions. For this reason, as well as the fact that the major dissociation channels involve C-I bond breaking,$^{10,11}$ the spectroscopic notation appropriate for discussions of the symmetry of linear molecules will generally be used.

A. IDENTIFICATION OF MOLECULAR CHANNELS.

In an early application of quantum theoretical models to molecular spectroscopy, Mulliken$^{12}$, using Pauling's valence bond approach, was able to draw qualitatively-correct potential curves for the HI valence states. The potential energy curves that correspond to rydberg electronic states may be superimposed on the Mulliken scheme with no difficulty. Three types of one-electron transition are now distinguishable:

a) $\sigma^2\pi^4 \rightarrow \sigma^2\pi^3\sigma^*$ ...valence-type

b) $\sigma^2\pi^4 \rightarrow \sigma^2\pi^3\text{nl}\lambda$ ...rydberg-type

c) $\sigma^2\pi^4 \rightarrow \sigma\pi^4\sigma^*$ ...valence-type
As will be shown below, significant configuration interaction occurs.

A paper by Fano$^{13}$ has demonstrated the essential equivalence of quantum defect and configuration interaction methods via the K-matrix. It is mixing of the states generated by these configurations that we must eventually try to sort out using GQDT methods. Guisti$^7$ has recently developed the formalism for rydberg-valence interactions in the context of dissociative recombination. The 2-dimensional configuration space of the radial coordinate of the rydberg electron and the intermolecular radial distance contains a region where the exchange of energy of these motions occurs. This region is evidently restricted by the total energy available to the system and is a generalization of curve-crossing arguments for diatomic systems. (See Jungen and Guisti$^5$ for a discussion of this configuration space.) Since the rydberg orbital is greatly extended spatially, interpretations of interactions of this type are dominated by considerations of the electron amplitude near the core (i.e., before the electron has emerged from the inner core region).

Prior to examining these particularly difficult aspects of molecular coupling, it would perhaps be best to mention some earlier efforts that provide a rationale for the direction this research has taken.

Concluding remarks contained in a paper by Wang et al.$^{14}$ on quantum defect analogies suggested the need for multichannel
approaches when the effective quantum number (i.e., the energy) becomes large. We recently published results which explored this possibility by bringing over directly the coupling problem for rare gas atoms. That paper is included in this dissertation as Appendix I. Many of the arguments given there have been superceded by the present analysis but it does represent a transitional stage in our effort, thus meriting its inclusion. Its main result (Figure 1 of that paper) is reproduced here in Figure 1. It should be borne in mind that the similarity between atomic and molecular Lu-Fano plots is partly built into the analysis and that, in fact, the actual coupling is much more complicated than the figure suggests.

To fully represent the problem, an enumeration of all channels must be undertaken. Restricting the number of channels to those that derive from the configurational excitations given above (i.e., to excitation from the highest-occupied MO's) it is found that for HX (X = C₂, Br, I) there are three ionization potentials to consider. (For CH₃I, a fourth occurs at energies a few electron volts higher than those of concern here¹⁵,¹⁶ but it is assumed that this channel is strongly closed in the sense of scattering theory and does not contribute significantly to the analysis of states in the energy range of interest. Furthermore, this higher ionization energy is found experimentally to be insensitive to halide substitution indicating that the orbital is primarily localized on the methyl group. Similar arguments apply to other alkyl derivatives). These energies are listed for several
molecules in Table I. The orbitals are portrayed in Figure 4 where, of course, the depiction is merely suggestive.

Since the QDT approach emphasizes the asymptotic behavior of atomic or molecular processes, we must consider in some detail the relationship between orbital ionization potentials\textsuperscript{15,16} and the states of the transitions given previously. Upon ionization, types a) and b) excited configurations go over to electronic continuum states in which the molecular ion core is in its ground electronic state \( \tilde{X}(2\pi,\tilde{\omega}=3/2, 1/2) \) while type c) results in the \( \tilde{A}(2\Sigma) \) core excited state. It would be expected, and is the case indeed, that ionization to the \( \tilde{X} \) state, and the rydberg transitions of type b, show little change in nuclear geometry whereas ionizations into the A manifold have significant vibrational activity along the C-I bond. In HI (see Fig. 5), the type c) transition gives rise to the state labeled \( \Psi' \Sigma^+ \) by Mulliken,\textsuperscript{12} the vibrational levels of which have been analyzed by Ginter et al.\textsuperscript{17}. Their results indicate a large change in rotational constant from that of the ground electronic state.

The methyl iodide photoelectron spectrum, for instance, exhibits sharp vertical transitions at 76930 and 81980 cm\(^{-1}\) corresponding to ionization to the two spin-orbit split level of the ground electronic state of the CH\(_3\)I\(^+\) molecular ion, \( \tilde{n} = 3/2, 1/2 \), respectively. As noted, at least 14 rydberg series may be seen to converge to these limits in high resolution spectra. The third ionization band has been attributed to the core excited
TABLE I. Photoelectron data for the lowest ionization events (in electron volts) of several simple halides. Values in column 5 refer to the onset of ionization. All values from Reference 15.

<table>
<thead>
<tr>
<th></th>
<th>1.</th>
<th>2.</th>
<th>3.</th>
<th>4.</th>
<th>5.</th>
<th>6.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HI</td>
<td>10.39</td>
<td>11.05</td>
<td>10.72</td>
<td>0.66</td>
<td>13.5</td>
<td>2.78</td>
</tr>
<tr>
<td>CH₃I</td>
<td>9.54</td>
<td>10.16</td>
<td>9.85</td>
<td>0.62</td>
<td>12.5</td>
<td>2.65</td>
</tr>
<tr>
<td>C₂H₅I</td>
<td>9.35</td>
<td>9.93</td>
<td>9.64</td>
<td>0.58</td>
<td>11.6</td>
<td>1.96</td>
</tr>
<tr>
<td>n-C₃H₇I</td>
<td>9.26</td>
<td>9.83</td>
<td>9.54</td>
<td>0.57</td>
<td>11.4</td>
<td>1.86</td>
</tr>
<tr>
<td>n-C₄H₉I</td>
<td>9.23</td>
<td>9.79</td>
<td>9.51</td>
<td>0.56</td>
<td>11.27</td>
<td>1.76</td>
</tr>
</tbody>
</table>

where

1. \( \text{RX}(X^1\Sigma_g^+) \rightarrow \text{RX}^+(X^2\Pi, \Omega = 3/2)+ e^- \)
2. \( \text{RX}(X^1\Sigma_g^+) \rightarrow X^+(X^2\Pi, \Omega = 1/2)+ e^- \)
3. the energy average of the values of column 1 and column 2.
4. the spin-orbit split of the ion core ground state, the difference between values of column 1 and column 2.
5. \( \text{RX}(X^1\Sigma_g^+) \rightarrow \text{RX}^+(\tilde{A}^2\Sigma, \Omega = 1/2)+ e^- \)
6. the difference between the values of columns 3 and 5.
FIGURE 4. Symmetry-breaking of orbitals and their energies for some related atoms and molecules. The well-resolved rydberg series of the simple halides are attributable to the persistence of atomic orbital structure on the halogen. The energies of these orbitals are obtained from photoelectron spectroscopy. Xenon and halogen orbital energies constitute an average over the two spin-orbit components. Units of energy are in electron volts. The salient feature illustrated here concerns the energies of orbitals of higher symmetry. For example, the triply degenerate \( 1f^2 \) orbital of methane at 14.2eV splits, in \( C_{3v} \) symmetry, into a doubly-degenerate \( 1e \) and nondegenerate \( 3a_1 \), the ionization of which in methyl iodide occur at energies above (15.0eV) and below (12.5eV), respectively, than that of the \( 1f^2 \) orbital in methane. A similar process for the \( 5p^6 \) subshell of Xe leads to the same result. It should be appreciated that the orbital energies of CH\(_3\)I are constrained by such considerations.
$5p^6(12.8)$  \hspace{1cm} $\pi(10.7)$  \hspace{1cm} $2e(9.8)$

Xe  \hspace{1cm} HI  \hspace{1cm} CH$_3$I  \hspace{1cm} CH$_4$

O(3)  \hspace{1cm} C$_{\infty v}$  \hspace{1cm} C$_{3v}$  \hspace{1cm} T$_d$
FIGURE 5. Potential energy curves for the bound valence state, $V$, for some simple iodides. Dissociation energies resulting from motion along the R-I internuclear coordinate are tabulated in Table II. The curve for the $V$ state of HI is reproduced from Reference 12 Figure 1 and has been vibrationally analyzed by Ginter et al., Reference 17. All alkyl iodide curves are speculative since no vibrational progressions have been identified. The shapes of these curves are deduced on the basis of the distribution of oscillator strength density, perturbations of nearby rydberg levels and comparisons with HI. The vibrational levels of the $V$ state in the alkyl iodides are assumed to form a quasicontinuum. This topic is discussed in more detail in the text. $R_e$ represents the equilibrium intermolecular distance for the $V$ state.
state $A^2\Sigma$ since the photoelectron spectrum\textsuperscript{15} shows several well-structured vibrational progressions extending from 96780 to 104850 cm\textsuperscript{-1} that involve C-I stretching motions, indicative of ionization of a sigma bonding electron.

Three trends become evident in comparing the effects of alkyl substitution. Inspection of the the data of Table I suggests that first, all bands shift to lower energy; second, a small, but consistent, reduction in the magnitude of the spin-orbit coupling occurs, as shown in column 4; and, third, the shift produced by alkyl substitution is larger for the third IP than for the lower ones. (Compare columns 4 and 6). In the corresponding rare gases, of course, only the two $p\rightarrow\pi^*$ ionizations to the $^2p_{3/2}$ and $^2p_{1/2}$ states are possible in this energy range. Figure 6 shows the spectra of several alkyl iodides aligned with respect to their lowest ionization potential.

The following conclusions which play a substantial role in the sequel can be stated:

1) ionization to the $\tilde{X}$ state involves removal of an electron of a halogen nonbonding electron;

ii) ionization to the $\tilde{A}$ state is clearly associated with the $R-X$ bond ($R = \text{-H,-CH}_3,\text{-CH}_2\text{CH}_3, \text{etc.}; X = \text{Cl, Br, I}$). This has been confirmed\textsuperscript{17} by vibrational analysis;
FIGURE 6. Photoabsorption spectra of some alkyl iodides, aligned on their respective first ionization potentials. The energy scales below each spectrum are in units of thousands of wavenumbers (cm$^{-1}$) and the abscissa variable is the effective quantum number relative to the first ionization potential. Many series levels, which are unresolved in this figure, actually make up the sharp bands that appear to converge on $I_1$. These levels have been completely resolved at high resolution and are the points plotted in Figure 2. It is important, also, to compare the intensity of levels along a series: in the neighborhood of $\nu_1=5.8$, bands in the CH$_3$I and CD$_3$I spectra show a sharp decrease in oscillator strength which is not the case for the spectra of other molecules shown. This region in CD$_3$I is shown in detail in Figure 8. Also, below $\nu_1=4.0$, a weak band, followed by two closely-spaced sharp and intense bands can be observed in the CH$_3$I spectrum. The weak band gains significant intensity and begins to overlap the sharper, high-energy bands in the other iodides. All these bands correspond to rydberg series members. Reasons are presented in the text that exclude rydberg-rydberg interactions from being the sole cause of these perturbations.
ALKYL IODIDES

\begin{center}
\textbf{ABSORPTION}
\end{center}

\begin{tabular}{c}
\hline
\textbf{ALKYL IODIDES} \\
\hline
\textbf{n-butyl} \\
\textbf{76} \\
\hline
\textbf{n-propyl} \\
\textbf{76} \\
\hline
\textbf{ethyl} \\
\textbf{76} \\
\hline
\textbf{methyl-d₃} \\
\textbf{76} \\
\hline
\textbf{methyl} \\
\hline
\end{tabular}

\begin{center}
\textbf{ABSORPTION}
\end{center}

\begin{center}
\textbf{\( \nu \)} \\
\textbf{40} \\
\textbf{50} \\
\textbf{60} \\
\textbf{70} \\
\textbf{\( \infty \)}
\end{center}
iii) the relative shifts of the $\tilde{X}$ and $\tilde{A}$ states will reappear below threshold as systematic shifts of the electronically and vibrationally excited manifolds that can be identified by appealing to the single channel concept. This is obviously correct only as a first approximation;

iv) under the assumption of MO separability, the coupling of rydberg states can be handled separately because all rydberg series are correlated to the alternate components of the ground state of the molecular ion, $\tilde{X}$. Furthermore, little vibrational activity is associated with these transitions;

v) all valence states of the simple halides can be obtained$^{10,12}$, from a consideration of the states of the neutral and ionic dissociation species: $R($ground state, $^2E) + X(^2P, = 3/2,1/2)$ and $R^+(^1A) + X^-(...np^61s_0)$;

vi) as discussed by Mulliken,$^{12}$ the $(R^+X^-)$ complex, to which the $V$ states correlates at large intermolecular distances, is stabilized by coulombic attraction. Consequently, dissociation of the molecule due to motion along this $R-X$ coordinate provides an alternative fragmentation channel that must be considered (See Figure 5); and, finally,
vii) the dissociation limit of the V state, viewed as a channel threshold, can be estimated from its relationship to the ion core states (cf., the systematic shifts of Table II.).

The energy region relevant to our discussion is just below the first ionization limit, in a region of the spectrum that may be termed the quasidiscrete electronic spectrum: in this region, the existence of lowlylying repulsive curves means that dissociation or predissociation are, strictly-speaking, accessible, or open, channels.

(Predissociation refers to indirect coupling of the dissociating state to the ground state via initial excitation to a bound state.)

The V state correlates to the Ā state of the ion and a comparison of the relative shifts of orbital energies of the ground and excited states of the ion core with respect to alkyl substitution gives predictive information on both the relative positions of the rydberg levels below threshold and the dissociation energy of the V state. Thus, knowledge of the internal and kinetic energies of the dissociated fragments relative to the molecular ground state of the molecule, the excited states and the ion is required to sort out the complete dynamics of the problem in this spectral range. The curves in Figure 5 are qualitative and merely serve to point out major differences regarding the shapes of the V state potential curves which can be estimated from spectroscopic data. The trend illustrated in the figure expresses the fact that ionic dissociation, which becomes rapidly coulombic beyond a few
TABLE II. Empirical and calculated dissociation limits of the bound valence state V in several alkyl halides.

<table>
<thead>
<tr>
<th></th>
<th>IP$_3^{a)}$</th>
<th>$D_1(V)^{b)}$</th>
<th>$D_2(V)^{c)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$I</td>
<td>12.5</td>
<td>9.2</td>
<td>9.1 - 9.2</td>
</tr>
<tr>
<td>C$_2$H$_5$I</td>
<td>11.6</td>
<td>8.3</td>
<td>7.7 - 8.1</td>
</tr>
<tr>
<td>n-C$_3$H$_7$I</td>
<td>11.4</td>
<td>8.1</td>
<td>7.4 - 7.6</td>
</tr>
<tr>
<td>n-C$_4$H$_9$I</td>
<td>11.27</td>
<td>7.9</td>
<td>(8)</td>
</tr>
</tbody>
</table>

a) The third ionization potential of the molecule. From column 5, Table I.

b) $D_1(V) \equiv IP_3$-constant. The constant here is 26700cm$^{-1}$, determined by fitting data for CH$_3$I. See text for discussion.

c) $D_2(V) \equiv IP(R) + EA(I) + D_0(RI)$. Refer to equation 4 of this Chapter for details. Large uncertainties exist for these values which were taken from a variety of sources. Only the CH$_3$I data is entirely consistent.
FIGURE 7. Photoabsorption spectra of some alkyl iodides, aligned at the calculated dissociation limit of the bound valence state, V. The energy scales below each spectrum are in units of thousands of wavenumbers (cm$^{-1}$). Breaks in the spectral curves correspond to slightly different experimental measurement conditions. The baseline is indicated by the dashed line. A comparison of certain rydberg series members, the bands marked (a), (b), (c) and (d); for example, undergo significant changes in intensity upon alkyl substitution. The distribution of the underlying oscillator strength density, df/dE, the variations of which we attribute entirely to the V state, follows the pattern shown at the bottom of the figure. From these observations and the data of Table II, we can construct the approximate shapes of the potential curves given in Figure 5. Moreover, from these observations, we can connect this perturbed region directly to the dissociation limit of the V state, which has been labeled D(V) in the figure.
ALKYL IODIDES

n-butyl

n-propyl

ethyl

methyl

\[ \text{ENERGY (CM}^{-1}) \]

\[ \frac{df}{dE} \]

D(V)
molecular radii in the hydrogen halides, is significantly tempered in the alkyl halides by additional forces which are present because the positive ion is not purely protonic. Concurrent with a softening of the potential well, there is also a gradual decrease in the energy of the dissociation limit of the V state as the alkyl chain increases. A major observation, which will be important at a later stage of this work, is that the rydberg levels overlap this dissociation limit in the alkyl halides whereas this limit lies above the first ionization threshold in the hydrogen halides. This overlap occurs in a region of the absorption spectra of all alkyl halides where the positions of rydberg series levels and their intensities appear perturbed, though spectra of sufficient resolution to permit equally-detailed analyses of halides other than CH$_3$I have not yet become available. This feature is shown in Figure 7 and discussed in the next section. An additional aspect of this problem must also be emphasized: the surprising paucity of vibrational activity in the spectrum of CH$_3$I. Indeed, even in the ethyl and higher derivatives which are of C$_s$ symmetry and less rigid, it is the electronic origins of rydberg levels that are most intense. An increased broadening is apparent, but even when observed, vibrational progressions remain weak in all cases. This is undoubtedly an effect of predissociation to purely repulsive states which, while an important spectroscopic feature, is not directly of concern here.
B. MULTICHANNEL COUPLING OF MOLECULAR RYDBERG STATES.

In what remains of this section, we will restrict ourselves to a discussion of the rydberg channel coupling problem.

The final state description, corresponding to the orbital electron plus the ion core, is appropriately described in \( (j_e, \tilde{\Omega}) \) coupling, the rotational energy levels of the core being neglected. As before, \( j_e \) is the total angular momentum of the electron and \( \tilde{\Omega} \) is the core momentum projection on the principal molecular axis. From this coupling limit arises the concept of what we will call a "rydberg multiplet" which, it should be noted, expresses not just the regularity of individual series but also emphasizes the fact that the orthogonality of rydberg orbitals, even in polyatomic molecules, is achieved by adding one additional node per unit effective quantum number. The concept of rydberg multiplets are more fully discussed in Appendix II.

The photoabsorption spectrum, Figure 8, shows a rydberg multiplet whose components can be clearly discerned. The lower energy set contains members of series which converge to the first ionization potential, \( I_1 = 76930 \text{cm}^{-1} \), which is associated with the \( \tilde{\Omega} = 3/2 \) core component, whereas the higher energy set contains members converging to \( I_2 = 81980 \text{cm}^{-1} \), which is associated with the \( \tilde{\Omega} = 1/2 \) core set. Members of series that relate
FIGURE 8. The photoabsorption spectrum of CD$_3$I in the energy region below the first ionization potential and including the first preionizing band system. The two sets of rydberg series levels, which we refer to as "rydberg multiplets", are nearly identical in relative ordering, intensity and bandshape. Each multiplet is made up of series members converging on the alternate ground state ion core states, $\tilde{n}=3/2$ and $1/2$. The lower energy component is identified as the (c) band in Figure 7. The horizontal dashed line in the lower portion of the figure indicates the perturbed region that is similarly distinguished in Figures 2 and 9. This region includes discrete perturbing levels and, in addition, the strongly attenuated multiplet located just below 74000 cm$^{-1}$. This multiplet is identified as the (d) band in Figure 7. For a discussion of the concept of rydberg multiplets, see Appendix II.
to the lower ionization potential can be located in the figure at
energies of roughly 72200, 73800, 74800, 75100, 75500 cm\(^{-1}\) and,
thereafter, at regular series spacings all the way up to \(I_1\).
Indeed, some series members in CH\(_3\)I have been followed to \(n = 30\)
and greater. The nearly identical shape of the band envelopes of
the two multiplet components shown in Figure 8 is unmistakably due
to predissociation of some of the lower members and preionization of
some of the upper ones. Recall that these processes represent
coupling of closed and open channels, or equivalently, bound and
continuum states. Consequently, the characteristically asymmetric
Beutler-Fano profiles are thus rationalized. The energy interval
indicated by the horizontal dashed line in the lower portion of
Figure 8 is more important to this discussion, however. The primed
levels appearing at energies intermediate to the upper and lower
multiplet components are the \(n-1\) members of series converging on
\(I_2\): the \(n\)th members of these series comprise the upper
component centered at 77200 cm\(^{-1}\). These perturbers (6d', 6d',
7p', 7p' and 8s') alter the positions of close-lying series members
which converge on \(I_1\). This rydberg-rydberg coupling can be
fully described in the MQDT formalism developed by Lu for atoms. It
is a well-known characteristic of rydberg series, clearly evident
in Figure 8 for those bands between 75500 cm\(^{-1}\) and \(I_1\), that
the oscillator strength decreases as a function of increasing \(n\).
For the hydrogenic situation, it is given by the following
proportionality:
\[
\frac{df}{dn} \propto n^{-3}. \quad (1)
\]

The intensity of the multiplet just below 74000 cm\(^{-1}\) is significantly less than expected based on this rule. (Obviously, it is the oscillator strength density \(df/dE\), that is being compared here; however, since rydbergs are viewed here as perfectly sharp transitions, the usage of the former quantity is justified.) It has been noted earlier in this section that this affected region is observed in all alkyl halide spectra we have examined (cf., Figure 7).

We will now demonstrate that this intensity anomaly cannot arise from interactions with the perturbers (i.e., that it is not due to rydberg-rydberg interactions) and must therefore result from rydberg-valence interactions. To show this, a solution of the channel interaction matrix is attempted by adapting the Lu-Fano graphical procedure to the molecular rydberg problem.

The qualitative solution is contained in Figures 2 and 9. Figure 2, strictly speaking, is not a Lu-Fano plot but represents instead the more familiar single-channel series classification. Below values of the effective quantum number \(\nu_2<3.2\), (i.e., the abscissa variable) the assignments are tentative for all but a few series members. The uncertainty is due to the fact that, below this value, the actual coupling scheme is not purely \((j_e, \tilde{n})\) as it clearly is for the rydberg multiplet of Figure 8 and is manifested in the striking constancy at high \(n\) in Figure 2. In fact, in this lower energy region, an intermediate coupling situation, where
neither \((j_e, \omega)\) nor \((n, \xi_e, j_e; \Lambda, S)\) coupling schemes describe the system very well, obtains. MQDT provides some information on the appropriate transformation but a joint effort using standard methods such as vibrational analyses and comparisons with the rotationally analyzed spectra of HX will be required to make definitive assignments and establish consistency. We will be satisfied with unraveling the spectrum at higher energies, \(v_2 > 3.2\) in the following.

In Figure 2, the association of electron angular momentum quantum numbers, \(\xi_e\) and \(j_e\), with particular series is meaningless in a multichannel scheme yet this association remains useful when contact with the linear correlation methods of Wang is made. The complicated spectral region, seen in Figure 2 and Figure 8, is indicated by the horizontal dashed line and the perturbers are also marked. As a generalization of the solution of channel mixing in Xe, the MQDT solution devolves on expressing the electronic BOA wavefunction in its asymptotic form and setting the coefficients of the exponentially rising component to zero, in conformity with the normal boundary condition for discrete states. This solution of a system of linear algebraic equations, yields an analytical expression for the effective quantum number \(v_1\) as a function of \(v_2\) and the parameters \(\nu_\alpha, U_{i\alpha}\)

\[
v_1 = v_2(v_2; \det |F_i(\nu_\alpha, U_{i\alpha})|)
\]

which, when plotted with the energy constraint relationship
\[ v_1 = v_2[1-R^{-1}(I_2-I_1)v_2]^{-1/2} \]
gives bound states at the intersection of the two curves.

A plot of \( v_1 \) vs. \( v_2 \) is most easily interpreted in the energy-independent format of Figure 1. The periodicity of the analytical curve, i.e., the solution of the determinant in equation 2, per unit effective quantum number, can be traced continuously from fairly constant \( v_1 \) values to rapid jumps corresponding to the location of perturbing \( v_2 \) channel members, with a gradual return to constancy. If one considers two noninteracting channels converging on different ionization limits, the result would be a graph composed of one horizontal and one vertical line. The positions of these lines would depend on the value, modulo 1, of the quantum defect, determined by the intersection of these lines with the diagonal line in Figure 1. The coupling matrix, \( U_{\alpha\alpha} \), is obviously diagonal and the eigenchannel description exact. A single coupling scheme suffices and so \( \alpha \) and \( i \) are identical. For two interacting channels, the lines do not intersect but form a single, continuous curve. The \( \alpha \) and \( i \) channel descriptions are now clearly linearly related to one another and the mixing strength of these channels is related to the nondiagonal elements of \( U_{i\alpha} \). The set of parameters in the equation, \( v_\alpha \) and \( U_{i\alpha} \), are varied and a best fit to the experimental data is obtained by trial and error. This method of solution is clearly intractable for a large number of channels, especially when the eigenvectors and eigenvalues
of the interaction matrix, $K_{ij}$, are not even approximately known. We may say that this is the essential difference between atomic and molecular problems. Some method of successive approximation is indicated: Lu approached the atomic channel coupling by initially assuming that s-d coupling could be neglected, or equivalently, that the matrix factored into a direct sum of $\lambda_e$ components. He based this approach on the fact that the pure (LS/jj) transformation is rigorously of this form (cf. the paper of Lee and Lu\textsuperscript{18}). This ploy failed completely when it was tried on the present data. Rather than factor according to $\lambda_e$, it has become clear that there is significant coupling between channels with the same $j_e$ implying that there are non-neglectable, nondiagonal elements in the interaction matrix which depend on spin. Figure 9 shows this factorization for $j_e = 1/2$ and $3/2$. The top part of figure 9 indicates their mutual interaction. Note especially that this is precisely the region denoted as strongly perturbed in Figures 2 and 8. Now, it may be argued that the presence of the rydberg interlopers is sufficient to cause these perturbations. This is not the case for the following reasons:

i) **spin interactions** in atomic rydberg states, and in particular for Xe, are unimportant. In fact, the spin-orbit coupling constant for Xe is about twice as large as for CH$_3$I so that, whatever the underlying
FIGURE 9. Lu-Fano plots for $j_e = 1/2$ and $3/2$ channels and their first-order coupling. Notation and format is exactly as in Figure 2. The perturbed region is marked by the horizontal dashed lines. The perturbers in that region can be observed in Figure 8. These curves, unlike those in Figure 1, are not the result of numerical fitting. They are hand-drawn because the effective quantum numbers of the data points in the perturbed region have additional phaseshifts (i.e., they are shifted to energies higher than would be consistent solely with rydberg-rydberg interactions) which, can only be attributed to rydberg-valence interactions.
cause of this molecular perturbation, it has no direct atomic analog;

ii) the residual negative slopes that are observed in the uppermost plot of Figure 9 are not artifacts of the procedure with the exception that the multidimensional problem has been projected onto a two-limit one. An actual two-limit problem does not admit negative slopes, a point that has been discussed in Reference 2; and,

iii) intensity variations of the rydbergs bands in this spectral region are inconsistent with rydberg-rydberg coupling or overlap, as we have mentioned above.

Therefore, in order to calculate the QDT parameters, a procedure that subtracts out these nonrydberg contributions to the phase shifts is needed. Perhaps more importantly, the nature of these interactions must be determined.
III. RYDBERG-VALENCE APPROACH

Let us now recall the main points made in previous sections. These are, in part, summarized in Figure 10. They are:

--- The electronic transitions of the alkyl halides resemble those of the hydrogen halides and the rare gases in that transitions of rydberg-type are predominant. This suggests that a two-limit MQDT approach should provide a good first approximation, it being thought that vibronic mixing ought to be energetically localized and not causative of perturbations to sequential series members.

--- Analysis of the data for CH$_3$I by MQDT methods leads to the conclusion that the rydberg levels of this molecule are strongly perturbed over a significant energy range both with respect to band energy and shape. This shows up, at first glance anyway, as a region of intensity attenuation. Attempts to understand the major channel-coupling effects suggest that this phenomenon is strongly spin dependent, with the largest effects occurring in the lowest j$_e$ channels.

--- The region of intensity attenuation has been seen in other alkyl halides and it correlates well with photoionization to the excited ion core state, $\tilde{A}^2\Sigma$. Because of the relationship between this ion state and the V$'\Sigma^+$ valence state and because the dissociation limit of the V state occurs in the appropriate spectral region, it seems reasonable to interpret these phenomena as a manifestation of rydberg-valence mixing, the effects of which are small except in the immediate vicinity of the V dissociation limit.
FIGURE 10. Summary of electronically excited states, collision channels and important discrete-continuum interactions for the simple halides. Orbital symmetry labels appropriate for linear molecules are used to identify transitions between ground and excited state configurations. The states that arise from these configurations can be i) purely repulsive (those denoted Q and T); ii) rydberg (Ryl and Ry2 converging on the alternate ion cores $\tilde{\Omega}=3/2$ and $\tilde{\Omega}=1/2$, respectively); or, iii) bound (the valence state V) where the vibrational manifold $v \rightarrow v'$ indicates a substantial change in nuclear geometry from ground to excited state. As an example, the three, close-lying threshold energies for photoionization and photodissociation are listed at the bottom of the figure for CH$_3$I. Discrete-continuum interactions are represented by processes (a) through (d), where (a) refers to predissociation; (b) to radiationless transitions to the vibrational manifold of the V state for $E<74100\text{cm}^{-1}$; (c) refers to predissociation to the ion-pair complex $R^+ + X^-$, for $E>74100\text{cm}^{-1}$; and (d) to preionization to the Ryl ionization continua for $E> I_1 = 76930\text{cm}^{-1}$.
configurational transition

\[ \pi \rightarrow \sigma^* \]

\[ \pi \rightarrow n \lambda \]

\[ \sigma \rightarrow \sigma^* \]

channel fragments

\[ R + X \]

\[ RX^+ + e^- \]

\[ RX^+ + e^- \]

\[ R^+ + X^- \]

\[ R + X \]

(\( RX = CH_3I \))

ENGLISH (CM⁻¹)

74100 76930 81980
While we have singled out the C-I coordinate for special consideration, we have not been specific about the role played by the actual many-dimensional potential surface. We have treated the alkyl radical as devoid of internal structure since the pertinent normal modes do not dissociate with significant probability\textsuperscript{10,11} to yield fragments such as CH\textsubscript{2} + HI or HCl + H\textsubscript{2}. All the remaining normal modes of the alkyl halides may be projected onto a generalized motion along the C-I coordinate and these motions constitute a quasicontinuum of vibronic levels built on the $\sigma^*\pi^*$ electronic transition. The coupling of rydberg to nonrydberg modes involves multielectron rearrangements with subsequent changes in nuclear geometry which, in the language of QDST, means passage of the system out of the reaction zone along the C-I coordinate. In large-molecule photophysics, such a passage is referred to as a radiationless transition (or electronic relaxation.) The implication of the above comment is that the important dynamics involve the C-I bond which, while it is diatomic-like, precludes an exact description because the vibronic manifold possesses a large number of unresolved states compared to an actual diatomic (i.e., an alkyl halide is simultaneously both a "large" molecule and a "small" one).

The dissociation limit for the valence state of CH\textsubscript{3}I is given by

$$D(V) = \text{IP(CH}_3\text{)} - \text{EA(I)} + D_0(\text{CH}_3\text{I}) \quad (4)$$
where

\[ IP(CH_3) = \text{ionization potential of the methyl radical;} \]

\[ EA(I) = \text{electron affinity of the iodine atom;} \]

and, \[ D_0(CH_3I) = \text{dissociation limit of methyl iodide to the ground state methyl radical and the iodine atom.} \]

This estimate places the dissociation threshold at about 74100 cm\(^{-1}\), well within the region referred to as "strongly perturbed." (See Figures 3 and 4.) Photoabsorption spectra of the alkyl halides, in contrast to the hydrogen halides, do not exhibit resolved vibrational progressions that can be associated with the V state. Presumably, the oscillator strength density of these progressions which, in the diatomic is necessarily localized into a single mode, is capable of being distributed among six normal modes in the methyl halides. Thus at the energies of interest, the density of the highly excited vibrational levels of the V state in the polyatomic is quite large because its dissociation limit \( D(V) \) is much less ionic than that of the diatomic.

Now, lacking direct evidence in the form of photodissociation-photofragmentation data, no definite conclusions can be reached on the actual passage of the molecule along a trajectory in the R-X coordinate. It is, moreover, likely that the actual details can
never be extracted simply because the density of states has approached the limiting conditions of a vibrational quasicontinuum at energies below the dissociation limit, $D(V)$, in the alkyl halides. We reiterate that this is not so in the hydrogen halides because $D(V)$ for these molecules is much higher in energy. Because the region of strong perturbation appears to be localized in an energy interval of roughly 2000 cm$^{-1}$ for CH$_3$I, it seems unlikely that any purely repulsive states are involved since the interactions should not be localized to the extent observed in this molecule. Therefore, the calculation of bandshapes in this region can be carried out by the MQDT generalization of Fano's theory of autoionization in atoms$^{19}$ by directly interpreting the phenomena that occur in this region as attributable to discrete states interacting with a quasicontinuum of vibrational levels of the V state.

Specifically, the oscillator strength density can be calculated by

$$\frac{df}{dE} \propto N|\sum_{\alpha} D_{\alpha} A_{\alpha}(\tau)|^2$$

(5)

where, as before,

$$\Psi = \sum_{\alpha} \psi_{\alpha} A_{\alpha}$$

and where $D_{\alpha}$ is the dipole moment of the $\alpha$th eigenchannel and $N$ is a continuum normalization integral. The rydberg-valence coupling parameters are manifest in the coefficients $A_{\alpha}$ where $\alpha$ now includes the V channel as well as the rydbergs. Note that in this case, the
V channel is open and has a continuous eigenphase-shift, \( \tau \). Fitting the calculated bandshapes to the experimental spectrum would, in practice, commence by giving non-zero values to the channel-coupling elements for \( j_e = 1/2 \) channels only. It has been implicit in all that we have discussed thus far that rigorous solutions are not known to exist for general problems in the spectroscopy of highly excited electronic states of polyatomic molecules. A survey that includes several members of the simple halides and involves the detailed extraction of MQDT parameters as well as an analysis of trends which might be expected upon halide or alkyl substitution will be the final arbiter of these methods. In addition, it must be stressed that every dimension of the problem has not been considered here. Indeed, only those that have appeared to dominate various points of the analysis of the present data have been discussed. We will leave further discussion of these related topics to the final chapter where future avenues of research on this problem are taken up.
REFERENCES:

CHAPTER THREE

PAST, PRESENT AND FUTURE.
I. PERSPECTIVE.

The present investigation has made contact with many areas of active research both in atomic and molecular photophysics and in molecular dynamics. By exploring some problems of molecular spectroscopy from the channel viewpoint, there appears to exist a considerable opportunity for much new insight into the electronic states of polyatomic molecules. It must be admitted, however, that the work described in the preceding chapters suffers from two types of shortcomings, those arising from problem conception and those from its execution. The latter, fortunately, can be enumerated and remedied. This will be done in the following section. The former, on the other hand, are not so readily encompassed and we will attempt discourse on them in our summary.

First, it is clearly inferred that the molecular orbital representation, while adequately descriptive of some features of the ground and low-lying electronic states (e.g., its connection via Koopmanns' theorem to photoelectron data), is not particularly suited for handling highly excited states, particularly those near ionization or dissociation thresholds. For rydberg series, we have introduced the concept of a rydberg multiplet (see Appendix II) based on a \( (j_e, \; \tilde{n}) \) coupling scheme that quite obviously focuses on a single electron and a molecular core. For the simple halides, the linear correlation approach suggests that this is a good approximation. In accord with this, we have found that deviations in results obtained by such an approximation can be used to uncover
possible rydberg-valence interactions in CH₃I. However, the lowest electronic states of this molecule have not been properly characterized and a transformation which adequately expresses the relationship between the alternative coupling schemes has yet to be obtained. Thus, a truly global representation of molecular electronic states is not yet at hand.

Recently, Ginter and coworkers¹ have extended their rotational analyses of the hydrogen halides to higher energy states. Their results will undoubtedly be important to any efforts to extrapolate the rydberg series of the alkyl derivatives to lower energies. This, of course, is not a new idea, but the graphical method of MQDT clearly provides constraints that were unavailable in previous analyses.

Second, the existing approaches to the electronic structure of polyatomic molecules are best viewed as confined electron gas models and the orbital approach as no more than an artifact of atomic and diatomic methodologies: rydberg series are "lost" as the atomic orbitals of an isolated atom mix increasingly with those of surrounding atoms, covalently, or otherwise, as the number of these atoms increases. The simple halides, accordingly, must be perceived as the most atomic-like of molecules, ones in which an external perturbation of Cᵥ symmetry has a large affect on the valence pσ subshell but leaves the pπ subshell relatively undistorted. The question of whether or not definite trends condition the change from one point group to another remains open. Multichromophore systems,
in which the orbitals associated with the individual chromophores, may exhibit considerable interaction, are also poorly understood. The definite link established between photoabsorption and photoionization data by the MQDT parameters suggests that an understanding of these questions is much closer than might be expected.

Third, this work shares many concerns with several areas of molecular dynamics and molecular energy transfer. The review article of Levine and Jortner,\textsuperscript{2} for example, addresses the problems of unraveling molecular processes which do not admit a complete resolution of the details of individual state-state interactions.

Photoabsorption spectra of the alkyl halides exhibit relatively sharp, strongly allowed rydberg states that are clearly coupled to the vibrationally active valence manifold. The decay into continuum states associated with this manifold should be followed, now that this region has been identified and the rydbergs assigned. Photodissociation experiments in the perturbed regions of CH\textsubscript{3}I and other simple halides seem likely to provide opportunities for testing these ideas. In this context, the simple halides are thought of as "large" molecules.

Fourth, the theoretical and computational efforts of Jungen and Guisti\textsuperscript{3} should provide a good foundation for much future work on the rydberg-valence mixing problem. Here, the "small" molecule aspects of this problem are emphasized.
Finally, the simple interpretation of the electronic states of CH₃I posited here, when and, if, fully substantiated by further efforts, will yield significant insight into the structure and spectra of polyatomic molecules.
II. PROSPECTS FOR FUTURE RESEARCH

In order to extend the methods and viewpoints that have been developed in the previous chapters to the class of molecules we have called the "simple halides" and so demonstrate the appropriateness of these techniques for polyatomics, further work on four aspects of the problem is required. The most important is certainly experimental. In particular, the high resolution photoabsorption spectra of several representative molecules are needed in order to generate Lu-Fano plots, extract coupling parameters and generate a more complete understanding of the systematics of channel coupling in polyatomics. It is clear that the major interactions cannot be sorted out unless the rydberg series are resolved up to n values high enough so that rydberg multiplets are easily discerned. In this regard, the synchrotron is currently the best light source available. It is anticipated that such synchrotron spectra will be obtained shortly. Photodissociation/photofragmentation experiments have been performed using laser excitations to probe the low-energy repulsive states of RX molecules and the ground and first excited state of RX+ ions. Unfortunately, the region discussed here requires a tunable VUV laser, namely a technology still in the process of becoming. Information on excited state lifetimes and fragment identifications is fully integrable by GQDT approaches in a manner coincident with the unified approach to photoabsorption and photoionization data provided by atomic MQDT.
Computational efforts will remain centered on extraction of parameters, $\mu_\alpha$ and $U_{1\alpha}$, as defined above, by a trial and error fitting of Lu-Fano plots of the data available in the quasi-discrete region. Additional efforts will be required in order to ensure consistency of the above parameters and to determine the dipole matrix elements $D_\alpha$ for the rydberg channels based on a fitting of the photoionization spectra of all related molecules. For example, it is expected, provided a good set of values are available for the parameter set of CH$_3$I, that it will be relatively easy to obtain approximate parameter values for all other simple halides by a straightforward fitting of the preionization band shapes, and then to use these values for the quasi-discrete region. Spin-orbit coupling, of course, will simplify the fitting procedure for discrete levels because multiplets to alternate core states will be better separated.

The rydberg-valence problem is amenable to a similar treatment by including the dissociative quasicontinuum as an open channel. Thus a synthetic spectrum for a predissociative event can be generated as readily as one as for a preionization event. This would clearly ensue later, after the initial estimates of the $\mu_\alpha$, $U_{1\alpha}$ and $D_\alpha$ for the rydberg channels had been separately obtained in a first approximation.

Considerable development of the methodologic area, particularly in our ability to conceive of relevant frame transformations is needed so that low energy states and their vibrational analyses can
be incorporated into the schema we have already set forth. Progress in this area evidently involves reciprocity between computational and experimental efforts.

Finally, the significance of correlations, or lack thereof, in the parametric sets that we expect to obtain for the simple halides, will make possible generalizations to other types of molecules. Finally, the meaningfulness of all this to any general understanding of molecular processes will need to be discussed, dissected, and criticized when all the data for these molecules has been examined.
III. CONCLUSION.

An important glimpse into the details of molecular structure has been provided by a many-channel analysis of the photoabsorption spectrum of methyl iodide. A systematic survey of the simple halides will establish whether or not the interpretation presented here for CH₃I is as general as claimed. Steps toward accomplishing this goal have been outlined earlier in this chapter. Furthermore, it has been shown that quantum defect-based methods are exceedingly useful for molecular problems because the stepwise application of channel interactions can be reconciled with, and are generalizations of such familiar molecular concepts as the Born-Oppenheimer Approximation and molecular orbital theory.
REFERENCES:


APPENDIX I:
Molecular Rydberg transitions.

Multichannel approaches to electronic

States: CH₃I

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These consist of pages:

Appendix I, pages 94-99 (Molecular Rydberg Transitions.)
APPENDIX II:
THE CONCEPT OF RYDBERG MULTIPLETS*
(A preliminary manuscript)

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*Supported by USDOE
ABSTRACT

Recent advances in the theory of atomic rydberg states have led to a reexamination of the modes of description of the highly-excited states of polyatomic molecules. The concept of a rydberg multiplet is introduced by generalizing the Mulliken theory of molecular rydberg states. It is shown that the rydberg multiplet concept provides a useful transitional device from the familiar molecular orbital picture of molecular spectroscopy to the recent many-channel approaches of Seaton's multichannel quantum defect theory (MQDT.)
I. INTRODUCTION

This paper attempts to clarify some notions regarding rydberg states in polyatomic molecules. These states have long been characterized by an elementary taxonomy based on series membership and near-constant quantum defects. In short, if the rydberg equation

\[ E = IP - \frac{R}{(n-\mu)^2} = IP - \frac{R}{\nu^2} \]

is satisfied for several sequential, but otherwise arbitrary values of \( n \), the electronic spectrum of the polyatomic molecule is presumed to be (at least partially) determined.

Justification for this approach rests primarily on the transferability of the average properties of rydberg states from atoms to molecules. Thus, in the absence of perturbing states, the average properties of atoms such as the intensity of a transition or the radial probability density maximum vary smoothly with principal quantum number. However, with the exception of the hydrogen atom and the alkalis, it is now well known that atoms generally do not possess simple rydberg series. Rather, the multichannel quantum defect theory (MQDT) of Seaton, and particularly the Lu-Fano\(^3,4\) formulation of it, provides a framework for the full treatment of perturbed series by extrapolating across the ionization
threshold the phase shift of scattering theory. A channel is
defined as all bound levels with a given set of internal quantum
numbers and its associated continuum (e.g., ionization or
dissociation.) In view of these substantial advances in atomic
theory, it is timely to attempt a reinterpretation of the analogies
that have made molecular rydberg series analyses meaningful. It can
also be anticipated that rydberg series will no longer be phenomena
that are isolated from molecular dynamics: by solving the
multichannel rydberg problem, rydberg-valence interactions can be
sensitively probed. The possibility of unraveling these
interactions has been facilitated in the experimental regime by
rapid advances in the highly-resolved vacuum ultraviolet (VUV)
spectroscopy and highly-selective VUV photoexcitation studies.

To this end, we consider diatomic-like molecules exhibiting
well-resolved rydberg series that can be described by a coupling
scheme (j_e, \tilde{\Omega}) where j_e is the angular momentum of the
rydberg electron and \tilde{\Omega} is the projection of the total core angular
momentum onto the principal molecular axis. Regardless of any other
consideration, only when the actual coupling approaches this limit
can regular progressions be observed. The rapidity with which the
system achieves pure coupling as a function of the principal quantum
number, n, is clearly dominated by the magnitude of spin-orbit
coupling in the ground state of the molecule, (i.e., by the extent
of initial decoupling).
Mulliken, in a well-known series of papers on molecular rydberg states, discussed atomic and molecular rydberg and core orbitals, in terms of Slater functions. We have something different in mind, however. We wish to extend the argument to an entire set of rydberg functions at once. For a given $\tilde{\Omega}$, there will occur a multiplet of terms \( \{ n, j_\pm, j_e; \tilde{\Omega} \} \) per unit effective quantum number $\nu$, which, barring the presence of interlopers, is generated by the addition of a single radial node to all components of the eigenset of hydrogenic wavefunctions. Orthogonality can be achieved in the above manner only when the overlap of the electron and molecular ion core is small enough so that noncentral forces are subordinate to the coulomb interactions. In this case, the term multiplet or, better, rydberg multiplet is given by \( \{(n_i, j_e, j_e; \tilde{\Omega}) \mid \nu_i = n_i - \mu, m < \nu_i < m + 1\} \) with $m$ any large integer, so that, except for a smooth decrease in oscillator strength with increasing $n_i$, a characteristic structure will be reproduced in the photoabsorption spectrum over each unit $\nu$.

It is clear that the magnitude of the quantum defect determines the principal quantum number of each component of their multiplet. The quantum defect $\mu$ is a function of $j_e$, of the effects of real and actual precursors, and of the extent to which channel mixing occurs within the core.
The main point here is that regular series progressions depend, as stated above, on the pertinent limit and on the previous appearance of all precursors belonging to a given multiplet.
II. ILLUSTRATION OF THE RYDBERG MULTIPLET CONCEPT

It is a well-established result that the photoabsorption spectrum of methyl iodide is largely composed of rydberg series converging to the alternate components of the ground electronic state X \( (\frac{3}{2}, \frac{3}{2}) \) of the molecular ion core.\(^7,8\) In high resolution a total of seven series,\(^9\) corresponding approximately to \( \lambda_e = s, p, d \) and \( f \), can be clearly traced to high \( n \) (up to \( n = 30 \)) for each \( \tilde{n} \) limit where the core splitting is roughly 5050 cm\(^{-1}\). MQDT results suggest the identifications listed in Figure 1, meaningless in a multichannel scheme, but useful outside the context nevertheless.

The two components of the multiplet bear a surprising mutual resemblance for very different reasons. Actually, the low energy component \( (\tilde{n} = \frac{3}{2}, \tilde{\lambda} \sim 7200 \text{cm}^{-1}) \) is rather strongly predissociated while the high energy one \( (\tilde{n} = \frac{1}{2}, \tilde{\lambda} \sim 77200 \text{cm}^{-1}) \) is mainly preionized. Configurational interactions are shown in Figure 2. The concept of the rydberg multiplet has been extremely useful for sorting out interactions especially in the region indicated in Figure 1 by the dashed line. Here, members of series converging on the \( 2^E_{1/2} \) core state (where next higher levels are those comprising the multiplet at 77200 cm\(^{-1}\)) are interspersed among the levels of three successive multiplets converging to the \( 2^E_{3/2} \) limit. We say that rapid variations of the quantum defects are therefore necessary to accommodate these interlopers into an orthogonal manifold. The MQDT graphical procedure maps these
variations explicitly as well as the return to simple node-adding regularity at slightly higher energy ( \( >75500 \text{ cm}^{-1} \).) We note in passing that the severely perturbed multiplet just below 74000 \text{cm}^{-1} clearly emerges\(^{10}\) as a rydberg-valence type interaction (see Figure 2.)
III. DISCUSSION

The rydberg multiplet can be a useful device in the interpretation of electronic spectra of polyatomic molecules. This is particularly true when there exists little or no prior information about any rigorous symmetry constraints and, hence, about rigorous coupling rules. As a concept, it is relevant insofar as it succeeds in bridging the gap between Mulliken's treatment of rydberg and core orbitals, the many channel approaches of MQDT, and the empirical methods by which spectroscopists have catalogued excited states in the past. Because, in the absence of perturbers, these multiplets are the result of regular, atomic-like behavior, the rydberg-rydberg and rydberg-valence interactions can often be untangled. It may be expected that the study of the variations of these interactions within classes of related molecules should contribute substantially to a much more detailed understanding of highly excited molecular states.

ACKNOWLEDGMENT

The author would like to thank Dr. W. S. Felps for providing the CD$_3$I spectrum.
REFERENCES:

6. Generally, atomic orbitals which have real precursors are penetrating. See Ref. 5, part III for a discussion.
FIGURE CAPTIONS:

FIG. 1. The photoabsorption spectrum of CD$_3$I in the region below the first ionization threshold I$_1$, and the first preionizing band system. These band systems are nearly identical in appearance and are made up of members of rydberg series converging on alternate molecular ion core states, $\bar{n} = 3/2$ and 1/2. The bands between these multiplet components are the next lower levels of those series whose members comprise the preionizing band at $E \approx 77200 \text{cm}^{-1}$. Notation is approximate and is given according to the following scheme:

$$\lambda_e = \lambda_e j_e (\bar{n} = \frac{3}{2})$$

$$\lambda_e = \lambda_e j_e (\bar{n} = \frac{3}{2})$$

where $\lambda_e$ can be s, p, d, or f.

and a prime, e.g., $\lambda'_e$, indicates series for which $\bar{n} = 1/2$.

FIG. 2. Energy scheme for the rydberg and valence transitions of alkyl halides. The channel structure (RHS) and the orbital designations (LHS) represent different aspects of the molecular dynamics which can be probed at high precision once rydberg-rydberg coupling is determined via MQDT. Orbital designations refer to the diatomic-like states given in Ref. 11. Only those interactions relevant to the discussion of Figure 1 are indicated (see text.)
VITA

John Arthur Dagata was born on February 24, 1952 in Washington, D.C. He was raised in Pawtucket, Rhode Island and was graduated from Tolman High School in 1970. He studied painting and the Chinese language before entering a science curriculum at Rhode Island College in the Fall of 1976. He was awarded the degree of Bachelor of Arts in Chemistry in the Spring of 1979. In August of that year, he began graduate studies at Louisiana State University, Baton Rouge, where he is presently a candidate for the degree of Doctor of Philosophy in the Department of Chemistry. On June 5, 1982, he was married to Shen I-Kuo. They currently live in Baton Rouge and are expecting their first child.
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