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Ultrafast study of photochemistry on Cr(CO)$_6$ using resonance Raman spectroscopy

Yu, Soo-Chang, Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1992
ULTRAFAST STUDY OF PHOTOCHEMISTRY ON Cr(CO)$_6$
USING RESONANCE RAMAN SPECTROSCOPY

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
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ABSTRACT

In this dissertation ultrafast photochemistry of Cr(CO)$_6$ using picosecond resonance Raman spectroscopy is studied. The advantage of the transient resonance Raman spectroscopy for this study is demonstrated along with a Raman differencing technique. This study is divided into two main parts.

The first part deals with the property of the electronic excited state of the Cr(CO)$_6$. The attempt to reveal the excited electronic structure of Cr(CO)$_6$ is tried with the help of Albrecht vibronic theory and wave packet description. Reaction coordinate and Jahn-Teller effects have been investigated in detail. Two possible reaction coordinates are found in contrast to the results reported by other group. The $v_2$ overtones are observed for the first time with both 213 nm and 266 nm excitations. The observation of the $v_2$ overtones implies that the $v_2$ can be a reaction coordinate. The appearance of two even overtones of the $v_7$ also implies that this mode can be a reaction coordinate along with the $v_2$. The singlet excited state is regarded as a photodissociative state as a consequence of the appearance of the overtones. The Jahn-Teller distortion study shows that the structure of the excited Cr(CO)$_6$ is not a perfect octahedron.

The second part deals with the vibrational relaxation of the solvated Cr(CO)$_5$. The transient band is found at 380 cm$^{-1}$. The vibrational relaxation time of this mode is about 80 ps in both cyclohexane and tetrahydrofuran solvents. Vibrational relaxation is confirmed with the help of the complementary dynamics
of the stokes and anti-stokes scattering. No direct evidence for the dynamics of solvent coordination, reorientation, and electronic relaxation is observed. However, the initial internal temperature of the molecule was found to be exceedingly hot. This non-equilibrium temperature persists for an unusually long time and are likely to play a major role in solvent coordination and solvent reorientation processes.
1. INTRODUCTION

Investigation of ultrafast phenomena has been of great utility in understanding photophysics in different solvent environments\(^{(1\text{-}18)}\). With the development of ultrafast laser techniques\(^{(19)}\), the photochemistry occurring in a fast time scale of \(10^{-9}\) to \(10^{-15}\) s has been extensively studied in the past several years\(^{(1\text{-}18)}\). Photodissociation, solvation, solvent reorientation, geminate recombination, and vibrational relaxation are primary steps in photochemical reaction occurring in liquids. By tracing the flow of an excess energy, these mechanism can be investigated during the course of reaction. The photochemistry of Iodine (\(I_2\))\(^{(1\text{-}9,18)}\) and chromium hexacarbonyl (\(Cr(CO)_6\))\(^{(10\text{-}17)}\) have been regarded as prototypes, and have been studied by many groups. However, data from different techniques often leads to different interpretation and this is somewhat discomforting\(^{(9\text{-}17)}\). Among many techniques, transient UV/visible absorption \(^{(4\text{-}5,10\text{-}12,15\text{-}18)}\), transient IR\(^{(13\text{-}14)}\), and transient resonance Raman spectroscopy\(^{(6\text{-}9)}\) have been widely used to study ultrafast phenomena in the condensed phase. The most widely used technique to study on the nature of excited electronic states is UV/visible absorption spectroscopy. However, the absorption technique has a limited capability due to its inherent poor resolution, especially for vibronic structure. On the other hand, resonance Raman scattering (RRS) as a spectroscopic technique provides more detailed information with less ambiguity.
The purpose of this dissertation is to discuss the ultrafast study of Cr(CO)₆ using a picosecond resonance Raman technique developed in our group. In the first part of this chapter, we present the basic understanding of the Raman scattering process with the help of simple mathematical expressions. In the second part, the details about resonance Raman scattering are explained by introducing Albrecht theory and its applications to the symmetry consideration. Detailed equations will not be derived, rather an attempt will be made to explain the physical insight described by the equations.

1.1. Theory of Raman Scattering.

In this section an introduction of the basic theory of Raman scattering is presented. An explanation is developed on the basis of the "Basic Physical Chemistry" written by Moore.²⁰

The Raman effect can be explained by understanding the addition or substraction of a quantum of vibrational energy to a quantum of incident radiation hv. The scattered quantum hv' is given by

\[ hv' = hv \pm (\epsilon_m - \epsilon_n) \]  

where \( \epsilon_m \) and \( \epsilon_n \) are two energy levels in the scattering substance. The Raman shift \( \Delta v = |v - v'| \) corresponds to the energy gap between two nearest quantum
numbers of $v = m$ and $v = m + 1$ ($m$ is an arbitrary integer) for vibrational energy.*

The Raman shift tells us how much energy was exchanged with a particular vibrational mode. From the Raman shift, the vibrational force constants can be deduced, and thus the rigidities of molecular bonds can be investigated.

The Raman effect occurs due to the oscillations of an induced dipole moment $\mu$ in a molecule by the electric field of the incident light wave. This induced dipole moment depends on the electric field strength, $E$ as $\mu = \alpha E$. For a given electric field, the induced dipole moment is proportional to the polarizability, $\alpha$, which is a tensor quantity. Polarizability is an intrinsic molecular property whose magnitude varies as the molecule oscillates. If we expand the polarizability with respect to the coordinate, the first approximation is

$$\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial x} \right) x$$  \hspace{1cm} (2)

Then the dipole moment is given by

$$\mu = \alpha_0 E + \left( \frac{\partial \alpha}{\partial x} \right) x E$$  \hspace{1cm} (3)

The exciting light wave has an alternating electric field,

$$E = E_0 \cos 2\pi v_0 t$$  \hspace{1cm} (4)

The coordinate $x$ of the molecule during the vibration with its own frequency $v_1$ is

* Only vibrational motions are considered in this dissertation since only vibrational Raman spectroscopy is considered.
From Eq. (2), (3), (4) and (5). The induced dipole moment is given by

\[ \mu - \alpha_0 E_0 \cos 2\pi v_0 t + \left( \frac{\partial \alpha}{\partial x} \right) x_0 E_0 \cos 2\pi v_0 t \cos 2\pi v_1 t \] (6)

Using trigonometric identities, the final equation for the dipole moment can be reduced to

\[ \mu - \alpha_0 E_0 \cos 2\pi v_0 t + \frac{1}{2} \left( \frac{\partial \alpha}{\partial x} \right) x_0 E_0 [\cos 2\pi (v_0 - v_1) t + \cos 2\pi (v_0 + v_1) t] \] (7)

The first term gives scattering with the same frequency as that of excitation, and is called Rayleigh scattering. The second term describes Raman scattering which gives smaller \((v_0 - v_1)\) or larger \((v_0 + v_1)\) frequency than the excitation frequency \(v_0\). The former process is called Stokes scattering, the latter is called anti-Stokes scattering. This is a basic theory of Raman scattering.

1.2. Process of Resonance Raman Scattering.

Resonance Raman spectroscopy can be used to determine the projection of the upper electronic state on the lower. This information provides great insight into bond displacement of the upper resonance state with respect to the lower. Using this method, \(\text{Cr(CO)}_6\) has been studied. In order to understand how the Raman spectrum can be interpreted, it is first necessary to summarize
Fig. 1. Comparison of the Non-Resonance and Resonance Raman Scattering.

A scheme for the comparison between non-resonance and resonance Raman scattering is diagramed. $S_0$ and $S_n$ represents an electronic ground and an electronic excited state, respectively. $V$ represents a vibrational state. a) In non-resonance Raman scattering, excitation reaches a virtual state in the electronic ground state which is indicated by dotted line. b) In resonance Raman scattering, excitation reaches any vibrational states in the electronic excited states. A pair of arrows (up: excitation, down: scattering) indicates Stokes (left) and anti-Stokes Raman scattering (right).
the theory of resonance Raman scattering. Normal Raman scattering results from a coupling between the vibrational and electronic states of a molecule\(^{53,54}\). In non-resonance Raman scattering (NRS)(Fig. 1.a), the scattered intensity due to a vibrational transition closely follows a \(v^4\) dependence

\[
I = (v_0 \pm v_k)^4
\]  

(8)

where \(v_0\) is the frequency of the exciting radiation, \(v_k\) is the frequency of the \(k\)-th vibrational mode, and the \(\pm\) refers to the anti-Stokes and Stokes radiation, respectively. However, the process of resonance Raman scattering (RRS)(Fig. 1.b) is different from that of NRS. Albrecht's development of the vibronic theory of resonance Raman scattering\(^{54}\) gives a simple method for deriving the basic formula from which symmetry considerations are feasible. For the development of Albrecht A-, B-, and C-terms the formula summarized by Gerrity will be simply used\(^{23}\). The dependence of the electronic transition moments on the normal coordinates \((Q_a)\) is described by Taylor series expanded about the equilibrium configuration of the ground electronic state. After neglecting all terms beyond the first order, the following equations are obtained.

\[
M_{\mu\nu} = \langle i | \langle g | \mu | e \rangle | \nu \rangle = \langle i | M_{\mu\nu} | \nu \rangle
\]  

(9)
Here, \( M_{ge} \) is the electronic transition moment between the ground state \(|g\rangle\) and the excited state \(|e\rangle\), \( i \) is the initial vibrational level, \( f \), the final vibrational level, and \( v \) is a vibrational level in the excited state. \( M^0_{ge} \) is the zero-order, \( \delta M_{ge}Q_a \) is the first-order nuclear coordinate dependent part of the g-to-e transition. The zero-order term can be thought of as the allowed component of the transition, while the first-order term, the vibronically coupled term. Taking account of the electric dipole matrix elements, the transition polarizability expression breaks down into the sum of three terms designated as A, B, and C-type activity:

\[
A = \Sigma_i \Sigma_v M^0_{ge} M^0_{eg} <i \mid \nu > <\nu \mid f > / \Delta \omega_{\nu} 
\]

\[
B = \Sigma_i \Sigma_v (M^0_{ge} \delta M^0_{eg} <i \mid \nu > <\nu \mid Q_a \mid f > / \Delta \omega_{\nu} + \delta M^0_{ge} M^0_{eg} <i \mid \nu > <\nu \mid Q_a \mid f > / \Delta \omega_{\nu}) 
\]

\[
C = \Sigma_i \Sigma_v \delta M^0_{ge} \delta M^0_{eg} <i \mid Q_a \mid \nu > <\nu \mid Q_a \mid f > / \Delta \omega_{\nu} 
\]

\[
\Delta \omega_{\nu} = \nu_{fe} - \nu_{0} + \Gamma_{\nu} 
\]
where $v_0$ is the laser frequency and $v_{ev}$ is the frequency of $|ev \rangle$ state. $\Gamma_{ev}$ is the dephasing rate of the $|ev \rangle$ state which has been loosely correlated with the half-width of a given excited state. In view of the fact that the enhancement depends on the symmetry of the vibrational mode at a given excitation, the information regarding the symmetry as well as equilibrium geometry of the excited state can be deduced.

If the excitation is in resonance with a strongly allowed electronic transition, only the totally symmetric vibrational modes will be enhanced. This is a result of the fact that the minimum of the potential energy surface (PES) of the excited state is displaced relative to that of the ground state only along the totally symmetric vibrational modes. The displacement of the PES of the excited state accounts for the non-orthogonality between two electronic wave functions. The vibrational wave functions in two different electronic states are also not necessarily orthogonal. In such a case, there are two factors to be considered for each mode. One is an electronic transition moment, the other is a Franck-Condon factor between two vibrational wave functions in the two different electronic states. The zero-order electronic transition moment terms will not go to zero since a strongly dipole-allowed transition is assumed. The products of the integrals $<i|v>$ and $<v|f>$ in Eq.(11) can be finite due to the non-orthogonality of vibrational wave functions. Thus, the A-term will dominate, and the fundamentals of the totally symmetric vibrational modes will be enhanced at a strongly dipole allowed transition. In the case of a large displacement in the
excited state relative to the ground state, there will be a progression of the overtones and possibly the combinations of these symmetric vibrational modes. This is again a simple consequence of the Franck-Condon factors.

If the excitation is in resonance with a weakly allowed electronic transition, the non-totally symmetric vibrational modes will be enhanced. A weakly allowed electronic transition arises from the mixing of the dipole-allowed with the forbidden transition along the normal coordinate of the non-totally symmetric vibrational modes. This weakly allowed electronic transition does not give rise to the displacement of the minimum PES of the electronic excited state relative to the ground state. Therefore, two vibrational wave functions in two different electronic excited states will be near orthogonal. In this case, $A$-term will be zero because the product of the zero-order transition moments, $M^0_{ge}$, $M^0_{eg}$ is zero. However, the product of the transition moments, either $M^0_{ge}\delta M_{eg}$ or $M^0_{eg}\delta M_{ge}$ will not go to zero since the transition from the electronic ground to electronic excited state is now allowed through the non-totally symmetric vibronic coupling modes. The summation of the integral products, $\Sigma \langle i|v>|v|Q_e|f\rangle = \langle i|Q_e|f\rangle$, does not go to zero either. Therefore, the $B$-term will dominate, and is responsible for the enhancement of the non-totally symmetric vibrational modes.

With a strictly forbidden transition, only the $C$ term is non-zero. In that case, the forbidden transitions cannot be sources of Raman scattering for non-totally symmetric fundamentals$^{54,61}$; the even overtones or combinations of the
non-totally symmetric vibrational modes which couple the forbidden states to the allowed states will be observed. The reason for this will be explained in the section of “Reaction Coordinate” of Chapter 4. However, as with the normal A-term, a given totally symmetric mode will be enhanced when the excited state is displaced relative to the ground electronic state along that normal coordinate.

1.3. Transient Resonance Raman Scattering.

1.3.1 General aspects.

Transient resonance Raman scattering refers to the resonance Raman scattering coming from a transient. The process of the transient Raman scattering is the same as that of resonance Raman scattering except that its intensity is usually very small. The reason for the small intensity of the transient species is mainly due to the small amount of the transients. The conversion efficiency from the parent to the transient molecule is usually as low as 10 to 20 percents. Therefore, the amount of the transient species is not comparable to that of the parent molecules. If the extinction coefficient of the transient species is smaller than that of the parent molecule at a given excitation (even if the excitation is in resonance with the absorption maximum of the transients), then the low extinction coefficient will be another factor of reducing the intensity.

The advantage of the transient Raman technique is that direct information is obtained about the vibrational coordinates as a function of time. Consider the process of vibrational relaxation of the transient after photodissociation in a
condensed phase. If the transient species has an excess energy right after the excitation, then the species will relax to the ground state to reach thermal equilibrium. During this process the energy will be transferred to the solvent through the V-V (vibrational to vibrational), V-R (vibrational to rotational) or V-T (vibrational to translational) energy relaxation. The question of interest is "how long will it take to finish the relaxation to the ground state?" or "which vibrational coordinates play the major roles in transferring energy?" We can get direct answers from the transient Raman spectrum. The beauty of studying vibrational relaxation by transient Raman spectroscopy lies in the fact that the Raman frequencies correspond directly to the quanta of energy that must be lost to depopulate the level. The time dependence of the Raman frequencies can then be used to probe the vibrational energy decay as a function of energy gap.

1.3.2. $I_2$ Example

One of the nice examples is the vibrational relaxation of the $I_2$ in the X state potential as shown in Fig.2. For the vibrational states observed in Fig.2, the frequencies for Raman scattering from any two adjacent vibrational levels $v \rightarrow v+1$ and $v \rightarrow v+2$ differ by a maximum of 2.3 cm$^{-1}$. Since the spacing between Raman bands from adjacent vibrational levels is so much smaller than the observed linewidth of an individual Raman band (23 cm$^{-1}$), only a distribution of states is observed. The arrows in Fig.2 illustrate the dynamics of the vibrational decay. From 0 ps to 100 ps the peak of the distribution shifts
towards the higher frequency vibrational levels located in the lower energy regions of the X state potential. In addition, the distribution appears to become more narrow at later times. This is a result of populating vibrational states with slower relaxation times which allows the population to collect in the lower vibrational levels.
Fig. 2. Pure Transient Spectrum of I₂ in Cyclohexane.

Pure transient spectrum of I₂ in cyclohexane obtained by subtracting the one color probe only background spectrum from the raw two color spectrum. In order to subtract, spectra have been normalized for transient absorption at 354.7 nm using solvent bands as an internal reference. Time delay between pump and probe lasers is given in figure. The band labeled A/A' in each frame corresponds to the excited electronic states denoted as such. Frequencies are in units of cm⁻¹.
2. EXPERIMENTAL

2.1. Raman Instrument

The Raman instrument has been designed in our laboratory\(^\text{\textsuperscript{21}}\) to study ultrafast phenomena occurring on the picosecond \((10^{-12} \text{ s})\) time scale. There are two important requirements to study ultrafast phenomena. Firstly, the pulse width has to be shorter than the time span during which the photochemistry finishes. Secondly, the repetition rate should be high enough to avoid nonresonant multiphoton effects which can be easily observed in many molecular species with power as low as \(6 \times 10^6 \text{ W/cm}^2\).\(^\text{\textsuperscript{19}}\) The transient Raman signal depends on the peak power of both pump and probe beam. However, this is limited because of multiphoton effects. Therefore, the peak power should be reduced not to generate this non-linear effects. The only way to solve this problem is to increase the repetition rate. The high repetition rate splits the same energy into the more pulses. The reduction in energy per pulse therefore reduces the peak power. Furthermore, the high repetition rate helps the signal to noise ratio (S/N). The S/N improves as \(N^{1/2}\), where \(N\) is a number of pulse averaged. The high repetition rate gives more pulses than the low repetition rate does at a given time.

A diagram of the system is shown in Fig.3. This laser system is designed to meet the requirement mentioned above well. Laser technique utilizes picosecond pulse compression and regenerative amplification in a CW Nd:YAG laser at 2 kHz. The output of the regenerative amplifier is about 500 \(\mu\text{J/pulse}\).
ω = 1.064 μm
8ps, 500 μJ / pulse
2 kHz

Fig. 3. Schematic Diagram of the Laser System.
at 1064 nm with $\approx 8$ ps pulsewidth. The harmonics of 532, 355, 266, and 213 nm are generated using KTP, and BBO crystals. After harmonic generation, the harmonics are separated by beamsplitters which are reflecting one color while transmitting the other color with high efficiency at 45 degrees with respect to the incident beam. One color is used for pumping the molecule into excited states, and the other color is used for probing the transient* generated by the pumping beam. One color is sent to an optical delay stage on which a retroreflector is attached. This delay stage is driven by the stepper motor, which is controlled by a computer. The distance by which the delay stage moves is calculated from the velocity of light. That is, the 1 mm movement corresponds to $3.33 \text{ ps}$ the light travelled. With this knowledge the probe beam is delayed with respect to the pump beam.

To find time zero, the dynamics of a stimulated emission of appropriate dyes has been used. For example, for the combination of 532 nm pump and 266 nm probe, the laser dye coumarin 500. Coumarin 500 has an emission spectra around 500 nm. When this dye is excited to the electronic upper level by 266 nm, it fluoresces with a maximum intensity around 500 nm. If the 532 nm probe is imaged onto the same spot on the sample, the intensity of the fluorescence changes in time because the photons at 532 nm deplete the upper state population through stimulated emission. Thus the time corresponding to

* Transient species refers to any species in different states from those of the original molecule after excitation.
a half maximum of the total intensity is regarded as time zero. Since the dynamics of the stimulated emission occurs within a pulse width, the time zero cannot be mislead. In case of the 4th and 4th, or 4th and 5th experiment*, the pulse limited depletion dynamics of Cr(CO)₆ has been used to determine time zero.

A mechanical chopper is used to chop the beams so that the signals coming from different beams are recorded separately. The chopper chops the beams alternately at several hundred Hertz. After being sensed by a photodiode the signals are recorded in a computer. When the pump beam is chopped, only the probe hits the sample and the signal coming from the probe beam is recorded. In the opposite chopping cycle two beams hit the sample. The subtraction (two color - one color) procedure gives a pure signal coming from only the transient species. The details about the differencing technique are described in a following section.

As for the sample holder we use either a spinning cell or a flowing jet depending on the molecules. The scattered light from the sample is collected by Raman pickup optics and then dispersed by a monochromator. The monochromator for these experiments is an Instruments SA U1000 1 meter dispersive double monochromator. The dispersed light is imaged onto a

*From now on the terms of "4th and 5th" will be used for "266 nm and 213 nm", respectively since they are the 4th and 5th harmonic of 1064 nm which is the Nd:YAG laser line.
photomultiplier tube (PMT) through the exit slit. The PMT signal is processed by a gated integrator and then stored in a computer.

2.2. Raman Differencing Technique.

In many cases transient signals are easily overshadowed by ground-state bands. When weak transient bands appear on the top of the strong bands their contribution to the total signals is almost negligible. The data acquisition problem is basically one of separation of a small signal from the huge ground-state bands. Basically, this problem can be solved by subtracting the ground spectrum from the mixture of the ground and transient spectrum. The subtraction method is described as follows.

1. To record the signals coming from both pump and probe beams. The spectrum coming from both beams is referred to as two color spectrum, whereas the spectrum coming from one beam is referred to as one color spectrum. The two color spectrum is responsible for Raman scattering, but in some instances there is a fluorescence contribution. Raman bands originate from both ground-state and transient bands.

2. To record the signal coming from the probe beam only. One color spectrum contains only ground-state bands, fluorescence, and background.

3. To record the backgrounds coming from PMT or electronics.
The subtraction procedure, 1-(2+3), gives the spectrum coming from only pure transient species.

If the pump beam contributes to the ground-state bands, then we need another chopper for the pump beam. In this case, two color signal -(pump only + probe only + background) signal gives transient signal. For the Cr(CO)$_6$ experiment, two combinations of the pump and probe beams are used. The first combination is the use of 266 nm for the pump and 213 nm for the probe. The 266 nm is red of the 213 nm, thus it does not interfere with the Raman signal coming from the 213 nm. Therefore it is not necessary to use two choppers. The other combination is the use of 266 nm for both the pump and probe. The pump definitely interferes with the probe. For the pump signal to be subtracted out two choppers must be used. The illustration for this examples is shown in Fig.13.

2.3. General Technique

Cr(CO)$_6$ was purchased from Aldrich Co. and used without further purification. The concentration of solution is 10 mM for every solvent. To avoid photochemistry from room light the samples were prepared just before taking the spectra. The samples were switched with a volume of 100 ml every two hours to avoid buildup of photochemical products. For the sample holder, a flowing jet system was used. It was found that spinning cell would not work because the Cr metal plated out onto the inside of the window of the cell. The
jet is made of glass tubing with a diameter of 3 mm. The end is squeezed under heat so that the thickness of the stream is about 1 mm. The flow rate of the sample is controlled by changing the speed of the pump so that the same sample region is not interrogated by consecutive pulses. The naked Cr(CO)₅ is easily oxidized with oxygen in the air. The oxidation product does not contribute to the transient spectrum over at least 2 hrs irradiation.

The angle of the scattered radiation is about 45 degrees with respect to the collecting lens attached to the monochromator. Finding a transient is dependent on the focusing of the pump beam and its overlap onto the probe beam. The transient is found from the following procedures. First align the probe beam on the biggest solvent band. Then overlap the pump beam onto the probe beam by looking at the beam spot on the solvent from the backside of the jet which is opposite to the direction of the incident light. The size of the probe beam is about 0.1 x 1 mm. The shape of the beam spot affects the intensity of the signal. The line shape is better than the round shape. If the beam is made too tight, it easily generates a plasma or multiphoton process. On the other hand, if the beam is defocused too much, some of the scattered radiation would not be imaged onto the slit. By making the shape of the beam linear, the undesired effects can be avoided because the energy per unit area becomes smaller while maintaining a smaller beam size. The size of the pump beam is controlled such that its peak power per cm² does not generate nonlinear effects.
To delay the probe beam, we have used a motor controlled delay stage on which a retroreflector is mounted. For the 4th and 4th experiment, the 2nd harmonic retroreflector has been used. The 2nd harmonic beam coming from the retrorefractor is converted to the 4th harmonic by putting the 4th harmonic crystal right after the delay stage. To reduce the beam size, a telescope is used before the 4th harmonic crystal. For the 4th and 5th experiment, a homemade retroreflector is used by putting the two 4th mirrors onto the metal plate folded by 90 degrees.
3. STUDY OF PHOTOCHEMISTRY OF Cr(CO)_6

3.1. Background of Cr(CO)_6

The group 6 transition metal carbonyl complexes have been the prototype molecules for understanding organometallic bonding and electronic structure. Cr(CO)_6 is one of the well-studied transition metal carbonyl complexes\(^\text{(22-52)}\). The characteristics of metal-CO bonding and electronic structure of the parent molecule of Cr(CO)_6 is reviewed to understand the importance of this molecule\(^\text{(34)}\).

The structure of this compound is six-coordinate octahedral, \(O_h\) symmetry with a zero oxidation state of the metal. It is believed that the bonding between CO and a metal is a combination of \(\sigma\) and \(\pi\) bonding\(^\text{(45)}\). Delocalization of lone pair \(\pi\)-d electrons from the central metal into the empty \(\pi^*\) CO orbital gives rise to \(\pi\)-back-bonding. Delocalization of the lone pair electron density of the carbon into the empty metal d orbital forms a \(\sigma\) interaction as diagrammed in Fig.4. The stronger \(\pi\)-back-bonding from low valent metal onto CO has a great tendency to delocalize electron density into the ligand. This back bonding is responsible for making Cr(CO)_6 highly covalent and rather stable. Thus the \(\pi^*\) CO orbitals play an important role in the stability of this molecule. The relative importance of \(\sigma\) and \(\pi\) interactions are difficult to assess. The electronic transition from the metal to the \(\pi^*\) CO orbital are attributed to substantial changes in bonding. This gives rise to the photosensitive excited states. This transition is called metal-to-ligand-charge-transfer (MLCT).
Fig. 4. σ- and π-Back-Bonding between Cr and CO

The bonding between Cr and CO is a combination of σ- and π-back-bonding. For the low oxidation state of Cr\(^{0}\) the π-back-bonding is responsible for the delocalization of the d electrons of the metal, thus enhancing the covalency of the bonding.
3.2. Electronic Structure

The electronic configuration of the Cr atom is [Ar]4s\(^1\)3d\(^5\). The ground electronic state has a \(t_{2g}\)\(^6\) electronic configuration and its symmetry belongs to \(^1\)A\(_{1g}\). One electron excitation to the \(t_{2g}\)\(^5\)e\(_g\)\(^1\) results in the \(^1\)T\(_{1g}\) and \(^1\)T\(_{2g}\) excited states on the basis of the ligand field theory\(^{46}\). The absorption spectrum of Cr(CO)\(_6\) is shown in Fig.5, and assignment for the bands are determined by Beach et al.\(^{48,49}\). The two strongest bands are assigned to the dipole-allowed (\(^1\)A\(_{1g}\) → \(^1\)T\(_{1u}\)) charge transfer transitions, and the shoulder (at 266 nm) of the blue side of the first charge transfer band (CT) is assigned to the weak d-d transition (\(^1\)A\(_{1g}\) → \(^1\)T\(_{2g}\)).

3.3. Structure of Chromium Pentacarbonyl.

The UV photolysis of the Cr(CO)\(_6\) generate coordinatively unsaturated Cr(CO)\(_x\) species (x=5,4,3,2), depending on the excitation wavelength in the gas phase\(^{28}\). The primary photoprocess in the condensed phase is different from that in the gas phase. Vibrational energy relaxation competes with Cr-CO bond breakage. It is found experimentally that only one CO is lost in solution\(^{24}\). Upon photodissociation of Cr(CO)\(_6\), Cr(CO)\(_5\) is produced within 1 ps in a condensed phase\(^{10-12,15-16}\). The naked Cr(CO)\(_5\) undergoes solvent coordination giving rise to the solvated Cr(CO)\(_5\) as a final product.

The appearance time of the final product may be dependent on the geometric structure of the initial photoproduct. The understanding of the
Fig. 5. Absorption Spectrum of Cr(CO)_6 in Cyclohexane.

The absorption spectrum is taken at 0.1 mM concentration. Two big bands are assigned to dipole-allowed C-T transitions (left: 2nd C-T, right: 1st C-T). The arrows indicate the wavelengths used to take the Raman spectra. The 2nd-CT band is off-scaled. This absorption spectrum was obtained on the Lakewood model 14DS, UV-VIS-IR spectrophotometer.
Fig. 5
geometric structure of Cr(CO)$_5$ is important to predict a photochemical pathway for the transient. There are two possible geometric structures for Cr(CO)$_5$. One is square-pyramidal (SP), the other is trigonal-bipyramidal (TBP) structure. The angular overlap model$^{(50)}$, extended Hückel calculations$^{(51-52)}$, and ab initio calculations$^{(31)}$ have determined that the SP structure is the preferred geometry for the singlet electronic ground state. However, for the electronic excited states the TBP structure is preferred. The reason for this is that the stabilization of this geometry over TBP is less than for Fe(CO)$_5$, which is known to adopt TBP geometry$^{(52)}$. Extended Hückel calculations$^{(52)}$ have confirmed that this configuration should have an energy minimum at the TBP structure. The TBP structure in the excited state finally shifts to the SP structure by way of the interconversion process of SP → TBP. The final SP structure is believed to be responsible for the solvation.

3.4. Polarization Study of Cr(CO)$_6$ and Cr(CO)$_5$

Polarized photochemistry of Cr(CO)$_5$ in N$_2$/Ar matrix has been done by Burdett et al.$^{(22)}$ From the UV/visible absorption study on the production of both N$_2$Mo(CO)$_5$ and Ar-Mo(CO)$_5$ with different polarizations it was concluded that the photoproduct of the parent molecule does not rotate during the solvation. If the same is true for Cr(CO)$_6$, it means that a certain polarized band of the transient species may retain the same polarization as that of the Cr(CO)$_6$. Suppose that $v_2$ vibrational mode of the transient is the same type of symmetry as $v_2$ of
Cr(CO)$_6$. In this case the Raman shift of $v_2$ of the transient is about the same as that of the parent molecule. In such a case, the two bands will almost be overlapped. The bands will have same polarization that is either parallel or perpendicular to the plane of polarization of the incident light since the solvated species (transient) does not rotate during the solvation. If the right polarization is not used for the ground-state band, the transient band will not be detected since both ground-state and transient bands have the same polarization. Therefore, the direction of the polarization should be carefully considered.

3.5. The Possibility of Dimer Cr(CO)$_5$-Cr(CO)$_5$

According to the ab initio calculation by Hay$^{(31)}$, there are two reasons why the Cr$_2$(CO)$_{10}$ dimer does not exist. The first reason is attributed to the presence of a "hole" in the d$^6$ shell. Cr(CO)$_5$ in the electronic ground state is represented as d$^5$ $a_1$ with a hole in the d$^6$ shell. Whereas, Mn(CO)$_5$ is represented as d$^6$ $a_1$ in the ground state without a hole. In the case of Mn(CO)$_5$, it readily forms Mn$_2$(CO)$_{10}$.

The formation of the dimer, Cr(CO)$_5$-Cr(CO)$_5$, needs the excited states of SP structure since the $a_1$ orbital of the SP is ideally suited for bond formation. The second reason why the dimer does not exist is related to the preference for the excited states of the monomer to exist as the TBP geometry. This geometry is unfavorable for dimer formation. Therefore the possibility of the formation of a dimer is ignored.
4. STUDY OF ELECTRONIC EXCITED STATE

4.1. Assignment of Bands.

Cr(CO)$_6$ has 33 normal vibrational modes. A representation of 33 vibrational modes is reduced to 13 fundamentals by $\Gamma = 2A_{1g} + 2E_g + T_{1g} + 4T_{1u} + 2T_{2g} + 2T_{2u}$ as shown$^{(30)}$ in table 1. Two of the Raman active modes, $\nu_1$ and $\nu_2$, belong to the totally symmetric $A_{1g}$ representation, and the rest belong to non-totally symmetric vibrational modes.

Two different Raman excitation wavelengths of 266 and 213 nm are used in our experiment. The 266 nm is off resonance. The 213 nm wavelength is in resonance with the second C-T transition. In view of symmetry considerations it is expected that two different types of vibrational modes will be differently enhanced depending on the excitation. The experimental data shown in Fig.6 indicate that the non-totally symmetric vibrational modes, $\nu_{10}$ (M-C-O bending) and $\nu_3$ (C-O stretching), are enhanced by 266 nm. On the other hand, the totally symmetric vibrational modes, $\nu_2$ (M-C stretching) and $\nu_1$ (C-O stretching)($\nu_1$ is shown only in fig.7), are enhanced by 213 nm. Basically we cannot tell any difference between the two spectra except for the intensity resulting from the different enhancement. Here, three overtones of the $\nu_2$ mode, $0 \rightarrow 2, 0 \rightarrow 3$, and $0 \rightarrow 4$, are observed at 760, 1135, and 1508 cm$^{-1}$, respectively$^{1}$. In fact, it is not easy to assign overtones because the anharmonicity for this molecule is not

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$^{1}$ The $0 \rightarrow 2$ overtone is apparent but the intensity of the $0 \rightarrow 3$ and $0 \rightarrow 4$ is about noise level. Therefore, the $0 \rightarrow 3$ and $0 \rightarrow 4$ overtones might be exaggerated.
Table 1. Fundamentals of the Vibrational Modes in Cr(CO)₆.

Fundamentals of all vibrational modes are shown in table 1. The frequencies from ref. are obtained in CCl₄ solution and ours are obtained in C₆H₁₂. The v₁ is obtained in CH₃OH solution. The accuracy is within ± 1 cm⁻¹. Jahn-Teller active modes belong to E₉ or T₂g representations.

<table>
<thead>
<tr>
<th>Fundamental</th>
<th>Activity</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref.*</td>
<td>Ours</td>
</tr>
<tr>
<td>1(A₁g)</td>
<td>Raman</td>
<td>2112</td>
</tr>
<tr>
<td>2(A₁g)</td>
<td>Raman</td>
<td>381</td>
</tr>
<tr>
<td>3(E₉)</td>
<td>Raman</td>
<td>2018</td>
</tr>
<tr>
<td>4(E₉)</td>
<td>Raman</td>
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</tr>
<tr>
<td>5(T₁g)</td>
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<tr>
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<tr>
<td>7(T₂u)</td>
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<td></td>
</tr>
<tr>
<td>13(T₂u)</td>
<td>Inactive</td>
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</tbody>
</table>

Fig. 6. Raman Spectra of Cr(CO)$_6$ in C$_6$H$_{12}$ at 266 and 213 nm Excitation.

The overtones of $v_2$ appeared in both 213 and 266 nm excitation spectra. The overtones appeared to be enhanced at 213 nm excitation as expected from Albrecht A-term activity. These overtones are confirmed by matching each other at two different excitations. $2v_2$ stands for the $0 \rightarrow 2$ overtone of the $v_2$. Likewise, $3v_2$ stands for $0 \rightarrow 3$, $4v_2$, $0 \rightarrow 4$ overtone, respectively. The solvent bands are represented by $S$. 
Fig. 7. Raman Spectra of Cr(CO)$_6$ in Cyclohexane and Methanol Solvents.

The spectra were obtained in two different solvents with 213 nm excitation. The overtones of $v_2$ appeared in both solvents. The ambiguity of the $v_2$ overtones in cyclohexane is cleared by comparing them with those in methanol. Especially, the $2v_2$ in methanol is apparent without being interfered by any solvent bands. The $v_1$ also appeared to be more enhanced at 213 nm excitation compared to 266 nm excitation in Fig. 6 implying that C-O is also displaced as expected from the Albrecht’s vibronic theory.
Fig. 7

Relative Intensity

Raman Frequency

Cr( CO )$_6$/C$_6$H$_12$

Cr( CO )$_6$/CH$_3$OH
known at this time. Nonetheless, these bands are assigned to overtones confidently by comparing the relative intensities between two spectra. The enhancement of the fundamental for $v_2$ band is much larger in 213 nm excitation than in 266 nm excitation because of a bigger enhancement. This is also true for the overtones, $0 \rightarrow 2$, $0 \rightarrow 3$ and $0 \rightarrow 4$. These overtones are not apparent in Fig.6 because of the interference of the solvent bands. However, they are clearly evident in methanol as shown in Fig.7 and Fig.8. In addition to these overtones, the activity of $v_7$ (M-C-O bending) and several combination bands are apparent.

This result is in contrast to that of Gerrity et al.\textsuperscript{(23)} in that their spectra did not show these overtones with 253, 266, and 281 nm excitation in the same solution. The reason for the apparent discrepancy is likely the result of their bad signal to noise ratio (S/N). In addition, the $0 \rightarrow 2$ band is not able to be separated from the solvent band in their spectrum. Also, the excitation wavelength of 266 nm does not enhance $v_2$ as much as that of 213 nm. Therefore, the small intensity of the $v_2$ overtones with 266 nm excitation is not enough to be separated from noise. However, in our spectrum it is confirmed that the overtones in the 266 nm Raman spectrum are not due to any artifacts by matching the overtones in 266 nm excitation spectrum with those in 213 nm spectrum. The appearance of the overtones in 266 nm excitation is not expected from the theory of vibronic Raman scattering. According to the theory the overtones for $v_2$ are not supposed to appear in the 266 nm spectrum since
Fig. 8. Raman Spectrum of Cr(CO)$_6$ in Methanol Solvent.

This spectrum is obtained in methanol with 213 nm excitation. There are several overtones of $\nu_2$ appeared with its combinations. The appearance of the combinations of $\nu_2$ with either totally or non-totally symmetric bands increases a credibility for $\nu_2$ being the reaction coordinate. Also, the $0 \to 2$, $0 \to 4$ overtones of $\nu_7$ appeared implying that the $\nu_7$ can be another reaction coordinate. The solvent bands are designated as "S".
the 266 nm corresponds to the d-d transition which is not the dipole-allowed transition. The reason for that is explained in the section of "interpretation of the overtones" and "Jahn -Teller distortion."

4.2. Interpretation of the Overtones.

The observation of the overtones for the totally symmetric mode, $v_2$, with either 266 nm or 213 nm excitation can be explained from the Albrecht vibronic theory. According to the theory, the overtones of a particular mode can appear only if the excited state is displaced with respect to the ground state along that vibrational mode. Experimentally it is found that this remains true. The appearance of the overtones of the $v_2$ is an indication that the excited state is displaced relative to the ground state along this normal mode. This reasoning does make sense in considering a transition in terms of molecular orbital (MO) theory.

The transition ( $^1A_{1g}(\pi) \rightarrow ^1T_{1g}(\sigma^*)$ ) corresponding to the 266 nm excitation accompanies one electron transition from the non-bonding $d(\pi)$ orbital in $t_{2g}$ electronic state to the anti-bonding $d(\sigma^*)$ orbital in $e_g$ electronic state (see Fig.9(B)). The transition from the non-bonding to the anti-bonding orbital results in two effects which decrease the bonding properties. The $\pi$ back-bonding decreases when one electron is removed from a lone pair $d(\pi)$ orbital in the $t_{2g}$ electronic state. The bonding is also reduced by population of the $\sigma^*$ anti-bonding orbital. These two cooperative effects cause the weakness of the
bonding between metal and carbonyl group. This mechanism accounts for the appearance of the overtones for the totally symmetric mode in this transition.

In the 213 nm Raman spectrum the totally symmetric mode, $v_2$, is enhanced by a factor of 3-4 compared to that in the 266 nm spectrum*. In addition, the fundamental of the C-O stretching mode, $v_1$, has shown up indicating the change of the bond length between the carbon and the oxygen atom. The 213 nm transition corresponding to the $^1A_{1g}(\pi) \rightarrow ^1T_{1u}(\pi^*)$ transition is different from that of 266 nm in that the former is strongly dipole-allowed whereas the latter is forbidden d-d transition. The depopulation of the non-bonding d($\pi$) orbital and the population of the $\pi^*$ CO in $t_{2u}$ electronic state are the sources for the displacement of the M-CO as well as the C-O bonding (see Fig.9 (C)). As with the 266 nm excitation, the depopulation of the non-bonding d($\pi$) decreases the strength of $\pi$ back-bonding, thus reduces the bond of M-CO. On the other hand, the population of the anti-bonding orbital of the $\pi^*$CO decreases the strength of the C-O bonding. In such a case, displacement of the C-O bond will take place. As a result, at 213 nm excitation the displacement of not only M-CO but also C-O bond can be observed. The appearance of the C-O stretching mode is also partially due to the enhancement in this strongly allowed CT transition.

* The numbers for the factor has been obtained by comparing the relative intensity between the totally and non-totally symmetric normal modes.
Fig. 9. Schematic Diagrams of the D-D and MLCT Transition.

A). The $d^6$ configuration in Cr metal before excitation.

B). The d-d transition accompanies one electron transition from the non-bonding $d(\pi)$ orbital to the anti-bonding $d(\sigma^*)$ orbital. The symmetry term for the electronic configuration of $t_{2g}^6$ is represented by $^1A_1g$, whereas, that of the $t_{2g}^5e_g$ is represented by $^1T_{1g}$(spin allowed).

C). The MLCT transition accompanies one electron transition from the non-bonding $d(\pi)$ orbital to the anti-bonding $\pi^*{CO}$ orbital. The symmetry for the resulting configuration is represented by $^1T_u$(spin allowed).
However, the comparison of the intensity between 266 nm and 213 nm spectra does not provide accurate information about the extent of the displacement. The reason is that the resonance effect rather than the extent of displacement may dominate. In order for a reaction to occur a particular vibrational mode has to be displaced largely. Therefore, if a large displacement occurs along that particular vibrational mode, that mode can be a reaction coordinate. The evidence for a reaction coordinate is the appearance of the overtones in a resonance Raman spectrum. Therefore, the \( \nu_2 \) mode could be a reaction coordinate. Nonetheless this mode as a reaction coordinate has been ignored by Nelson et al.\(^{16}\) by reason that it is unlikely that all six CO are displaced by the same amount during the reaction.

It is interesting to compare our results for \( \text{Cr(CO)}_6 \) with those for \( \text{Mn}_2(\text{CO})_{10} \) of Nelson et al.\(^{16}\). \( \text{Mn}_2(\text{CO})_{10} \) dissociates through two channels depending on the excitation wavelength. One of the channels is the cleavage of the Mn-Mn bond. The normal mode responsible for this cleavage is the Mn-Mn stretch. This mode belongs to the totally symmetric modes. If the Mn-Mn stretch appears with its overtones, it could be easily considered as a reaction coordinate since this is the mode corresponding to the bond required to be broken. In fact, they observed its fundamental and overtones, and assigned it as the very mode along which photocleavage occurs. The only difference between two molecules is that in \( \text{Cr(CO)}_6 \) six Cr-CO bonds are involved, whereas one Mn-Mn bond is involved in the same type of vibrational mode.
(totally symmetric stretching mode). A vibrational mode with high overtones gives more confidence in assigning it as a reaction coordinate. Therefore, it is quite possible that the $v_2$ of Cr(CO)$_6$ is a reaction coordinate. The question remained is that: Does this mode contribute to the reaction coordinate solely? or partially with the other modes? Since the $v_7$ has been reported as a reaction coordinate$^{16}$, it is possible that the $v_2$ mode is coupled with that mode, so that either of them becomes a final reaction (cleavage) coordinate. Now, the possibility of the $v_7$ as another reaction coordinate is investigated in the following section.

4.3. Reaction Coordinate.

For the reaction coordinate, the $v_7$ mode has been considered by Nelson et al.$^{(16)}$ by reason that it is an asymmetric stretching mode, and its $0 \rightarrow 2$ overtone has been observed with the 351 nm excitation. The $v_7$ is IR active as an asymmetric stretching mode of Cr-CO, therefore its fundamental should not appear in the Raman spectrum. However, its even overtones could appear in two cases when the forbidden d-d transition is used. When it plays a role of either a coupling mode or reaction coordinate*, its even overtones are supposed to appear.

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* A coupling mode is the mode which can couple the forbidden transition to the strongly dipole-allowed transition. A reaction coordinate is the coordinate along which a displacement occurs giving rise to a reaction.
If it is a coupling mode, from the symmetry consideration only even overtones appear. This can be visualized by taking account of the Franck-Condon factors between two vibrational wave functions. As shown in Eq. (11-13) the polarizability responsible for the Raman intensity is proportional to the Franck-Condon factors. To begin with, the case of $0 \rightarrow 2$ overtone as an even overtone will be considered. Assuming that the vibrations are harmonic, the Eq.(13) will be as follows.

$$\alpha = <\text{1}|Q|\text{v}> <\text{v}|Q|\text{f}> = <2|Q|\text{v}> <\text{v}|Q|0>.$$  \hspace{1cm} \text{(15)}

$$= <3|\text{v}><\text{v}|1> + <1|\text{v}><\text{v}|1> \hspace{1cm} \text{(16)}$$

where $Q$ is a coupling mode and plays the role of a ladder operator. $V$ is a vibrational level in the excited state. The product of the first term in Eq.(16) corresponds to the $0 \rightarrow 2$ overtone, and the product of the second term, Rayleigh scattering. These two terms do not vanish because the Franck-Condon overlap between two odd wave functions does not go to zero. Hence, the even overtones of the coupling modes will appear in the strictly forbidden transition.

If the case of the $0 \rightarrow 3$ overtone is considered for a odd overtone, then the Eq.(13) will be as follows.

$$\alpha = <3|Q|\text{v}> <\text{v}|Q|0>$$ \hspace{1cm} \text{(17)}

$$= <4|\text{v}><\text{v}|1> + <2|\text{v}><\text{v}|1> \hspace{1cm} \text{(18)}$$

The products of the even and odd functions in Eq.(18) go to zero. The first term corresponding to the $0 \rightarrow 3$ overtone vanishes. This is also true for the second
term corresponding to the fundamental. Therefore, only even overtones would appear if there exists a coupling mode.

If the $v_7$ mode plays a role of a reaction coordinate, its even overtones will appear not only in a forbidden but also in a dipole allowed transition. But, if an excitation is in resonance with a dipole allowed transition, the $v_7$ overtones would be more enhanced than if the excitation is in resonance with the forbidden transition. Therefore, the observation of the even overtones ($0 \rightarrow 2, 0 \rightarrow 4$) of the $v_7$ with the 213 nm excitation is evidence for this mode being a reaction coordinate. The appearance of its higher even overtone ($0 \rightarrow 4$) in the 213 nm spectrum shown in Fig.8 clearly confirms the $v_7$ as a reaction coordinate since higher overtones will appear only in a large displacement.

This can be better understood by introducing the wave packet description. Originally using this concept, Lee and Heller\textsuperscript{(55)} described the time-dependent theory of Raman scattering, and Kinsey et al.\textsuperscript{(56)} applied this wave packet concept to the study of CH$_3$I photodissociation. Later Nelson et al.\textsuperscript{(16)} applied it to the Cr(CO)$_6$ to reveal the reaction coordinate.

When a molecule is excited into a dissociative energy level, it comes apart in roughly a molecular vibrational period or less ($\approx 10^{-14}$). As it comes apart, the dissociating molecule sweeps through the dissociative potential energy surface. Thus a propagating wave packet gives rise to Franck-Condon overlap with highly excited vibrational levels of the ground state. The cross section $\alpha_{1+}$ of Raman process is given by
\[ \alpha_i = \int_0^\infty \exp\left( -\epsilon_i \right) \exp\left( -\Gamma t \right) dt \]  

where \(|i(t)\rangle\) is the wave packet after propagating on the excited surface for a time \(t\), \(\Gamma\) is the electronic dephasing rate, and \(\epsilon_i\), energy of a vibrational state \(|i\rangle\). If we promote the wave packet from the electronic ground state to the excited state at \(t=0\) using the sudden approximation, the wave packet is still the initial vibrational wave function. With time it evolves as \(|i(t)\rangle\), thus it overlaps with higher vibrational states \(<f|\) as a function of \(t\). For a given vibrational progression, the overlap will develop continuously from the lowest level to the higher levels, depending on the amount of displacement of the coordinate for the excited state. The absolute square of \(\alpha_i\) is directly proportional to the intensity of the overlap at a certain excitation wavelength. Ideally at exact resonance with photodissociation, only the integral part of \(<f| i(t)\rangle\) will affect the intensity because the damping rate would be almost zero. If the excitation is not an exact resonance with photodissociation, the damping rate \(\Gamma\) will have a contribution. Therefore, the dynamics on a time scale that decreases with increasing \(\Delta E (E_{ev}-E_0)\) is sampled. In the limit of very large \(\Delta E\), only dynamical process taking place on a time scale much shorter than the dissociation time will contribute the Raman intensity. Thus the high overtones corresponding to late developing dynamics will disappear more rapidly than the earlier developing fundamentals. For this reason, if an exact resonance is used for an excitation,
the dynamical process occurring on a longer time scale on the order of the
dissociation time results in high overtones.

If the excitation is in resonance with a strongly allowed electronic
transition, the minimum of the PES of the excited state of the totally symmetric
vibrational mode will be displaced relative to the ground state. For totally
symmetric vibrational modes, the wave packet in the excited state picks up
overlap with the overtone levels in the ground state while it moves back and
forth. Since the minimum energy of the PES can be different for totally
symmetric vibrational modes, the Frank-Condon overlap will not be canceled out
in any case. In other words, the Franck-Condon overlap will not come from the
complete phase matching between two wave functions. Hence, the overlap
between even and odd function will not be exactly out of phase. Therefore all
the overtones with its fundamental can appear in this case. For asymmetric
modes, the minimum of the PES of the excited state is not displaced with
respect to the ground state. So the wave function in the excited state is phase
matched with that of the ground state at a given normal coordinate. Thus the
Frank-Condon factor corresponding to the even and odd functions will be
completely out of phase. Therefore, only the even overtones are enhanced in
this case.

The appearance of the overtones also provides information about the
photodissociative state where dissociation occurs. Dissociation can occur either
in a singlet or a triplet state. Nasielski and Colas\(^{(32b)}\) addressed that
photodissociation occurs in a triplet state by reason that the quantum yield for
dissociation in a similar W(CO)$_6$ is independent of wavelength. The resonance
Raman study also supports this result by reason that the overtones of any
normal modes responsible for the reaction coordinate has not been observed.
However, the triplet state as primary dissociation channel has been refuted by
the femtosecond UV/vis absorption study$^{(16)}$. According to the femtosecond
UV/vis absorption study the photodissociation takes place in about 500 fs, and
solvation follows right after for 0.5 - 5 ps. If there is a dynamics due to the
intersystem crossing to the triplet state, it has to appear between 0 and 500 fs
temporal range. In Cr(CO)$_6$, Mo(CO)$_6$, and W(CO)$_6$ the identical dynamics in
form and time scale were found implying that no intersystem crossing takes
place. This result is based on the expectation that the different time scale for the
intersystem crossing due to the different spin-orbit coupling should influence the
dissociation time in the 0-500 fs range. Since this was not observed in the
femtosecond study it was concluded that the reaction proceeds directly from the
initially excited singlet state with no intersystem crossing necessary.

Our Raman spectra support the femtosecond study. Suppose that
dissociation occurs in the triplet state through intersystem crossing; then
overtones would come from the triplet state. In such a case the Raman cross
section will be zero, since it is a spin forbidden transition. Thus it will not be
possible to observe them in resonance Raman spectra; Raman bands are
attributed to the product of the vibrational wave functions between the singlet
electronic excited and the ground state. On the other hand, if the singlet state is responsible for the dissociation, the activity of the overtones will show up in resonance Raman spectra since the projection of the displacement will appear as overtones, while the higher overtones indicating the large displacement. Therefore, the appearance of the overtones of $v_2$ and $v_7$ implies that the singlet state is responsible for the photodissociation in our excitation. The triplet state may be responsible for the photodissociation to some extent after fast ($\leq 100$ fs) intersystem crossing\(^\text{(16)}\). The intersystem crossing can occur during the wave packet of the singlet state evolves giving rise to overtones. Since the time scale and the quantum yield of the intersystem crossing are not known yet, the triplet state could not be ruled out as being responsible for photodissociation. Nonetheless, this fact does not change our conclusion that the singlet state is mainly responsible for photodissociation.

### 4.4. Jahn-Teller Distortion

The structure and properties of a molecular system are determined by the interaction between electrons and nuclei. The big difference in masses between electron and nucleus leads to approximation in quantum mechanical treatment of their motions. According to this approximation, a large difference of the masses causes a significant difference in their velocities of motion, and thus the electronic state is sustained as stationary for every instantaneous nuclear motion, whereas the latter are moving in the averaged field produced
by electrons. This approximation is called the adiabatic approximation\(^{(57)}\). The deviations from this adiabatic approximation were found by Jahn and Teller and are known as the Jahn-Teller effect. The Jahn-Teller theorem states that for a nonlinear molecule in an electronically degenerated state distortion must occur to lower the symmetry, remove the degeneracy, and lower the energy.

For example, Cu\(^{2+}\) ion such as in Cu(NH\(_3\))\(_6\)\(^{2+}\) with O\(_h\) symmetry\(^{(59-60)}\) is illustrated. The electronic configuration of Cu\(^{2+}\) ion is t\(_{2g}\)^6e\(_g\)^3. This ion possesses one hole in the e\(_g\) orbitals. The electronic state of the ion is a degenerate E\(_g\) state\(^*\). According to the Jahn-Teller theorem the octahedral symmetry is no longer perfect but is a distorted octahedron. The reason for the distortion can be visualized by a simple physical description. Suppose that of the two e\(_g\) orbitals (d\(_{x^2-y^2}\), d\(_{z^2}\)), the d\(_{x^2-y^2}\) orbital is doubly occupied, and the d\(_{z^2}\) is singly occupied as shown in Fig.10. In such a case, the four negative charges or the negative ends of dipoles in the xy plane will be more screened from the electrostatic attraction of the central Cu\(^{2+}\) ion than will the two charges on the z axis. Then, the two ligands on the d\(_{z^2}\) orbital will be more closely attracted than the other four ligands. Thus, not all the distances between metal and ligands are same. This is a simple example to illustrate how the Jahn-Teller distortion works. But, the theorem gives no explicit prediction of the geometrical nature of the distortion or how great it will be.

\(^*\) The label of E\(_g\) represents the ground state of t\(_{2g}\)^6e\(_g\)^3 from the symmetry point of view. Whereas, the label of e\(_g\) represents the electronic state.
Fig. 10. A Schematic Diagram of Jahn-Teller Distortion.

A). The $e_g$ orbitals ($d_{x^2-y^2}$, $d_{z^2}$) will be degenerated if they are filled up with 4 electrons. In such a case a perfect octahedron is formed. B). The $e_g$ orbitals are splitted due to the unbalance of the electrons in the $e_g$ orbitals. The splitting of the $e_g$ orbitals results in the distortion from the perfect octahedron.
The Jahn-Teller theorem also applies to the excited states. The Cr\(^{0}\) has no \(E_g\) component in the ground state since no electrons are occupied in \(e_g\) state. Hence, the Jahn-Teller distortion can not be applied to Cr(CO)\(_6\) in its electronic ground state. If one of the six electrons in \(t_{2g}\) move to the \(e_g\) or other state, the Jahn-Teller distortion will take effect.

In the presence of the Jahn-Teller effect, the electrons do not adiabatically follow the motion of the nuclei. The nuclear states are determined not only by the averaged field of electrons but also by the coupling between the electrons and nuclei. The factor playing a role for coupling is vibration. Therefore vibronic mixing of electronic states gives rise to the deviation from the adiabatic approximation and its effect is not negligible.

It is interesting to study how much this Jahn-Teller distortion affects excited state of Cr(CO)\(_6\). The study for Cr(CO)\(_6\) has been done recently by Gerrity et al.\(^{23}\) using resonance Raman spectroscopy. The observation of the enhancement of the fundamentals of the \(\nu_3\) (\(E_g\)) and \(\nu_{10}\) (\(T_{2g}\)) modes is evidence for the existence of the Jahn-Teller distortion.\(^{57}\) They observed an enhancement of the fundamentals of the Jahn-Teller active modes with 253 and 282 nm, which corresponds to the 2nd and 1st CT transitions, respectively. Their conclusion is as follows; 1. The enhancement of the fundamentals of the \(\nu_3\) and \(\nu_{10}\) modes by the first CT band , and apparently by the second CT bands as well, is almost certainly due to a Jahn-Teller effect in the excited states of these transition. 2. The absence of binary overtones and combinations of
these Jahn-Teller active modes in the Raman spectrum, corresponding to C-type activity, indicates that the induced components are much weaker than the allowed components of the transition moment, and therefore, the Jahn-Teller coupling in these molecules must be interpreted as being weak. Thus, the distortion in the excited states is not large. However, our results do not completely agree with their results. Firstly, the Jahn-Teller distortion did not occur to the same extent in our 1st and 2nd CT transitions. Secondly, the combinations of the Jahn-Teller active modes are observed (see Fig.8) in our spectra implying that the Jahn-Teller coupling is relatively large, thus the distortion in the excited state is large.

In our experiment 266 nm, which is the same as what was used by Gerrity et al.\(^{(23)}\), and 213 nm, which is very near the maximum of the 2nd C-T transition in the absorption spectrum, are used. In the 266 nm Raman spectrum the non-totally symmetric vibrational modes, \(v_{10}\) and \(v_{3}\), are dominating even though the activity of the totally symmetric mode, \(v_{2}\), appeared. On the other hand, in the 213 nm Raman spectrum, the totally symmetric mode, \(v_{2}\), dominates, whereas the non-totally symmetric modes, \(v_{10}\) and \(v_{3}\), are dramatically reduced.

The 266 nm excitation is assigned as a forbidden d-d transition even though the assignment of this transition as the d-d transition is still under debate. Assuming it is a forbidden d-d transition as assigned by Beach et al.\(^{(48)}\), the fundamentals of the non-totally symmetric modes, \(v_{10}\) and \(v_{3}\), are not
supposed to be observed. Instead, the fundamentals, overtones, and combinations of the totally symmetric modes and even overtones of the non-totally symmetric vibrational modes should appear as coupling modes. Our results, showing an enhancement of not only the totally symmetric but also the non-totally symmetric modes, are not consistent with an expectation from the theory; this activity is not a C-type but a B-type activity.

A plausible explanation for the abnormality of d-d transition can be found by considering the Jahn-Teller distortion. The d-d transition of this molecule results in the $t_{2g}^5e_g^1$ configuration for the central metal. As a consequence, the splitting of the degeneracy takes place in both $t_{2g}$ and $e_g$ orbitals. In such a case, the effect of Jahn-Teller distortion would be even bigger compared to the "one hole system" like $t_{2g}^6e_g^1$. As a result, the intensity of the Jahn-Teller vibrational modes would be enhanced. Therefore, the observation of a relatively large enhancement of the $v_{10}$ and $v_3$, corresponding to the Jahn-Teller vibrations, is evidence for the existence of the Jahn-Teller distortion. This result agrees with that of Gerrity et al. (23)

The 213 nm Raman spectrum is different from the 266 nm spectrum in that at 213 nm excitation the totally symmetric band, $v_2$ as well as its overtones are strongly enhanced, whereas the non-totally symmetric bands, $v_{10}$ and $v_3$ are dramatically reduced. The appearance of the totally symmetric vibrational modes is indicative of Albrecht's A-type activity. But the presence of the non-totally symmetric vibrational modes can be explained by a small extent of Jahn-Teller
distortion. This small extent of Jahn-Teller distortion is due to the promotion of one electron in non-bonding orbitals, $t_{2g}^6$ to the anti-bonding $\pi^*CO$ orbitals. The electron removed from $t_{2g}$ orbital does not enter the anti-bonding $e_g^*$ orbitals as in the case of 266 nm excitation. Thus the promotion of one electron to the $\pi^*$ CO orbital does not split the $e_g^*$ orbitals as much as in the case of 266 nm excitation. Therefore only a small extent of Jahn-Teller distortion has been observed in 213 nm excitation. However, it is noticed that even this small extent of Jahn-Teller distortion is enough to give rise to a displacement of the excited state contrary to the results of the Gerrity et al.\textsuperscript{(23)}

In summary, there are several important features to be pointed out by comparing our works with Gerrity’s similar works.\textsuperscript{(23)}

1. The overtones of the totally symmetric vibrational mode, $v_2$, has been observed in both 266 nm and 213 nm excitation. The observation of the overtones indicates that there is a large distortion along this totally symmetric vibrational mode. This is consistent with a reaction coordinate from this electronic state which leads to CO loss.

2. The singlet excited state appears to be responsible for photodissociation even if an extent of a contribution cannot be determined. This is proven by the appearance of the overtones for the totally symmetric vibrational mode, $v_2$ in both forbidden and dipole allowed transitions.
3. The Cr-C bond has a large displacement in both dipole allowed and forbidden transition. The activity of the C-O stretching mode tells us that this bond is also displaced but not as much as the Cr-C bond is.

4. The observation of the even overtones of the asymmetric vibrational mode, \( v_7 \), is evidence for this mode being a reaction coordinate, and also clearly shows that photodissociation takes place through the cooperation among the possible modes.

5. The Jahn-Teller distortion has been found in the 266 nm excitation to a large extent. On the other hand in the 213 nm excitation only a small extent of Jahn-Teller distortion has been found.
5. TIME-RESOLVED RAMAN STUDY USING PUMP AND PROBE TECHNIQUE.

5.1. The Historical Review of Time-Resolved Study on This Work.

With the availability of new instruments which can detect very fast time scale of pico- or sub pico-seconds, the interaction between the molecule and solvent has been of interest. The mechanism of the flow of an excess energy after being dumped into the molecule is also one of the fields that has become possible. Simon et al.\(^{(10)}\) reported the solvation time of \(\leq 0.8\) ps for naked \(\text{Cr(CO)}_5\) in cyclohexane solvent after photodissociation of \(\text{Cr(CO)}_6\) using transient uv/visible absorption technique. He insisted that the photofragment of \(\text{Cr(CO)}_5\) upon photodissociation deactivates the excess energy via interconversion between SP and TBP resulting in solvation in its electronic ground state. Therefore no vibrational relaxation could be observed in this system even though a theoretical study predicted the possibility of relaxation from the electronic excited state\(^{(48)}\). The rate for the dissociation of the parent molecule is so fast that the rise time is ascribed to the solvation time. In methanol solvent they observed 2.5 ps rise time and assign it to the reorganization of the local solvent. Their interpretation is that the reorganization time of the local solvent before coordination affects the rise time. According to their results the breaking of solvent hydrogen bonds is not the step which occurs prior to solvation. It is supported by the fact that the Debye relaxation time for hydrogen-bonded methanol molecules is \(\approx 50\) ps. In addition, the
coordination time is faster than the rotational diffusion time of Mo(CO)\textsubscript{6} assuming similar results would be expected for Cr(CO)\textsubscript{6}. From the above facts Simon \textit{et al.}\textsuperscript{(10)} reached the conclusion that only a small change in the local solvent environment is necessary for solvent coordination to occur.

However, controversial results have been reported by Spears \textit{et al.}\textsuperscript{(13)} using picosecond IR transient absorption technique. They observed dynamics of \approx 200 \text{ ps} and interpreted this as transient naked Cr(CO)\textsubscript{5} comprising two kinds of structures; one is SP, the other is TBP. The dynamics are due to two channels with different rate constants. The TBP has more reactivity than SP by a factor of 2.3 suggesting that the geometry or electronic configuration of unsaturated coordination is important in reactivity. In their results the solvation time is much longer than 0.8 ps reported by Simon \textit{et al.}\textsuperscript{(10)} Since two results are contradicting each other, several groups have been involved to resolve this problem. Nelson \textit{et al.}\textsuperscript{(15-16)} used the transient absorption technique with femtosecond time resolution. They found three different dynamics in methanol solution; a pulse duration-limited rise, a rapid (< 500 fs) non-exponential decay, and a slow (1.6 ps) exponential rise. Nelson \textit{et al.}\textsuperscript{(15-16)} interpreted the three temporal regions of the data correspond as 1. photoexcitation, 2. photodissociation, and 3. solvent complexation processes. Their results support the solvation time which Simon \textit{et al.}\textsuperscript{(10)} found. Nelson \textit{et al.}\textsuperscript{(15-16)} also observed a long time scale of 70 ps and interpreted it as both electronic and vibrational relaxation. Harris \textit{et al.}\textsuperscript{(17)} reported dynamics of 17 ps
using transient uv/visible absorption technique. They insisted that vibrational relaxation is followed by solvation since the transient molecule has extra energy after rejecting one CO group. The questions that remain are as follows. 1. Does solvation take place so fast that naked Cr(CO)₅ cannot be observed? 2. Does vibrational relaxation occur before or after solvation? 3. Do they observe a real vibrational relaxation other than electronic relaxation?

Recently our group reported long time dynamics of ≈ 100 ps using picosecond Raman spectroscopy and ascribed it to the vibrational relaxation after solvation. Since the transient Raman technique gives an unambiguous evidence for the vibrational relaxation with the help of complementary results of both Stokes and anti-Stokes scattering, the vibrational relaxation from the other dynamics such as electronic relaxation and conformational change can be separated.

The solvent reorientation is another subject of controversy. Spears et al. reported solvent reorientation time of ≈ 700 ps in THF (tetrahydrofuran) solution. THF has two different kinds of elements in terms of electron affinity. One is a hydrogen, the other is an oxygen. Initially the hydrogen of alkane complexes attack the vacant site of Cr(CO)₅. With time increment, the alkane complexes rearrange to the thermodynamically more stable hydroxyl group. On the other hand Simon et al. observed < 200 ps corresponding to the solvent rearrangement. The other groups, however, failed to observe the solvent
rearrangement either in THF or alcohols which both have two different functional groups.

In this study the investigations of the controversial results are carried out using picosecond Raman spectroscopy technique. In section 5.2, the way how to interpret the dynamics of 100 ps as vibrational relaxation is described with the help of the complementary results of the Stokes and anti-Stokes Raman spectra in cyclohexane solvents. In Chapter 6, the solvation, electronic relaxation, and vibrational relaxation times are studied in details.

5.2. The Role of Vibrational Energy in the Ultrafast Photodissociation of Cr(CO)₆

In this section an investigation is presented of the photodissociation of Cr(CO)₆ and the subsequent reaction dynamics of the photoproducts using picosecond transient Raman spectroscopy. Contrary to the common perception that non-equilibrium vibrational energy does not contribute to condensed phase reactions, it is found instead that the appearance time of the thermally equilibrated Cr(CO)₅ photoproduct is rate limited by vibrational energy decay. This result has important implications to recent ultrafast studies of the photochemistry of Cr(CO)₆. Transient absorption experiments have discovered(10-12,15-16) that photoexcitation of Cr(CO)₆ results in the formation of solvated Cr(CO)₅ which appears in a time of < 0.8 ps in hydrocarbon solvents. However, in contrast to these results a controversy now exists due to the
experiments of Spears et al.\textsuperscript{(13-14)} where transient picosecond infrared data has been interpreted to show that solvated Cr(CO)\textsubscript{5} appears to be produced by several different mechanisms on a much slower time scale. In contrast to this interpretation, time dependent shifts in the absorption maximum of solvated Cr(CO)\textsubscript{5} have been attributed\textsuperscript{(15-17)} to vibrational energy relaxation which occurs\textsuperscript{(17)} in 17 ps.

The results reported in this section remove the present controversy by directly probing the vibrational coordinates of the photoproducts using transient Raman spectroscopy. The experimental apparatus has been previously described in detail.\textsuperscript{(6-9,21)} Fig. 11 shows the picosecond transient Raman spectra obtained at various optical delays for 266 nm excitation of Cr(CO)\textsubscript{6} in cyclohexane. Two 5 ps pulses at 266 nm are used in this experiment. The first pulse photodissociates Cr(CO)\textsubscript{6} and the second probes the resonance Raman spectrum of Cr(CO)\textsubscript{5}. The advantage of detecting resonance Raman scattering at this wavelength is that the ultraviolet absorption band of Cr(CO)\textsubscript{5} is very strong\textsuperscript{(64)} ($\epsilon = 3 \times 10^4$ at 240 nm) and relatively insensitive to solvent interactions. The spectra contain only pure transient Raman bands after removal of solvent and ground state Cr(CO)\textsubscript{6} bands using a spectrum differencing technique. This was achieved by alternately exciting the sample with a single interrogation laser pulse or a double pump-probe laser pulse sequence. The pure transient spectrum shown in Fig. 11 is obtained by subtracting the one pulse background spectrum from that obtained in the double pulse sequence.
Fig. 11. Pure Transient Picosecond Stokes Raman Spectrum in Cyclohexane

This spectrum is obtained by two pulse pump and probe at 266 nm as described in the text. The Raman intensity represents a temporal average over the pulse width of the laser which is specified in each frame. The colored-in bands are those assigned to solvent coordinated Cr(CO)$_5$. Asterisks are used to denote noise due to Raman bands of the solvent molecules which have been subtracted out of each spectrum. Laser intensity was 20 μJ/pulse at 2 kHz in a 0.2 mm beam waist. This laser intensity is two times less than that used in the previous transient infrared experiments. Concentration is 10 mM. Frequency is in units of cm$^{-1}$. 
Comparing frames A-D in Fig.11, it is readily apparent that a single transient appears with a time scale of roughly 100 ps. The metal-CO stretch at 381 cm\(^{-1}\), and the CO vibration at 1935 cm\(^{-1}\) indicate that the transient is a metal carbonyl complex which is assigned to Cr(CO)\(_5\). The bands marked with asterisks are the result of noise generated by the spectrum differencing technique at the frequencies of the cyclohexane solvent bands. The negative going peaks are ground state Cr(CO)\(_6\) bands which appear in the transient spectrum as a result of population bleaching. The ground state 383 cm\(^{-1}\) metal-CO stretch of Cr(CO)\(_6\) appears as a bleach in the 30 ps spectrum and gradually fills in at later times due to the growth of the Cr(CO)\(_5\) transient band at 381 cm\(^{-1}\).

The dynamics of vibrational cooling can be investigated by comparing the Stokes and anti-Stokes band intensities. Figure.12 illustrates the transient anti-Stokes spectrum in the region of the 381 cm\(^{-1}\) band assigned to Cr(CO)\(_5\). The results indicate that the anti-Stokes spectrum from the hot vibrational state decays in 100 ps. The observation that the anti-Stokes and Stokes spectrum have complementary dynamics is consistent with vibrational relaxation. The appearance of thermally equilibrated Cr(CO)\(_5\) is therefore believed to represent the time required for the photoproduct to approach thermal equilibrium with the solvent. This conclusion clearly demonstrates the importance of non-equilibrium vibrational energy in condensed phase photochemistry and provides an alternative explanation for the dynamics observed in the transient infrared\(^{13-14}\).
Fig. 12. Pure Transient Picosecond anti-Stokes Raman Spectrum in Cyclohexane

This spectrum is obtained under similar conditions to those given in Figure 11. Time delay between pump and probe pulses is given separately in each frame. Ground state bands have been subtracted out of the spectrum as described in the text. Spectra are normalized to the intensity of the ground state chromium band at 532 cm$^{-1}$ in the un-subtracted spectrum. Frequency is in units of cm$^{-1}$.
experiments. It is interesting to note that the time scale we observe for complete vibrational relaxation is approximately the same as that observed\(^{36}\) for the CO stretching vibration in Cr(CO)\(_6\). In that experiment, a relaxation time of 145 ± 25 ps was observed in n-hexane. Similar rates would be expected in these two experiments if the latter dynamics represent the time required for energy randomization followed by vibrational relaxation through the entire manifold of vibrational levels. There is no direct way to compare our results to the faster dynamics attributed to vibrational decay in the transient absorption\(^{15\cdots17,37}\) experiments. It is likely that the latter results represent initial decay from upper vibrational levels which are difficult to characterize using electronic absorption spectroscopy.

In summary, results are presented which demonstrate the importance of vibrational energy in the photodissociation of Cr(CO)\(_6\). A single Stokes transient is observed to appear at a rate similar to the decay rate of a species with a vibrationally hot anti-Stokes spectrum. The probe wavelength (266nm) should\(^{64}\) be equally sensitive to detection of both naked Cr(CO)\(_5\) and Cr(CO)\(_5\)·C\(_6\)H\(_{12}\). Even so, we do not find a thermally equilibrated precursor to the final product. This suggests that one of the following two reaction schemes\(^{65}\) is operative. Here # indicates non-thermal vibrational energy and -S solvent coordination.

\[
\text{Cr(CO)}_5^* \rightarrow (100 \text{ ps}) \text{ Cr(CO)}_5 \rightarrow \text{(fast)} \text{ Cr(CO)}_5 \cdot \text{S} \quad (20)
\]

\[
\text{Cr(CO)}_5^* \rightarrow \text{(fast)} \text{ Cr(CO)}_5^* \cdot \text{S} \rightarrow (100 \text{ ps}) \text{ Cr(CO)}_5 \cdot \text{S} \quad (21)
\]
In both mechanisms, vibrational relaxation is the rate limiting step and is found to be remarkably long requiring over 100 ps for complete thermalization.
In this chapter the details of the vibrational relaxation and solvent coordination have been studied using the 4th (pump) and 4th (probe) technique. Using this technique transient Raman investigation is presented to determine if the vibrational relaxations reported from other techniques are actually vibrational relaxations. If so, what is the difference between these dynamics and the 100 ps dynamics reported in our earlier communication? Also, an attempt to separate vibrational decay from solvent reorientation is tried.

6.1. Introduction

The photochemistry of Cr(CO)$_6$ has been extensively investigated.$^{(34)}$ Recent research has focussed on understanding the ultrafast dynamics following photodissociation of Cr(CO)$_6$ in the solution.$^{(9-17)}$ The dynamics of the Cr(CO)$_5$ photoproduct are of interest as a probe of condensed phase processes such as: solvent coordination, solvent reorientation, and energy relaxation.$^{(9-17,37)}$

In the gas phase single-photon absorption can result in ejection of more than one CO group.$^{(33,66-67)}$ However, only Cr(CO)$_5$ is produced in the condensed phase.$^{(44)}$ Pentacarbonyl is highly reactive with the solvent and generates the solvent-complexed pentacarbonyl species, Cr(CO)$_5$-S, where S is the solvent. In this chapter the pentacarbonyl transient is referred to as Cr(CO)$_5$-? in cases where we do not know if it is naked or complexed with the
solvent. Where it is important to distinguish between the solvent uncomplexed or solvent complexed species, the terminology "naked" or "solvent complexed" is used respectively.

There are currently several controversies for the time scale and mechanisms of formation of the solvent coordinated Cr(CO)\textsubscript{5} photoproduct.\textsuperscript{(9-17)} Cr(CO)\textsubscript{5} should be formed in the excited electronic state in a C\textsubscript{4\nu} square-planar configuration.\textsuperscript{(31)} This state decays electronically through a trigonal-bipyramid configuration into the ground electronic state. \textit{Ab initio} calculation,\textsuperscript{(31)} matrix isolation\textsuperscript{(22,66)} and recent femtosecond absorption\textsuperscript{(15-16)} studies provide evidence for the existence of the excited electronic state. However, it is not yet clear whether solvent coordination occurs from the ground state or the excited C\textsubscript{4\nu} state.

Simon \textit{et al.}\textsuperscript{(10-12)} first reported that photodissociation of Cr(CO)\textsubscript{6} results in the formation of solvated Cr(CO)\textsubscript{5} which appears in a time of 0.8 ps in cyclohexane. Their interpretation was that solvation occurs in the electronic ground state of naked Cr(CO)\textsubscript{5}. In this model solvation takes place after dissipation of the excess energy by electronic relaxation.

However, in contrast to these results the picosecond transient infrared experiments of Spears \textit{et al.}\textsuperscript{(13-14)} suggest a much longer solvation time of 200 ps. These results were interpreted as a consequence of two channels leading to solvation. That is, both the square-planar ground state and trigonal-bipyramid excited state geometries are believed to form the solvated Cr(CO)\textsubscript{5}-S complex.
Efforts to solve the discrepancy between these two results have been made by other groups.

Femtosecond transient absorption experiments by Nelson et al.\(^{(15-16)}\) showed two different time scales of 300 fs and 70 ps in methanol. The short time scale was interpreted as photodissociation immediately followed by solvation. The long 70 ps time scale was assigned to both electronic and vibrational relaxation from the electronic excited state of the Cr(CO)\(_5\)–S complex.

Further transient absorption studies by Harris et al.\(^{(17,37)}\) have been interpreted as vibrational relaxation in the pentacarbonyl photoproduct. Their data suggest a time scale of 4 to 17 ps for vibrational relaxation.

To provide further insight into this photochemistry, we have used transient picosecond Raman spectroscopy to directly probe the vibrational spectrum of the photoproduct. In a previous communication\(^{(9)}\) vibrational relaxation has been reported to occur on a time scale of 100 ps. This conclusion was made with the assistance of complementary Stokes and anti-Stokes data. In that communication\(^{(9)}\) our experimental method was limited to times longer than 30 ps.

In this chapter a detailed transient Raman investigation is presented to determine if the 4 to 17 ps dynamics observed by Harris et al.\(^{(17,37)}\) is actually vibrational relaxation. If so, what is the difference between these dynamics and the 100 ps dynamics reported in our earlier\(^{(9)}\) communication?
Cr(CO)$_6$ is photodissociated at 266nm and the transient species, Cr(CO)$_5$\textsuperscript{-}? is probed at the same wavelength with a second laser pulse. The ultraviolet absorption band of Cr(CO)$_5$\textsuperscript{-}? is very strong ($\varepsilon_{\text{max}} = 3 \times 10^6$ dm$^3$mol$^{-1}$cm$^{-1}$ at 240 nm) and relatively insensitive to solvent interactions.$^{(68)}$ Raman interrogation of Cr(CO)$_5$\textsuperscript{-}? at 266 nm should therefore experience a strong resonance enhancement. Details for the vibrational relaxation of solvated Cr(CO)$_5$ are presented in cyclohexane and THF.

In alcohols there are two possible solvent bonding sites to Cr(CO)$_5$. Coordination can occur to a hydrogen atom or the oxygen atom of the solvent. The latter is thermodynamically more stable. This suggests the possibility that a molecule which is initially coordinated to a solvent-hydrogen atom, can reorient and bond to a solvent-oxygen atom. The dynamics of this solvent reorientation process are currently a matter of controversy.$^{(11,14,37)}$

In the present chapter, Raman spectroscopy is used to attempt to separate vibrational decay from solvent reorientation processes. This is done by carefully measuring the dynamics of the intensity and frequency shifts of Raman bands assigned to transient Cr(CO)$_5$\textsuperscript{-}? . The intensity of the strong Raman bands are apparently not sensitive to solvent coordination. However, frequency shifts related to vibrational population relaxation are observed. An analysis of the time dependent vibrational temperature is presented. The effects of this non-equilibrium temperature on solvent coordination are discussed.
6.2. Experimental

The experimental apparatus has been previously described in detail.\(^{(6-9,21)}\) The laser system\(^{(21)}\) consists of a high repetition rate (2 kHz) chirped pulse regenerative amplifier which provides 1 mJ pulses with an 8 ps pulse width at 1.064 \(\text{\mu m}\). The 266 nm frequency quadrupled pulse has a width of 5 ps. A mode-locked cw Nd:YAG laser in combination with a single-mode fiber-optic is used to produce the seed pulse to the regenerative amplifier. Laser excitation occurs in a free flowing jet which moves the solution at a speed sufficient to ensure that no two successive pulses interrogate the same region of sample. Raman scattering is dispersed by an Instruments SA U1000 double monochromator. The signal is detected by a photomultiplier tube, and processed by a gated integrator.

Accurate absolute Raman shifts are obtained by recording a complete spectrum of the sample of interest which includes a feature corresponding to the attenuated Rayleigh line. This spectrum is generated in a single continuous scan of the monochromator. Raman shifts are directly measured from the spectrum as the difference in frequency between the band and the Rayleigh line. The accuracy of the monochromator is specified at 1 cm\(^{-1}\) over 5000 cm\(^{-1}\). This has been checked many times by measuring the Raman shift of the gas phase \(\text{N}_2\) band\(^{(69)}\) at 2329.917 cm\(^{-1}\). Repetitive scans indicate that the accuracy of this frequency calibration method is .5 cm\(^{-1}\). Frequency positions are obtained by fitting the line shape to a gaussian function using a Levenberg-Marquardt
The standard deviations for the peak positions are obtained from the same fitting routine and these values are quoted in the figure captions with a confidence limit of 1 cm$^{-1}$.

The pump-probe technique used in this experiment uses 266 nm light for both the pump and probe pulses. The 1064 nm Nd:YAG pulse is frequency doubled in a KTP crystal and the 532 nm doubled to 266 nm using a BBO crystal. After frequency separation, the remaining 532 nm light is optical delayed and then frequency doubled with a BBO crystal to make the second 266 nm pulse. Both 266 nm pulses are then imaged onto the sample. The intensities of the two pulses varied from day to day. However, the approximate relative intensities are 15 μJ for the pump and 2 μJ for the probe pulse.

The pure transient Raman spectrum is obtained by using a spectrum differencing technique. This is accomplished by rapidly chopping (mechanically) the pump and probe beams and recording the total two pulse signal as well as the individual one pulse background spectra. The pure transient spectrum is obtained by subtracting the one pulse background from the raw two pulse spectrum.

Dynamics are obtained by varying the optical delay between pump and probe pulses using a retroreflector and 1 m long computer controlled delay stage. The timing between pulses was measured experimentally using the dynamics of the anti-Stokes spectrum of the Cr(CO)$_5$-S transient. As the delay between the two 266 nm pulses is increased, the anti-Stokes Raman signal
increases to a maximum value and then falls off to a steady state value. (An example of such data is shown in Fig. 19) Since both pulses have identical wavelengths, either pulse can function as the pump or probe. The time axis in the spectrum corresponds to the optical delay with respect to perfect temporal overlap at time zero. As a result, the time "minus" data corresponds to one of the pulses acting as the probe and the time "plus" data to the other pulse acting as the probe. However, there is a large difference in the intensity of the pump and probe pulses. For this reason the two spectra have drastically different intensities. The observation of these two independent dynamics was used to establish time zero. The accuracy of this method is approximately 15 ps.

The linearity of the delay stage was checked over a range of 800 ps. Stimulated emission in laser dye C500 was used for this purpose. Excitation of the dye at 266 nm was followed by an optically-delayed 532 nm pulse. Fluorescence from the dye is observed in the backscattering direction. Stimulated emission causes a decrease in the fluorescence. This signal is used to measure the spatial overlap of the two beams as the optical delay is scanned. For the present experiment, the 532 nm beam is frequency doubled after the delay stage and used as a probe beam at 266 nm.

Cr(CO)$_6$ (99% purity) was purchased from Aldrich and used without further purification. The concentration was 10 mM in every solvent. Cyclohexane was purchased from Aldrich and was of spectrograde purity. Tetrahydrofuran
(THF) and n-propanol were HPLC grade purity and were purchased from Mallinckrodt.

6.3. Results

6.3.1. Identity of the Transient

Fig. 13 illustrates the two pulse technique used to measure the transient Raman spectra. Fig. 13A shows the total Raman spectrum which results when both beams are imaged on the sample. This spectrum is almost identical to the one pulse spectrum shown in frame B. It is not surprising that the two pulse and one pulse spectra appear to be almost identical. In the two pulse spectrum each pulse creates a large background spectrum consisting of ground state Cr(CO)$_6$ and solvent bands. In comparison to the ground state bands, the transient signal is very small. Frame C shows the transient spectrum which is obtained by taking the two pulse spectrum (frame A) and subtracting the one pulse spectrum from each laser pulse. As described below, this spectrum must be corrected before it can be readily interpreted.

The transient Raman spectrum in Fig. 13C contains negative-going peaks. This is caused by a change in the optical density of the solution due to the transient absorption of the photoproducts and the photobleaching of ground state Cr(CO)$_6$. The first laser pulse creates the transient photoproduct and simultaneously bleaches Cr(CO)$_6$. When the second laser pulse interrogates the sample, the effective optical path length in the solution has been altered by the
Fig. 13. Illustration of Two Pulse Differencing Technique for Cr(CO)$_6$ in THF.

Both laser pulses are at 266 nm with 100 ps time delay between pulses. Pump pulse is 15 μJ and probe pulse is 2 μJ. All spectra are normalized on an separate relative scale. Chopped laser excitation is used to record: X = two pulse spectrum, Y = pulse one by itself, Z = pulse two by itself. The data in the four frames labeled A-D are: A) = X, B) = Y, C) = X-Y-Z, D) = X-Y-Z*factor. The factor is chosen to make the solvent band labeled S subtract to zero. Frame D) represents the pure transient spectrum of Cr(CO)$_5$.?
photochemistry created from the first laser pulse. In this experiment, the transient absorbs more strongly than ground state Cr(CO)₆. This has the effect of reducing the optical path length experienced by the second pulse. When both pulses are interacting with the solution, the ground state Raman spectrum from the second laser pulse is weaker compared to the Raman signal from the second laser pulse by itself. When the transient spectrum is computed, the Raman spectrum of the solvent and ground state Cr(CO)₆ appears to bleach.

The effects of the optical density change can be removed from the spectrum by using the solvent bands as an internal standard. This is achieved mathematically by computing the transient spectrum as: \( \text{Transient} = \text{Two Pulse} - \text{Pulse A} - \text{Pulse B} \times \text{factor} \). The factor is adjusted such that the solvent bands subtract to zero in the computed transient spectrum. The result of this procedure is shown in Fig.13D. This spectrum is believed to be the pure transient spectrum. The ground state Cr(CO)₆ band at 580 cm⁻¹ still appears to go below the baseline due to population bleaching. The Cr(CO)₆ band at 381 cm⁻¹ does not appear to bleach because of the large positive transient band at or near the same frequency. All of the transient spectra shown throughout the rest of this chapter are corrected in this manner.

The Raman spectrum of Cr(CO)₆ is well known. The corresponding Cr(CO)₅⁻ transient Raman spectrum has been reported in frozen matrices. The transient Raman spectrum in Fig.14 is assigned to Cr(CO)₅⁻ based on the expectation that photoexcitation of Cr(CO)₆ produces Cr(CO)₅⁻ with a quantum
Fig. 14. Long Range Transient Difference Spectrum of Cr(CO)$_5$-? in Cyclohexane.

Time delay between pulses is 400 ps. This spectrum has been corrected by the method described in the text and illustrated in Fig. 13. The filled peaks correspond to the transient band. Negative-going peaks are ground state Cr(CO)$_6$ bands. The dotted region of the spectrum has a low signal-to-noise due to the subtraction of intense cyclohexane solvent bands.
Fig. 14

- **Relative Intensity**
- **Raman Frequency (cm⁻¹)**

- **Transient**
- **Ground**
yield\(^{32}\) of 0.7. It is possible that the transient is the result of subsequent photochemistry caused by the probe pulse at 266 nm. However, the transient signal is observed to depend on the time delay between the pump and probe pulses. It is therefore unlikely that the observed transient is \(\text{Cr(CO)}_n\), where \(n \leq 4\). There is no obvious reason why sequential absorption of two 266 nm photons would require a time delay. There are additional arguments which support the assignment of the transient:

1. The transient spectrum in Fig.14 has two bands analogous to those of \(\text{Cr(CO)}_6\). The normal ground state Raman spectrum\(^{71}\) of gas phase \(\text{Cr(CO)}_6\) has a \(\nu_3\) CO stretch at 2019 cm\(^{-1}\) and the \(\nu_2\) Cr-CO stretch vibration at 381 cm\(^{-1}\). The transient in cyclohexane has strong bands at 1935 cm\(^{-1}\) and 380 cm\(^{-1}\) which are likely to be CO stretching and Cr-CO stretching vibrations, respectively.

2. The extinction coefficient for \(\text{Cr(CO)}_5^-\) is very large at the probe wavelength. It is therefore expected that the resonance Raman enhancement for \(\text{Cr(CO)}_5^-\) is large.\((\epsilon_{\text{max}} = 3 \times 10^4 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1} \text{ at } 240 \text{ nm}^{(68)})\)\)

3. The peak power used in this experiment is 0.003 J/cm\(^2\) for the pump pulse. The probe laser fluence in this experiment of 0.0003 J/cm\(^2\) is about 10 times less than that in the pump pulse. The linearity of the transient signal was checked over a range of laser powers from 5 times greater to 5 times less than those typically used. Only at the highest laser powers was a nonlinear signal observed. In fact, the transient signal was found to decrease at high fluence.
The observation of a transient signal linear in both pump and probe laser power is a good indication that the transient is Cr(CO)$_5^-$ and not Cr(CO)$_n$, where $n \leq 4$.

4. The laser fluence used in this experiment is 10 to 25 times weaker than that used in the previous transient infrared$^{(13-14)}$ or transient UV-visible absorption$^{(3, 15-17, 37)}$ studies where only Cr(CO)$_5^-$ was identified as a photoproduct.

5. The magnitude of the transient signal did not change as the sample was irradiated for times up to 1 hour. A sample volume of 100 ml was recirculated for this time and then replaced with a fresh sample. During this irradiation time it is possible for only 20% of the sample to be converted to Cr(CO)$_5^-$. This is a worst case estimate. It assumes all photons are used to convert Cr(CO)$_6$ to Cr(CO)$_5^-$ with a quantum yield of 0.7. Loss of Cr(CO)$_5^-$ by back reaction with CO to form the starting material is ignored in this calculation.

6. The lifetime of the transient is found to be $>1$ ns. This is consistent with the known microsecond lifetime$^{(28)}$ for solvated Cr(CO)$_5$. It is important to note that a lifetime of $>1$ ns proves that the transient is not vibrationally hot Cr(CO)$_6$ formed by geminate recombination or radiationless relaxation. The transient we observe is distinctly different from Cr(CO)$_6$ for times significantly longer than 1 ns. (We observe no change in the Stokes Raman intensity for times between 400 ps and 1 ns.) If vibrationally hot Cr(CO)$_6$ were formed, a transient spectrum would be observed. However, the spectrum of a hot Cr(CO)$_6$ would completely subtract out of the two color transient difference spectrum as
soon as vibrational cooling was complete. A vibrational cooling time constant of >1 ns is very unlikely\(^{(72)}\) for \(\text{Cr(CO)}_6\). It should be noted that an analogous experiment has been performed by our group on deoxyhemoglobin.\(^{(73)}\) In this case photoexcitation of deoxyhemoglobin leads only to a vibrationally hot heme. A transient Raman spectrum of the hot heme appears and then completely disappears within 40 ps as the heme reaches thermal equilibrium with the environment.

In summary, there is strong evidence to support the conclusion that the observed transient is \(\text{Cr(CO)}_5\)\(^2\)-. The resonance enhancement at 266 nm should be equally sensitive to both the solvent coordinated and the uncoordinated species. It is anticipated that these two species can only be separately identified through shifts in the observed Raman frequencies.

6.3.2. Dynamics in Cyclohexane

6.3.2.1. Vibrational Relaxation

The Stokes and anti-Stokes vibrational spectra of \(\text{Cr(CO)}_5\)\(^2\)- obtained at various time delays are shown in Fig. 15 and 16. The intensities of these spectra are only accurate to approximately 20%. These data are pure transient spectra which have been corrected by the previously described method. There are several important features found in these data. The band shown in the Stokes spectra (Fig. 15) increases in intensity during the first 20 ps. In addition, the position of the band shifts to higher frequency during the first 20 ps.
Fig. 15. Stokes Transient Difference Spectra of Cr(CO)$_5^-$ in Cyclohexane.

Time delay between pulses is given in a box. The spectra have been normalized to reflect the true relative intensity at each time delay. These spectra have been corrected by the method described in the text and illustrated in Fig. 13.
Fig. 15

Stokes Raman Frequency (cm⁻¹)

Relative Intensity

- 400 ps
- 20 ps
- 0 ps
Fig. 16. Anti-Stokes Transient Difference Spectra of Cr(CO)$_5$-$^+$ in Cyclohexane.

Time delay between pulses is given in a box. The spectra have been normalized to reflect the true relative intensity at each time delay. These spectra have been corrected by the method described in the text and illustrated in Fig. 13.
Fig. 16
In contrast to the results found in the Stokes spectra, the same band in the anti-Stokes spectra has a maximum intensity at 0 ps and decreases rapidly in intensity during the first 50 ps. The position of the band shifts to higher frequencies during the first 50 ps. The magnitude of this frequency shift is more than 13 cm$^{-1}$ and is found to be reproducible.

The Stokes and anti-Stokes band positions are approximately equally for each time delay. It is therefore likely that the Stokes and anti-Stokes spectrum result from the same transient. The complementary observation of a growing Stokes spectrum and a decaying anti-Stokes spectrum is interpreted as vibrational energy relaxation. For a 380 cm$^{-1}$ vibration, the ratio of the population in $v=1$ to $v=0$ is 0.16 at 300 K. Thus, most of the Stokes scattering occurs from $v=0$ at room temperature. Similarly, the majority of the anti-Stokes scattering occurs from $v=1$.

The shift of the band to higher frequencies is consistent with population relaxation to lower quantum states. Vibrational energy gaps typically increase for lower quantum levels as a result of the anharmonicity of the potential. Similar frequency shifts have been previously observed for vibrational relaxation of naked Cr(CO)$_5$ in the gas phase. In this case transient infrared spectroscopy of the CO stretching vibration was used to measure the gas phase cooling process. An alternative possibility that all or part of the band shift arises from solvent coordination is discussed below. However, it is important to note that the complementary dynamics of the intensity of the Stokes and anti-Stokes
s spectra are only consistent with vibrational energy relaxation and cannot be explained by solvent coordination. Although solvent coordination may, in part, be responsible for the frequency shifts, there is no doubt about the time scale for vibrational cooling.

6.3.2.2. Electronic Relaxation

Naked Cr(CO)₅ is believed⁴ to be initially formed in its excited electronic state with C₄ᵥ symmetry. Suppose that the excited state is initially produced and has a lifetime longer than the 5 ps laser pulse width. In this case, an excited state transient might be observable in the transient Raman spectrum. If so, we would expect to observe a Stokes and an anti-Stokes band which had a peak intensity at early times. These two bands should decay together at the rate of electronic relaxation. Instead, we observe the decay of the anti-Stokes spectrum at the same rate as the rise of the Stokes spectrum. These dynamics are assigned to vibrational relaxation. This result indicates that electronic relaxation is too fast to observe with the present time resolution.

6.3.3. Dynamics in THF

The vibrational spectrum of transient Cr(CO)₅⁻ has been obtained in the solvents THF and n-propanol. These spectra are plotted in the same way as the data in cyclohexane. Fig.17 and 18 show the data for the Stokes and anti-Stokes spectral regions in THF.
Fig. 17. Stokes Transient Difference Spectra of Cr(CO)$_5$-? in THF.

Time delay between pulses is given in a box. The spectra have been normalized to reflect the true relative intensity at each time delay. These spectra have been corrected by the method described in the text and illustrated in Fig. 13.
Fig. 17

RELATIVE INTENSITY

STOKES RAMAN FREQUENCY (cm$^{-1}$)

--- 400 ps
--- 0 ps
Fig. 18. Anti-Stokes Transient Difference Spectra of Cr(CO)$_5$-? in THF.

Time delay between pulses is given in a box. The spectra have been normalized to reflect the true relative intensity at each time delay. These spectra have been corrected by the method described in the text and illustrated in Fig. 13.
RELATIVE INTENSITY

Fig. 18

300
350
400
450
500

ANTISTOKES RAMAN FREQUENCY (cm⁻¹)

- - - - 0 ps
- - - 20 ps
- - 50 ps
The data in Fig. 17 and 18 exhibit the same trends as the data in cyclohexane. The anti-Stokes spectrum shifts to higher frequency and decays in amplitude during the first 50 ps. The Stokes spectrum increases in intensity and shifts to higher frequency during the first 50 ps. The complementary dynamics of the Stokes and anti-Stokes data are the spectral signature expected for vibrational relaxation. The dynamics occurring during the first 50 ps are therefore assigned to vibrational relaxation.

6.4. Discussion

The dynamics of the vibrational spectra can be used to quantitatively determine the internal temperature in the photoproduct. Of course this assumes a Boltzmann distribution of vibrational population within the photoproduct. This is not a good assumption particularly for a molecule like Cr(CO)$_5$-? which has a heavy atom at the center. It is precisely this kind of molecule which might be expected to exhibit weak coupling between the internal vibrational modes.$^{(74)}$ Nonetheless it is still useful to determine the magnitude of the internal temperature that a Cr(CO)$_5$ molecule would have in order to produce the observed vibrational cooling dynamics.

Before energy relaxation, the initial vibrational temperature of Cr(CO)$_5$ can be crudely estimated in the following way. The internal vibrational energy is given by a sum over states
\[
\langle E - E_0 \rangle = \sum E \frac{\rho(E) \exp(-E/k_B T)}{\sum \rho(E) \exp(-E/k_B T)}
\] (22)

Where \( \rho(E) \) is the density of states estimated by the method of Stein and Rabinovitch.\(^{39}\) This calculation was done using the normal modes\(^{72}\) of \( \text{Cr(CO)}_6 \). Excitation at 266 nm produces \( \text{Cr(CO)}_5 \) with a maximum of 26760 cm\(^{-1}\) of internal energy\(^{75}\) assuming a Cr-CO bond dissociation energy\(^{76}\) of 36.8 kcal/mol. In a similar calculation, Harris et al.\(^{37}\) assumed that 20% of the available energy is carried off by the leaving CO. This assumption was based on experimental results\(^{76}\) from a molecular beam study of \( \text{Fe(CO)}_4 \). We make the same assumption and calculate that the \( \text{Cr(CO)}_5 \) photoproduct should have an initial internal energy of 21400 cm\(^{-1}\). Eq.(22) indicates that this amount of internal energy corresponds to a temperature of 1400 K. This value is higher than the 1250 K internal temperature calculated by Lee and Harris\(^{37}\) due to the more energetic excitation wavelength in our experiment.

The temperature in \( \text{Cr(CO)}_5 \) can be estimated spectroscopically from the dynamics of the Stokes and anti-Stokes Raman bands. For two quantum levels denoted 0 and 1, the ratio between vibrational populations for level 1 at two different temperatures indicated by \( T \) and \( T^0 \) is given by

\[
\frac{N_1^0}{N_1} = \frac{N_0^0}{N_0} \exp\left(\frac{\Delta E}{k_B}\left(\frac{1}{T} - \frac{1}{T^0}\right)\right)
\] (23)
$\Delta E$ is the energy spacing between quantum levels. The intensity of the anti-Stokes band is directly related to the population in quantum level 1. The ratio $N_1^0/N_1$ is the change in the intensity of the anti-Stokes Raman band determined at the two temperatures. Similarly, the ratio $N_0^0/N_0$ is the equivalent quantity for the Stokes band.

The time dependent change in the anti-Stokes and Stokes spectrum between $t=0$ and $t=50$ ps can be used to determine the temperature of Cr(CO)$_5$-. We assume that the internal energy is statistically distributed. It is also assumed that equilibrium with the solvent has been achieved after 50 ps. With these assumptions Eq.(23) gives 1100 K as the initial temperature at $t=0$. This is remarkably hot considering that the present experiment measures a temperature averaged over the 5 ps laser pulse width. Even so, a major fraction of the initial energy remains in the photoproduct on a picosecond time scale. The Raman data in Fig.19 indicate that the cooling occurs with a rate constant of 80 ps.

It is important to recognize that this temperature estimate is not affected by uncertainties in the relative Raman enhancement for the Stokes and anti-Stokes bands. The temperature is estimated from a ratio of the change in the anti-Stokes band intensity compared to the change in Stokes band intensity. Thus, it is not necessary to know the relative strengths of the resonance Raman enhancement for the Stokes or anti-Stokes band.
Fig. 19. Dynamics of the Intensity of the Transient Anti-Stokes Band

The anti-Stokes dynamics spectrum in cyclohexane is obtained at Raman shift 380 cm$^{-1}$. Positive times correspond to pump followed by delayed probe. Relative energies are approximately 15 $\mu$J for the pump and 3 $\mu$J for the probe. Step size of the optical delay is 5 ps. The signal is symmetric in time but asymmetric in intensity since the pump and probe pulses have the same wavelength but different energy. Circles represent data points. The thick line through the data is the calculated fit to the equation $y(t) = 1.0 \times \{(1-\exp(-t/5)) \times \exp(-t/80)\}$ for $t > 0$, $y(t) = 0.2 \times \{(1-\exp(-t/5)) \times \exp(-t/80)\}$ for $t < 0$. Times are in picoseconds. This equation represents a 5 ps rise time with a decay component of 80 ps.
Fig. 19

RELATIVE INTENSITY

TIME (picoseconds)
Fig. 19 Illustrates the dynamics of the intensity for the anti-Stokes band at a single frequency. The band position chosen for this measurement corresponds to the final frequency of the band (after all frequency shifting has taken place) after 50 ps. The signal is symmetric in time but asymmetric in intensity since both the pump and probe lasers have the same wavelength but different energy (See experimental section). The dynamics represent both the frequency shifting and intensity changes of the band. Nonetheless, it is observed that the frequency shift is almost pulse-width limited. The signal intensity decays by a factor of 3 with a time constant of 80 ps. It is this factor of three which is used in the temperature calculation. It is believed that this value represents the change in the vibrational population for the v = 1 level between the extremes in temperature.

There is one possible source of error in this calculation. Higher vibrational levels also contribute to the Raman spectrum. However, the signal from higher levels is shifted to lower frequency. Nonetheless, the wings of the Raman bands from higher levels contribute to the Raman signal detected at 380 cm$^{-1}$. If the resonance Raman enhancement increases substantially for the higher levels, the calculation will overestimate the change in the anti-Stokes signal. This will cause the calculated temperature to be somewhat higher than it should be.

In summary, the 80 ps cooling dynamics of the 380 cm$^{-1}$ band are quite clear. The temperature estimate is admittedly very crude. However, it does point
out the possibility of large internal temperatures in the Cr(CO)$_5$ photoproduct. This observation may well be important in understanding the chemistry of the solvent coordination reaction.

6.4.1. Solvent Coordination

A mechanism for solvent coordination has been proposed by Harris et al.\(^9\) In this model, solvent coordination is viewed as a rapid (≤1 ps) event. However, the amount of solvent coordination is determined by the equilibrium constant. As the naked Cr(CO)$_5$ molecule cools, the amount of solvent coordination is predicted to increase due to the temperature dependence of the equilibrium constant

$$\text{Cr(CO)$_5$ + S} \leftrightarrow (k_{eq}) \text{Cr(CO)$_5$-S.}$$

The results of this experiment demonstrate that Cr(CO)$_5$-? remains very hot for relatively long times (10's of picoseconds). This conclusion comes entirely from the complementary behavior of the intensities of the Stokes and anti-Stokes band. (A decaying anti-Stokes band and a growing Stokes band was observed. The observed band shifts are consistent with vibrational cooling but it is the dynamics of the intensities that establishes vibrational cooling.) It is therefore quite possible that a large fraction of the solvent coordination and (H-bonding to O-bonding) solvent reorientation occur at a rate similar to the vibrational cooling rate. In fact, solvent coordination may be responsible for part of the frequency shift observed for the Cr-CO vibration. If so, the time scale for
the frequency shift of 20-50 ps is consistent with solvent coordination occurring at a similar rate to vibrational relaxation.

6.4.2. Bonding Properties and Vibrational Frequencies of Cr(CO)₅

Solvent coordination to Cr(CO)₅ should affect the vibrational frequencies of the Cr-CO and CO stretching vibrations. Vibrational frequencies can be rationalized from a simple molecular orbital picture of bonding in metal carbonyls. It is well known that the metal-CO bond is formed through a combination of a σ-bond and a π-bond formed by back donation of electrons from the metal into an anti-bonding orbital on the CO. The CO stretching frequency has been widely used to measure the amount of metal back donation to CO in metal hexacarbonyl coordination compounds.\(^{(77)}\)

When a CO ligand comes off Cr(CO)₆, there is additional electron density on the chromium atom which increases the metal-ligand back bonding. For the naked Cr(CO)₅ species, this results in a weaker CO bond and a lower frequency vibration is expected. This effect has been observed in the gas phase by observation of the CO stretching frequency.\(^{(28)}\)

We are not aware of any experimental data on the frequency of the Cr-CO stretch in Cr(CO)₅\(^{-}\). The π-bond and σ-bond respond in opposite ways to the electron density on the chromium atom.\(^{(78)}\) It is therefore difficult to predict whether the Cr-CO bond in Cr(CO)₅\(^{-}\) will be stronger or weaker than in Cr(CO)₆. This is an important consideration which may help to make a more
definitive statement about solvent coordination. Further work is in progress to measure the Cr-CO stretching frequency in weakly interacting solvents where solvent coordination effects are minimized.

We have attempted to measure Raman lineshapes for the CO stretching vibration of the transient. However, the Raman intensity of this band is weak. In addition, this band is very close in frequency to the large Cr(CO)$_6$ ground state band. Depletion of the Cr(CO)$_6$ ground state band as shown in Fig. 14 makes accurate lineshape measurements of the corresponding transient band exceedingly difficult.

6.4.3. Comparison to Previous Results

Two components of 20 ps and 50 ps were previously found for the absorption dynamics reported from other laboratories. These dynamics were assigned to electronic or upper level vibrational relaxation and pure vibrational relaxation, respectively. Nelson et al.$^{(15-16)}$ reported a dynamics of 50 ps which was assigned to vibrational and electronic relaxation in cyclohexane, hexane, and THF. This time scale is in excellent agreement with our transient Raman results. Harris et al.$^{(17-37)}$ reported exponential decay of 4 to 17 ps in the electronic absorption spectra and attributed this to vibrational relaxation. We do not observe the $\approx$20 ps dynamics. If this component results from vibrational relaxation it must involve levels which we do not observe.
The longer time scale of 80 ps observed in this experiment and (less accurately) in our previous\(^9\) communication is probably relaxation from slow relaxing vibrational levels. A similar 100 ps transient was also observed in absorption and attributed to slow vibrational relaxation.\(^{37}\) It is not clear whether these levels are low energy states or weakly coupled levels at higher energies. There is evidence from other experiments which support the existence of vibrational levels with relaxation rates longer than 200 ps. For example, Heilweil \textit{et al.}\(^{36}\) have measured relaxation from CO vibrations in Cr(CO)\(_6\) in a variety of solvents using transient infrared techniques. Their data suggest\(^{36}\) that the CO vibrations are weakly coupled and relax with a rate of 145 ps in n-hexane.

The third temporal region is the solvent reorientation time in specific solvents such as THF and alcohols which have two different functional groups. According to the results of Harris \textit{et al.},\(^{37}\) the decay time of 20 ps in the electronic absorption dynamics is also found for cyclohexane and THF. No evidence for solvent reorientation was found.\(^{37}\) Our results indicate that non-equilibrium internal energies in Cr(CO)\(_5\)-? are likely to affect solvent coordination during the first 50 ps. No band shifts were observed on a time scale \(\geq 50\) ps which could be attributed to solvent coordination or reorientation.

\textbf{6.5. Conclusion}

Picosecond transient Raman spectroscopy has been used to measure the dynamics of the vibrational spectrum of the photoproduct Cr(CO)\(_5\)-?.
No direct evidence was found for the dynamics of solvent coordination. However, the initial internal temperature of the molecule was found to be exceedingly hot. A crude estimate indicates that the average temperature is over 1100 K during the first 5 ps sampled by the finite width of our laser pulse. These high non-equilibrium temperatures persist for an unusually long time and are likely to play a major role in solvent coordination and solvent reorientation processes. The dynamics of vibrational energy relaxation were measured from the decay of the anti-Stokes signal form the 380 cm$^{-1}$ vibration. A time constant of 80 ps was observed for the relaxation time.

No direct evidence was found for electronic relaxation. This result suggests that electronic relaxation is too fast to observe with the 5 ps time resolution of the apparatus.
7. CONCLUSIONS.

The power of picosecond resonance Raman spectroscopy is proven to give lots of information about photochemistry in a condensed phase. There are two main parts studied in Cr(CO)$_6$. One is the time independent study of the excited state of the Cr(CO)$_6$ molecule, the other is the time dependent dynamic study of the vibrational relaxation of the solvated Cr(CO)$_5$ species.

In study of the excited state of the Cr(CO)$_6$, the followings are revealed:
1. The overtones of the totally symmetric vibrational mode, $v_2$, has been observed in both 266 nm and 213 nm excitation. The observation of the overtones indicates that there is a large distortion along this totally symmetric vibrational mode.
2. The singlet excited state appears to be responsible for photodissociation even if an extent of a contribution cannot be determined.
3. The observation of the even overtones of the asymmetric vibrational mode, $v_7$, is evidence for this mode being a reaction coordinate, and also clearly shows that photodissociation takes place through the cooperation among the possible modes.
4. The Jahn-Teller distortion has been found in the 266 nm excitation to a large extent. On the other hand in the 213 nm excitation only a small extent of Jahn-Teller distortion has been found.

In study of the time dependent dynamics of solvated Cr(CO)$_5$:
1. No direct evidence was found for the dynamics of solvent coordination.
However, the initial internal temperature of the molecule was found to be exceedingly hot. A crude estimate indicates that the average temperature is over 1100 K during the first 5 ps sampled by the finite width of our laser pulse. These high non-equilibrium temperatures persist for an unusually long time and are likely to play a major role in solvent coordination and solvent reorientation processes. The dynamics of vibrational energy relaxation were measured from the decay of the anti-Stokes signal form the 380 cm\(^{-1}\) vibration. A time constant of 80 ps was observed for the relaxation time. This results suggest that electronic relaxation is too fast to observe with the 5 ps time resolution of the apparatus.
8. REFERENCES.


65. The anti-Stokes and Stokes vibrational frequencies for the transient species are identical and therefore suggest that both can be assigned to the solvated pentacarbonyl indicating that Eq. 21 is correct. However, we do not know how much solvent coordination will shift the Raman frequencies and can not rule out Eq. 20.


75. We have added the internal energy of Cr(CO)$_6$ at 300K of 2040 cm$^{-1}$ to find the total energy Cr(CO)$_5$ after photodissociation.


9. VITA

Soo-Chang Yu was born in Puan, Chonbuk, Korea on February 9, 1958. He graduated from Chonju high school in Chonju, Korea in February 1977. In March 1977, he entered Chonbuk National University where he received his Bachelor of Science Degree in Chemical Education in February 1984. In June 1978, he volunteered for his military service and served for 31 months. After finishing military service, he continued his study and received B.S. Degree in 1984. In February 1984 he entered Master program in the Department of Chemistry of Chonbuk National University where he received Master Degree. After that, he gained teaching experience in a high school for one year. In August 1987 he came to Louisiana State University, where he is now candidate for the degree of Doctor of philosophy in the Department of Chemistry. He married Keunok Han in May 3, 1987. He is the father of one daughter, Jin.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Soo-Chang Yu

Major Field: Chemistry (Physical)


Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

Dec. 4, 1991