Ultrafast Measurement of Chemical Dynamics in the Condensed Phase Using Transient Vibrational Spectroscopy.

Xiaobing Xu
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ULTRAFAST MEASUREMENT OF CHEMICAL DYNAMICS IN THE CONDENSED PHASE USING TRANSIENT VIBRATIONAL SPECTROSCOPY

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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by
Xiaobing Xu
B.S. University of Science and Technology of China, 1986
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I am most grateful for my parents for their love, support and encouragement. My parents have not seen me and talked to me for more than four years due to inconvenient communication and transportation. Their suffering cannot be described in words. I dedicate this work to them.

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ABSTRACT

Geminate recombination and vibrational energy relaxation of iodine in the condensed phase are investigated using picosecond transient Raman spectroscopy. The advantages of transient Raman in measuring vibrational energy relaxation and separating different reaction dynamics are demonstrated in this dissertation.

Using transient Raman spectroscopy we have for the first time directly observed geminate recombination and vibrational energy relaxation of I$_2$ on both $X$ and $A'$ $^3\Sigma_{2u}$ states. For the $X$ state, energy relaxation from vibrational levels ranging from $v=52$ to $v=1$ have been observed. These levels correspond to absolute energies of 9,300 to 210 cm$^{-1}$ above the zero point in the $X$ potential. The importance of vibrational to vibrational (V-V) energy transfer pathways has been studied and the V-V transfer efficiency is found to be very solvent dependent. The results suggest that the vibrational coupling between the excited iodine oscillator and the solvent is drastically affected by the nature of the normal mode character of the solvent vibration. For the $A'$ state, geminate recombination rate is found to be significantly slower than the $X$ state. Evidence is reported which suggests the possible role of iodine atom-solvent complexes in the reaction step leading from photodissociated atoms to formation of the excited state. Electronic relaxation is investigated and is found to be largely the result of the formation and decay of I$_2$•Solvent exciplexes.

Geminate recombination between iodine radical and iodine molecule is directly observed by dissociating iodine dimer. The geminate recombination time of
I+I₂ in cyclohexane is measured to be 50–100 ps. The slower recombination rate of I + I₂ in comparison with the fast geminate recombination of I + I provides direct experimental evidence for the existence of an activation barrier for the former reaction. Recombination rates in different solvents decrease in the order n-hexane > neo-hexane ≥ deuterated cyclohexane ≈ cyclohexane. The lifetime of I₃ is determined to be greater than 500 ps.
1. GENERAL INTRODUCTION

In this dissertation I will describe the first direct measurement of vibrational energy relaxation of iodine in the condensed phase using picosecond transient Raman spectroscopy.

1.1 History

Despite the fact that there is a wealth of experimental data on the reaction dynamics in the gas phase, there is relatively less direct information available about the reaction pathway and energy transfer in the condensed phase. In contrast to the gas phase there are many experimental difficulties in measuring reaction dynamics in the condensed phase. Due to the constant interaction between solvent and solute, vibrational and rotational structure which are well defined in the gas phase become smeared in solution. This is particularly true for electronic spectroscopy. In this case the linewidth broadening is determined by the electronic dephasing time. Electronic states are very sensitive to collisions and nearest neighbor interactions. Typical electronic dephasing times are on the order of $10^{-13}s$, which gives a spectral linewidth of $\approx 50\text{cm}^{-1}$.(1) For $I_2$ in $n$-hexane the electronic dephasing time is determined to be $\approx 3\times 10^{-13}s$,(2) this dephasing time gives a linewidth of $\approx 20\text{cm}^{-1}$. With this linewidth the detailed vibrational structure which exists in the gas phase is removed in the solution phase absorption spectrum. Due to the extraordinary high collisional frequency in the condensed phase, a lot of important dynamics occur on fast time scales such as picosecond and femtosecond time regimes. The information about how the solvents affect the electronic potentials of a molecule is critical
in understanding the reaction barrier and curve crossing process in the condensed phase. The detailed mechanism of energy dissipation in a reaction is also very important in understanding the condensed phase reaction dynamics.

The iodine photodissociation reaction has served as a prototype in understanding the reaction dynamics in the condensed phase for more than half a century. This reaction has the advantage of simplicity, since it only involves bond breakage and formation of two homonuclear atoms. The interest of this reaction in solution was inspired by the discovery of a so-called solvent “cage effect” in the 1930's.(3-5) In solution two photodissociated atoms are surrounded by the solvent cage. The probability of recombination of iodine atoms is much larger than that of cage escape. The recombination of the same two iodine atoms to form one parent molecule is termed geminate recombination. The geminate recombination yields in different solvents have been extensively studied by Noyes et al.(6-9) They have measured the solvent viscosity dependence and the excitation wavelength dependence of caging efficiency. However, detailed information about this geminate recombination was not obtainable until the advent of ultrafast lasers.

The first time resolved measurement of iodine photodissociation was performed by Eisenthal and coworkers(10) using 5ps laser pulses. Iodine molecule in solution was excited with a 532nm photon and probed at the same wavelength. The measured transient absorption signal is depleted within about 25ps and it recovers in 70ps in hexadecane and 140ps in CCl₄ solutions. On the long time scale, the signal is not completely recovered. This result is interpreted as the observation of
geminate recombination of iodine atoms. The long time offset is due to the fraction of iodine atoms which escape the solvent cage.

The iodine recombination process was simulated by several groups.\textsuperscript{(11-16)} The recombination is divided into two processes. One is direct recombination without encountering solvent molecules. The time for this process is calculated\textsuperscript{(17)} to be \(< 1\text{ps}\) in high density fluids. This recombination is much faster than the experimentally determined 100ps time scale. The other process is recombination after intervention of a solvent molecule. The intervention of solvent will prevent immediate recombination of iodine atoms. This process is roughly controlled by the rate of iodine diffusion and the time for this process is calculated to be about 100ps. It seems that the experimental results can be explained by this mechanism. The recombination is controlled by iodine diffusion in the solvent.

However, this interpretation was questioned as oversimplified.\textsuperscript{(11)} Absorption at 532nm is essentially from lower vibrational levels of the ground state iodine. The bleach recovery is measuring the sum of processes of geminate recombination and population relaxation from top of the potential to the bottom. Nesbitt and Hynes \textit{et al.}\textsuperscript{(11-12)} have done a series of calculations on the geminate recombination and vibrational energy relaxation in iodine ground state which is the $X$ state for highly excited oscillator. They calculated the overall vibrational relaxation time from the top of the $X$ state potential based on the mechanism of vibrational to translational energy transfer (V-T). In principle, this process is the predominant channel of energy transfer, since the high collision frequency between solvents and solutes in
solution facilitates the V-T process. Their result indicates that the overall energy transfer efficiency through V-T channel is quite low, especially for the lower vibrational levels of the $X$ state. The estimated vibrational energy relaxation time is as long as 1ns for iodine in $\text{CCl}_4$ solution if only V-T transfer is important. The possibility of vibrational to solvent vibrational energy transfer (V-V) was also considered for iodine in $\text{CCl}_4$ solution.$^{(11-12)}$ It is assumed that if a solvent molecule has a vibrational mode close to the vibrational energy gap of iodine $X$ state, the energy transfer rate will be greatly enhanced. This consideration accelerates the vibrational relaxation in the lower vibrational levels of $X$ state. The overall VER rate is reduced to as short as 200ps! This is very close to the measured absorption recovery time of 140ps.

Great efforts have been made to separate the geminate recombination from vibrational relaxation experimentally. Two groups$^{(18-21)}$ have measured transient absorption of iodine in $\text{CCl}_4$ solution. If vibrational energy relaxation is much slower than the geminate recombination, transient absorption band should shift to the shorter wavelength region at later time. This wavelength shift reflects the dependence of the spectrum on the Franck-Condon factor of the absorbing energy level. If geminate recombination is the predominant process, no wavelength shift should be observed. However, two contradictory results were obtained. Wilson et al.$^{(18-19)}$ have measured transient absorption from 595nm to 840nm in alkane and haloalkane solutions. They found that the transient band shifts to the short wavelength in about 100ps. Therefore they concluded that the 100ps dynamics is
due to the vibrational energy relaxation in iodine $X$ state and that geminate recombination is very fast. Kelley et al.$^{(20-21)}$ measured the same process from 590nm to 750nm in alkane and chloroalkane solvents. They did not observe spectral shifts with time. They concluded that vibrational relaxation is much faster and geminate recombination takes 100ps as originally proposed.

The most complete data to verify vibrational relaxation in iodine $X$ state were later obtained by Harris et al.$^{(22-25)}$ They measured transient absorption from 295nm to 1000nm using laser pulses of 1ps duration. Their results clearly indicate that vibrational relaxation in iodine $X$ state takes about 100–200ps and geminate recombination occurs in less than 1ps.

The successful proof of vibrational energy relaxation (VER) in the solution phase is not the end of the story. The ultimate goal of the study of vibrational energy relaxation in condensed phase is to understand how the energy transfer process is different from the gas phase. It is necessary to obtain the information about the vibrational level dependence and solvent dependence of VER rate. The transient absorption technique has its inherent restrictions in studying the mechanisms of vibrational energy relaxation. First, transient absorption is measuring electronic transitions which contains information of vibrational population. The validity of conclusions about vibrational energy relaxation from such measurements relies on the *indirect* interpretation of electronic absorption data. Second, different electronic states might have the same absorption. It is almost impossible to separate
different electronic states which have similar dynamics. This problem was encountered by Harris et al. in studying the vibrational relaxation in alkane solvents\(^{(23)}\) in which the \(X\) state vibrational relaxation has similar dynamics as \(A'\) state. (The \(X\) and \(A'\) states are two electronic states of iodine. Their potentials are shown in Figure 1.2.) Third, it is very difficult to differentiate vibrational relaxation from electronic relaxation for an excited state using transient absorption. In fact, the vibrational energy relaxation in the \(A'\) state is neglected in the transient absorption measurements. Fourth, the highest vibrational levels observed in the \(X\) state is only about \(v = 38\) due to the limitation of probe laser wavelength. Therefore transient absorption can not provide detailed information about vibrational relaxation in the upper region of the potential. The best technique for studying vibrational relaxation is to use transient vibrational spectroscopy.

There are two kinds of commonly used vibrational spectroscopy: infrared and Raman. Measurement of transient infrared spectra requires the use of picosecond or femtosecond infrared laser pulses with broad wavelength tunability. To measure the vibrational mode of \(200\,\text{cm}^{-1}\), which is the vibrational mode of iodine ground state, the laser wavelength must be as large as \(50\mu\text{m}\)! This kind of laser system is very hard to construct under current experimental condition. Even if the system exists, there are still two experimental difficulties. First, the infrared light is invisible, this increases the difficulty of experimental operation. Second, the sensitivity of detection device such as photomultiplier tube in IR region is much smaller than in the uv-vis region. The alternative is to use transient Raman spectroscopy.
The use of transient Raman spectroscopy can not only overcome the disadvantages of uv-vis transient absorption but also offer the opportunity to study vibrational energy relaxation using currently available laser systems. Since Raman process is a scattering process, Raman scattering occurs in almost all kinds of wavelengths. In another words, Raman spectroscopy moves the vibrational spectroscopy into uv-vis (200nm-700nm in wavelength) region. Next section will be dedicated to describe the Raman scattering process in detail.

1.2 Raman Spectroscopy

Raman scattering is one of the phenomena which result from the interaction of electromagnetic radiation with molecules. When a photon is incident on a molecule, the scattering radiation either has the same energy as the incident photon (termed as Rayleigh scattering) or has different energy as the incident photon. The difference in energy between scattering radiation and incident radiation is independent of the incident wavelength. This scattering is called Raman scattering. In Raman scattering the energy difference strictly corresponds to the energy gap between two vibrational levels of an oscillator.

Classically, Raman scattering process can be understood assuming that the electromagnetic radiation induces a vibrating dipole in the molecule. For an electromagnetic wave with a periodically varying intensity, the electric field can be described as

\[ E = E_0 \cos(2\pi \nu_0 t) \]  

(1.1)
Here $E_0$ is the intensity amplitude of the electric component, $\nu_0$ is the wave frequency, and $t$ is time. The induced electric dipole moment can thus be written as

$$\mu_{\text{ind}} = \alpha E_0 \cos(2\pi \nu_0 t) \quad (1.2)$$

The parameter $\alpha$ is called polarizability of the molecule which characterizes the size and shape change of the molecule corresponding to the molecular vibrations. The polarizability tensor $\alpha_{ij}$ may be expanded as a function of the normal vibrational coordinate $Q$.

$$\alpha_{ij} = (\alpha_{ij})_0 + \left( \frac{\partial \alpha_{ij}}{\partial Q} \right)_0 Q \quad (1.3)$$

If we present the polarizability tensor in the form of a matrix

$$\begin{pmatrix} \alpha_{ij} \end{pmatrix} = \alpha$$

$\alpha$ can be written as a function of the normal vibrational frequency $\nu$ of the molecule. Therefore

$$\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial Q} \right)_0 A_\nu \cos(2\pi \nu t) \quad (1.4)$$

Here $A_\nu$ is the amplitude of the given normal vibration of the molecule frequency $\nu$. Substituting this expression for $\alpha$ into the expression of $\mu_{\text{ind}}$ in equation (1.2) gives

$$\mu_{\text{ind}} = \alpha_0 E_0 \cos(2\pi \nu_0 t) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial Q} \right)_0 A_\nu E_0 \left\{ \cos[2\pi(\nu_0 - \nu)t] + \cos[2\pi(\nu_0 + \nu)t] \right\}$$

Therefore, from classical theory the vibrating molecule can be the source of scattered radiation of three different frequencies.
The radiation which has the same frequency as the incident radiation is called Rayleigh scattering. The radiation which has different frequency from the incident radiation is Raman scattering. The difference in frequency corresponds to the vibrational frequency of the oscillator. There are two types of Raman scattering. One is called Stokes Raman scattering which refers to scattering radiations with less energy ($\nu_0 - \nu$) than the incident light ($\nu_0$). The other one is called anti-Stokes Raman scattering which refers to scatterings with higher energy ($\nu_0 + \nu$) than the incident light ($\nu_0$).

The semi-quantum mechanical and full quantum mechanical treatment of Raman scattering can be found in many classic books of Raman spectroscopy.\(^{(26-27)}\) Since the interpretation of our time resolved Raman spectroscopy does not require complicated calculation of Raman scattering, I will not go into the details of the tedious quantum mechanical derivation. Instead I will discuss several aspects of Raman scattering which are relevant to our experiments from quantum mechanical point of view.

Figure 1.1 shows a schematic diagram of Stokes and anti-Stokes scattering. Raman scattering is a two photon process. In Raman scattering two vibrational levels from same electronic state and one higher intermediate states are involved. As shown in pairs of arrows in Figure 1.1, Stokes Raman originates from scatterings at lower vibrational level (such as $\nu = 0$) and ends at higher vibrational level (such as $\nu \geq 1$). The anti-Stokes Raman originates from scatterings at higher vibrational level (such as $\nu = 1$) and ends at lower vibrational level (such as $\nu = 0$). Normally,
the anti-Stokes signal is much weaker compared to the Stokes signal, since the vibrational population for higher vibrational levels are much smaller than that at the vibrationless level at room temperature.

For a harmonic oscillator only those transitions with change of vibrational quantum numbers by one are allowed. Theoretically only one Raman band corresponding to the oscillator vibrational frequency will be observed in the spectrum. For an anharmonic oscillator, the selection rule indicates that not only \( v = \pm 1 \) transitions are allowed but also \( v = \pm 2, \pm 3 \ldots \) transitions are allowed. Raman bands correspond to \( v = \pm 2, \pm 3 \ldots \) are called overtones. In a Raman spectrum one would observe a progression of bands with vibrational spacing getting smaller and smaller and intensity getting weaker and weaker as the vibrational frequency becomes higher. From the band positions of overtones, one can easily calculate the dissociation energy of the potential well and the anharmonicity of the potential if assumptions are made about the shape of the potential (such as Morse potential). Overtone bands can therefore provide information about the potential well for that electronic state. Examples are given in Chapter 4.

However, in normal Raman scattering process it is not easy to observe the overtone bands, since the transitions with vibrational quantum number change other than one are much weaker. The intensity of normal Raman scattering, which is often called nonresonance Raman scattering is only about \( 10^{-3} - 10^{-4} \) of that of the Rayleigh scattering. The Rayleigh scattering is in turn only \( 10^{-3} - 10^{-4} \) of the
Figure 1.1

Schematic diagram of Raman Scattering. Left scheme is a sketch of nonresonance Raman scattering. In a nonresonance Raman scattering, the intermediate state is a virtual energy level which is indicated by the dashed line in the figure. Right scheme is a sketch of resonance Raman scattering. In a resonance Raman scattering the intermediate state is (or close to) one of the real vibronic level which is indicated by solid lines in the figure. \( S_0 \) stands for ground electronic state. \( S_n \) stands for one of the excited electronic states. Each pair of arrows represents Stokes and anti-Stokes process respectively.
intensity of incident radiation. In order to observe a strong Raman signal or even overtone, resonance Raman enhancement has to be utilized.

The difference between normal Raman scattering and resonance Raman scattering is also sketched in Figure 1.1. In a normal Raman scattering process shown in the left scheme, the excitation frequency reaches a virtual energy level (indicated by the dashed line in Fig. 1.1) of the molecule. In resonance Raman scattering shown in the right scheme, the excitation frequency reaches a real energy level (indicated by solid line in Fig. 1.1) or close to the real level. Therefore, resonance Raman scattering occurs when the excitation radiation frequency approaches or enters the electronic or vibronic absorption band of molecule. In resonance Raman scattering the intensity of Raman band is several magnitudes higher than normal Raman scattering. There are several publications\(^{2,26,28-29}\) dealing with the quantum mechanic treatments of resonance Raman scattering. I will not go into the details of the theory, since the interpretation of our Raman band intensity does not require rigorous theoretical justification. There are two factors affecting the intensity of resonance Raman scattering. One is the energy defect between the incident photon and the energy gap of two real energy levels. The smaller the defect, the stronger the Raman intensity. The other factor is the vibrational overlap integral between the initial vibrational state and the upper intermediate vibrational state (in an excited electronic state) and the overlap between the intermediate state and the final vibrational state. This part is obviously vibrational level dependent and will dramatically affect the band shape and intensity of Raman spectra as we will see in Chapter 3
and Chapter 4. In order to calculate this term, detailed information about the excited state potential well is required. This increases the difficulty in predicting the resonance Raman band profile. In Chapter 3 we have done some very simple calculations for $X$ state to explain the observed unsymmetry of transient $X$ state Raman band.

Another distinctive feature of resonance Raman spectrum is that Raman band is accompanied by a progression of overtones. The resonance between the exciting photon and the electronic transition of the molecule will enhance both fundamental and overtone bands. Using the frequencies of overtones for the excited state we can calculate the anharmonicity and well depth of that electronic state. In Chapter 4 I will display such calculation to obtain the information for excited $A'$ state.

1.3 $I_2$ Photophysics and Photochemistry

In order to understand the energy flow in iodine in the condensed phase following photoexcitation, it is necessary to have knowledge about the electronic potentials in iodine molecule. Figure 1.2 is a plot of the gas phase potential surfaces in iodine. The potentials for all electronic states are obtained from known literatures to the best of our knowledge. The only plotted electronic states are those which are pertinent to our experimental measurement. The state labeled $X$ is the ground state. The electronic state is $^1\Sigma_g^+$. States labeled $A(^3\Pi_{1u})$ and $A'(^3\Pi_{2u})$ are excited electronic states. At infinite nuclear separation, all these three states will lead to the generation of two ground state iodine atoms $I(^2P_{3/2})$. State labeled $B(^3\Pi_{0u}^+)$ is also a bound excited state which corresponds to one ground state iodine atom and
one excited state atom at dissociation limit. The higher lying bound excited state $D$ is called ion-pair state which corresponds to the formation of iodine ions at dissociation limit. The dashed curve in Fig. 1.2 is solvent shifted $D$ state potential. There are several repulsive curves (such as $^1\Pi_u$ and $a^3\Pi_{1g}$) crossing with the $B$ state at the bottom of the potential well. They are very similar to each other. These repulsive states will directly lead to the dissociation of iodine molecule to form two ground iodine atoms. In Figure 1.2 only one repulsive state $a^3\Pi_{1g}$ is plotted.

The excitation wavelength we used is 532nm. This wavelength excites a mixture of excited electronic states. Estimates of transition strengths in the gas phase suggest that $\approx 85\%$ of the excitation goes to the $B^3\Pi_{0+u}$ state and $\approx 15\%$ to the $^1\Pi_u$ state with excitation near 532nm.$^{(31)}$ Excitation at 532nm into the $B^3\Pi_{0+u}$ state is expected to populate vibrational levels$^{(32)}$ near $\nu=31$. Excitation to these vibrational levels will predominately lead to predissociation of $B$ state. In the gas phase the predissociation$^{(33-40)}$ of $B$ state via repulsive curve has been extensively studied. The natural and magnetic predissociation of the $B^3\Pi_{0+u}$ state involves the $^1\Pi_u$ state,$^{(33-35,41)}$ whereas the primary exit channel in collisional induced electronic predissociation is the $a(3\Pi_{1g})$ dissociative state.$^{(42)}$

The electronic predissociation$^{(36-39)}$ time of the $B$ state was found to be dependent on the vibrational level of the $B$ state. Generally the predissociation time is on the order of microseconds. The predissociation of $B$ state is the predominant process so that the vibrational relaxation can be neglected. In the solution phase,
Figure 1.2: Gas phase potentials of I$_2$. Bound electronic states $X$, $A'$, and $B$ potentials are plotted respectively. The gas phase $D^1\Sigma_u^+$ state is plotted as the solid line and the estimate of the solvent shifted potential as a dashed line.$^{(30)}$ The repulsive curve is $a^3\Pi_1g$ state. Arrow (1) indicates $B \rightarrow X$ excitation at 532nm. Arrow (2) indicates the predissociation via the repulsive state after photoexcitation. Arrow (3) and (4) indicate the geminate recombination on $A'$ and $X$ states. The dashed vertical line with arrow indicates the resonance Raman probe of $X$ state levels using the $D \rightarrow X$ transition. Energy is in units of cm$^{-1}$; internuclear separation is in units of Å.
Figure 1.2

POTENTIAL ENERGY (cm⁻¹)

INTERNUCLEAR SEPARATION

A'

(1)

X

(2)

(3)

(4)
the high collision frequency enhances the predissociation rate of $B$ state. As a matter of fact, the transient absorption measurement by Harris and coworkers\cite{22,25} using 1ps laser pulse indicates that predissociation through $B$ state occurs in less than 2ps. The actual $B$ state predissociation rate was recently determined to be about 300fs.\cite{43} Therefore photoexcitation with a 532nm photon will lead to instant dissociation of iodine within our 8ps time resolution. The newly generated iodine atoms are surrounded by the solvent cage. Geminate recombination will occur subsequently on both the $X$ state and $A'$ state. Immediately following recombination, the nascent iodine molecule contains more than 12,000 cm$^{-1}$ internal energy at the top of the $X$ state potential well. This amount of energy is dissipated through the vibrational ladder by transferring one or several quanta of vibrational energy to its surrounding solvents. Using transient Raman spectroscopy we have for the first time directly observed geminate recombination and vibrational energy relaxation on both $X$ state and $A'$ state.

The term "vibrational energy relaxation" (VER) is used to distinguish two different vibrational relaxation processes. One is the relaxation due to vibrational population change. This process is often referred to as its lifetime "$T_1$". The other process is relaxation due to vibrational dephasing. This process is often referred to as its lifetime "$T_2$". The commonly used term "vibrational relaxation" is a sum of both processes. In our time resolved Raman spectroscopy, we are directly measuring the vibrational population change at different vibrational levels. Therefore we define the "$T_1$" process in our measurement as "vibrational energy relaxation".
1.4 Organization

This dissertation will be organized as following. In Chapter 2, I will describe the experimental technique to measure the transient Raman spectroscopy. The laser system and experimental setup will be discussed therein. In Chapter 3, I will present first direct measurement of geminate recombination and vibrational energy relaxation in the $X$ state. The solvent dependence of VER and detailed energy relaxation pathways are discussed. In Chapter 4, I will present the results on the study of geminate recombination, vibrational energy relaxation and electronic relaxation of excited electronic $A'$ state. Both Chapter 3 and Chapter 4 are based on two separate papers which have been published in the *Journal of Chemical Physics*. In Chapter 5, I will present results on the study of geminate recombination of radical iodine and molecular iodine. This chapter is based on a paper which is going to be submitted to the *Journal of Chemical Physics*. In Chapter 6, I will summarize the results and conclusions of our study on the geminate recombination and vibrational energy relaxation of iodine in the condensed phase.
2. EXPERIMENTAL Technique

In this chapter I will describe the experimental technique to measure transient Raman spectrum. I will address three aspects of the technique in obtaining a high signal-to-noise ratio transient Raman spectrum: special requirements on laser system; unique experimental setup, namely, pump-probe technique and spectrum subtraction technique.

2.1 Ultrafast Laser System

Because Raman scattering signal is so weak, the laser intensity of incident radiation must be high enough to observe Raman signal. For the transient Raman signal we are seeking, the signal is even weaker since normally only about 10% to 20% of the molecules are excited. However, the laser power cannot be increased indefinitely. High intensity laser pulse could easily reach the threshold of nonlinear artifact. High intensity light also has the risk of sample damage. One way to avoid using high intensity laser pulse is to use a laser with high repetition rate. Instead of delivering all the power in one giant pulse, in a high repetition rate laser each pulse only delivers very small portion of the total power.

High repetition rate is not the only requirement for measuring time-resolved transient Raman spectrum. The laser system must be capable of providing enough peak power and high time resolution. The laser system used in our laboratory employs the amplification of 100-MHz mode-locked NdYAG laser (Quantronix Model 416ML) pulses using a high repetition rate regenerative amplifier (Quantronix Model 117). The seed pulse is frequency chirped by a fiber optic and then injected
into the regenerative amplifier. The amplified pulse is compressed by a pair of gratings. The initial mode-locked laser pulse has a pulse width of 80ps and peak power of 60nJ/pulse. After compression and amplification the output laser pulse has peak power of 1mJ/pulse and pulse width of 10ps. The laser system is running at a repetition rate of 2kHz. This is the highest repetition rate ever achieved in this system.\(^{(44)}\)

### 2.2 Experimental Setup

Figure 2.1 shows a typical experimental setup for measuring the transient Raman spectrum. A pump-probe two-color scheme is used to measure the Raman spectrum and dynamics of transient. This technique has been described in detail in two publications\(^{(45-46)}\). The output fundamental IR beam at 1.064\(\mu\)m is frequency doubled, tripled and quadrupled using nonlinear crystal KTP and BBO to generate light at different wavelengths. The second harmonic at 532nm is used as a pump beam to excite iodine molecule. Both third harmonic at 354.7nm and fourth harmonic at 266nm are used to probe processes subsequent to photodissociation. The probe beam is optically delayed by a motorized delay stage. Since light travels at a speed of \(\approx 3 \times 10^{10} \text{ cm/s}\), the delay time between pump and probe can be obtained by comparing the distance travelled by each beam. The precise delay time is achieved by the use of a computer program. A retroreflector is mounted on the delay stage to insure that the probe beam stays at same position in space as it travels. Typical energy used for pump 532nm is 70\(\mu\)J and typical energies for probe 354.7nm and 266nm are 20\(\mu\)J. Both beams are focused to the beam waists of 250 to 500 \(\mu\)m. To
obtain the spectrum of pure transient, both one color (probe only) Raman spectrum and two color (pump+probe) spectrum are measured. This is achieved by chopping the pump beam using a chopper at 200Hz. A computer sorts the Raman signal from each laser pulse into two bins according to the phase of the chopper. In this way both one color and two color spectra are obtained simultaneously. The pure transient Raman spectrum is generated by subtracting one color background from the raw two color spectrum.

The Raman scattering was imaged onto an Instruments SA double monochromator which was positioned to collect at the 180° backscattering geometry. The angle between the laser beam and a line normal to the sample is near 50°. Both pump and probe beams are approximately collinearly incident on the sample by using a dichromatic beam combiner. The signal from each laser pulse was detected with a photomultiplier tube, processed through a Lecroy 2249SG CAMAC based gated integrated, where the information is analyzed by a DEC 11/73 computer. The laser power from each laser pulse is measured using a photodiode. Those laser pulses with fluctuations in laser energy by more than 20% are discarded by the computer. Repetitive scans are taken and then summed to increase the signal-to-noise ratios of the spectrum.

Accurate Raman shifts are obtained by recording a complete spectrum of the sample of interest which includes a feature corresponding to the attenuated Rayleigh line. Raman shifts are directly measured from the Rayleigh line. Most spectra are shifted according to the ground state iodine Raman band in solution.
Figure 2.1

\[ \omega = 1.064 \, \mu m \]

8ps, 500 \mu J / pulse

2 kHz

\[ \text{Flowing jet solution} \]

\[ \text{Raman pickup optics} \]

ISA U 1000

Monochromator
which is at 212 cm\(^{-1}\) or to the known solvent bands. All Raman spectra at different time delays are shifted same way so that the relative shift of Raman band with time can be correctly accounted for.

In measuring the dynamics of transient Raman band, the timing between pump pulse and probe pulse was determined using fluorescence depletion dynamics of coumarin dye C500 in methanol. Upon excitation of 354.7nm and 266nm, the coumarin 500 dye emits at blue region. When a second photon at 532nm is incident on the sample, stimulated emission will result in the depletion of the fluorescence intensity in the backscattered direction. This is due to the removal of population from the emitting state by the second photon. The depletion occurs faster than our pulselength. The observed depletion dynamics is thus pulselength limited. The position where the emission intensity decrease to 50% of the maximum is taken as time zero. The delay stage is about one meter long. However the longest delay we ever measured is 3ns, which corresponds to 0.45 meters delaying distance on the stage. The linearity of this mechanical delay stage was checked by measuring the transient Raman spectrum of the lowest excited triplet state of \([\text{Ru(bpy)}_3]^{2+}\) which has a decay time\(^{(47)}\) of 580ns in water at 25\(^\circ\)C.

Two sampling systems are used in our experiments. One is the free flowing jet system. In this system a flowing solution was sprayed through a home-made glass nozzle which produce a low turbulence optical quality jet with a path length of 1mm. The flow rate is fast enough so that each laser pulse interrogates a new region of the sample. The other system used is a spinning cell. The cell is made of Teflon
which is inert to iodine and most solvents. The cell assembly is sealed by a suprasil window. In the spinning cell iodine sample does not degrade under photoexcitation for at least 48 hours. Temperature dependence measurements are achieved using flowing jet system by inserting the solution container into the bath of a temperature controller.

Iodine is bought from Aldrich company and used at stated purity of 99.999%. Solvents were also purchased from Aldrich, which are of highest grades available. They were used without further purification. The concentration of iodine was varied from 0.5mM to 20mM. Except in measuring the dynamics of $X$ state the concentration used is 3mM, all other concentration changes are indicated in text.

2.3 Spectrum Difference Technique

The Raman spectra shown in this dissertation are all transient Raman spectrum. They are obtained by subtracting one color only background from the raw two color spectrum. The one color only spectrum comprises ground state iodine band and solvent Raman bands. The raw two color spectrum comprises bands from one color spectrum plus excited state bands and Raman bands of new transients. Normally the excited states and new transient bands are much weaker than the ground state bands and solvent bands. Sometimes they are heavily overlapped. From the measurement of raw two color spectrum only, it is very difficult to separate the excited states and transients from ground state and solvent bands. The sensitivity of
this spectrum difference technique in recovering the weak transient signal is illustrated in Figure 2.2

Figure 2.2 is the Raman spectrum of iodine in CCl$_4$. The raw two color spectrum is shown in Frame A. The one color only background spectrum is shown in Frame B. Frame C is the subtracted spectrum. After the removal of solvent bands the very small excited bands at 106 cm$^{-1}$ is completely recovered. There are two new bands merged. One is at 204 cm$^{-1}$ and the other one is at 299 cm$^{-1}$. They are indiscernible in the raw two color spectrum due to the existence of huge solvent bands. These two bands are \textit{not} the experimental error due to the subtraction procedure. They are the overtones of the excited state band at 106 cm$^{-1}$. These same two overtones are also observed in other solvents where there are no solvent bands nearby. Figure 2.2 clearly displays how powerful and important this subtraction technique is in studying the dynamics of transients.

Strictly speaking, the pure transient Raman spectrum must also subtract the background from pump only spectrum. Because the pump beam is more than 9000 cm$^{-1}$ away from the probe beam, the effect of pump only background on the total spectrum can be neglected. In addition, we measured the pump only background in the region we probed. It is indeed the case.

The formula used in obtaining the transient Raman spectrum is

$$\text{Transient} = \text{RawTwoColor} - \text{factor} \times (\text{OneColor}).$$
Pure transient difference spectrum of I\textsubscript{2} in CCl\textsubscript{4} obtained by subtracting the one color spectrum in frame B from the raw two color spectrum in frame A. Spectra were obtained simultaneously in a single scan of the monochromator using chopped laser excitation. The bands at 217 and 313.5 cm\textsuperscript{-1} in frames A and B are solvent bands.\textsuperscript{48} The solvent band at 217 cm\textsuperscript{-1} is overlapped with the ground state I\textsubscript{2} band. Optical delay between pump(532nm) and probe(354.7nm) lasers is 500ps. Frequency units are in cm\textsuperscript{-1}.
If no factor is applied ($factor = 1$), the subtracted spectrum shows that both the ground state Raman band and solvent bands are all depleted. This is due to the optical density change resulting from the photoexcitation of iodine molecule. After photoexcitation of iodine molecule by the pump beam, iodine will dissociate and recombine again into the vibrationally excited $X$ and $A'$ states. The absorption of the $A'$ state is stronger at both 354.7nm and 266nm than the vibrationless $X$ state. This effect changes the optical density of the molecule so that the solvent molecule actually absorbs less than when no pump beam exists. In the subtracted spectrum, the depletion of iodine ground state band is due to both depopulation of vibrationless state and optical density change. The depletion on the solvent bands is purely due to the optical density change upon the excitation of pump beam. For the solvent there is no photochemical process under the influence of both pump and probe beams. We can correct the optical density change by removing the depletion of solvent bands. Since the pump only Raman band for solvent is always stronger than the two color band, the factor we applied is always less than one. All the transient Raman spectra shown here are corrected to remove the depletion on solvent bands.
3. GEMINATE RECOMBINATION AND VER OF X STATE

3.1 Introduction

Photodissociation of iodine has been widely used as a source of reactive atoms to investigate chemical dynamics in the condensed phase. The specific reaction of the geminate atoms, termed geminate recombination, has been extensively studied as a model of condensed phase reactivity. Following recombination at the top of the potential energy well, the iodine molecule contains over $12,000 \text{ cm}^{-1}$ of internal energy as shown in Figure 1.2. This energy is initially distributed within the vibrational modes of the newly formed iodine molecule. In the condensed phase, vibrational energy relaxation (VER) will cool the internal energy of the hot iodine molecule into the heat bath comprised of the solvent coordinates. This is a key process in condensed phase reactions and is poorly understood at the present time. The rates and mechanisms by which this energy relaxation occurs are the primary topics of this chapter.

The energy gaps separating adjacent vibrational levels range from near zero at the top of the $X$ state potential to $210 \text{ cm}^{-1}$ for the lowest energy levels at the bottom of the potential. With such a wide range of energy gaps it has been suggested\(^{(11-12)}\) that the dominant mechanism of VER can change as the energy gap varies. As a result different relaxation mechanisms can become important as the vibrational population distribution relaxes within the $X$ state potential. The experimental technique utilized in this work is transient picosecond resonance Raman spectroscopy. This approach is unique in that it provides a direct measure of
the vibrational kinetics at a given vibrational energy spacing—that is, at any point on the $X$ state potential the vibrational energy spacing is precisely the value of the experimentally determined Raman shift. In principle it is possible to observe the dynamics over the entire range of vibrational levels. However, in practice there is an experimental limit imposed by the necessary condition of a strong resonance Raman enhancement. Since the electronic absorption strength depends on the originating vibrational level, the resonance Raman enhancement will likewise be affected. For this reason several different probe wavelengths (266nm, 354.7nm, and 532nm) are used in this experiment to obtain the vibrational dynamics over the entire range of energy levels.

Harris et al. have investigated\(^{(24)}\) VER in the $X$ state by comparing calculated Franck-Condon absorption strengths to experimental transient absorption data. There are two points of concern with these results. First, the Franck-Condon calculations were performed using gas phase potentials. Although it is not expected\(^{(24,49)}\) that the potentials will shift in non-interacting solvents, this assumption remains to be validated. The second concern involves the dynamics observed in alkane solvents. As first pointed out by Kelly et al.,\(^{(20)}\) there are strong absorption signals originating from the electronic absorption of the $A'$ excited states.\(^{(20)}\) To interpret the VER dynamics using absorption data the excited $A'$ state signal must be removed. Harris et al.\(^{(24)}\) have carefully considered this problem. However, in alkane solvents both VER on the $X$ state and electronic decay of the excited $A'$ state have very similar dynamics. This makes it difficult to separate the data into the two
different components. For iodine in chlorinated-methane solvents the excited $A'$ state signal is easily removed.\(^{(24)}\) In these solvents the VER dynamics have been interpreted\(^{(24,50)}\) to indicate that vibrational to translational (V-T) relaxation is a dominant pathway. This result is consistent with theoretical predictions.\(^{(11-12)}\) In addition, Harris et al. have interpreted their results to indicate that vibrational to rotational (V-R) relaxation pathways are also important. These effects have been traditionally ignored in condensed phase theories but recent calculations\(^{(51)}\) indicate that V-R may be of nearly equal importance to V-T energy transfer. In addition, they have determined\(^{(24,50)}\) that vibrational to vibrational (V-V) relaxation is apparently of less importance than originally predicted.

Using transient Raman data, it is possible to separate the $A'$ and $X$ components even in alkane solvents. This information can then be used to interpret the mechanisms of VER in complex solvents where both V-T and V-V energy relaxation pathways are possible. These results are compared to the experimental results of Harris et al. in chlorinated-methane solvents\(^{(24)}\) and to theoretical predictions for V-T and V-V energy relaxation. The importance of additional considerations is suggested from the transient Raman results.

The distribution of excited vibrational states in the $X$ state potential well is an important measure of the mechanisms of energy transfer. This information has been previously obtained by the inversion of transient absorption data for long times on the order of 50ps after geminate recombination.\(^{(24)}\) Using transient Raman spectroscopy, vibrational distributions\(^{(52)}\) can be directly obtained in the first
few picoseconds. During the initial relaxation time much higher vibrational states are populated. In this chapter we discuss the dynamics of the vibrational population of $X$ state over the complete range of times from 0 to 500ps.

3.2 Results

3.2.1 Raman Detection at 354.7nm

The sensitivity of the two-color transient Raman technique is shown in Figure 3.1 for excitation at 532nm and Raman interrogation at 354.7nm. The raw two-color spectrum containing both the transient and one-color background signal is shown in Figure 3.1A. The one-color spectrum is shown in Figure 3.1B and exhibits two features. The first consists of the wing of the Rayleigh line, which rises at low frequencies. The second feature is the ground state iodine band at 210 cm$^{-1}$, which is weak as a result of the relatively small resonance enhancement at 354.7nm. The pure transient spectrum shown in frame C, is obtained by subtracting frame B from frame A. This spectrum corresponds to several transient species with two prominent features at 106 and 195 cm$^{-1}$.

In the gas phase the $v$=0-1 vibrational spacing in the excited $A'$ ($A'$ $^3\Pi_{2u}$) state has a value of 104.3 cm$^{-1}$. Flynn et al. proposed that the $A'$ state is formed by geminate recombination following photodissociation of iodine at 532nm. The dynamics of the $A'$ state have been measured by Kelly et al. and Harris et al. using transient absorption spectroscopy. The dynamics of the 106 cm$^{-1}$ Raman band match the absorption dynamics attributed to the $A'$ state.
Pure transient Raman difference spectrum of I$_2$ in cyclohexane obtained by subtracting the one color spectrum in frame B from the raw two color spectrum in frame A. Spectra were obtained simultaneously in a single scan of the monochromator using chopped laser excitation. The filled-in parts in frame A highlight the two weak transient Raman bands in the raw data. The rising signal at lower frequencies in both raw two color data and one color data are due to the influence of Rayleigh line. Optical delay between pump(532nm) and probe(354.7nm) lasers is 50ps. Frequency units are in cm$^{-1}$. 
The band at 106 cm\(^{-1}\) is therefore assigned to the excited \(A'\) state based on these spectroscopic and dynamic arguments. This band is marked \(A/A'\) in the figures to indicate the possibility that this Raman band may originate from both the \(A^3\Pi_{1u}\) and \(A'\) electronic states. The next chapter considers the spectroscopy of the \(A^3\Pi_{1u}\) and \(A'\) state transients.

The broad feature at 195 cm\(^{-1}\) in Figure 3.1A is assigned to the Raman spectrum due to hot vibrational states in the \(X\) state potential. The pure transient Raman difference spectrum at various optical delays is shown in Figure 3.2. The broad feature assigned to the \(X\) state is indicated by the arrow in each frame. As time progresses from 5 to 55ps, this feature shifts from a peak position at 155 cm\(^{-1}\) to 195 cm\(^{-1}\). These dynamics are assigned to vibrational cooling on the \(X\) state potential. In the \(X\) state potential vibrational energy gap increase from 0 cm\(^{-1}\) at the top of the potential to 212 cm\(^{-1}\) at the bottom of the potential. In a transient Raman spectrum, Raman frequencies correspond directly to the quanta of energy that must be lost to depopulate the level. As vibrational cooling proceeds, the observed Raman band should shift to higher frequencies. In addition, the Raman spectrum represent an ensemble of unresolved vibrational levels. This is consistent with the expectations for the Raman spectrum from adjacent vibrational levels in the \(X\) state. The frequencies for Raman scattering from any two adjacent vibrational levels \(v \rightarrow v + 1\) and \(v + 1 \rightarrow v + 2\) differ by a maximum of 2.3 cm\(^{-1}\) based on gas phase spectroscopic constants.\(^{57}\) Since this difference is small compared to
the observed line width for condensed phase iodine (20 cm\(^{-1}\)), only a distribution of states is observed.

It is interesting to note that the transient spectra in Figure 3.2 do not show evidence for depletion of ground state iodine. This is a result of the extremely weak resonance enhancement for the thermally populated \(v=0,1,2,3\) vibrational levels. The absence of population bleaching in the spectrum is simply due to the magnitude of the transient Raman spectrum compared to the fraction of population removed by the pump laser. Under the laser conditions used in these experiments about 1\% of the I\(_2\) is photodissociated. The magnitude of the bleach should therefore be on this order. However, the Raman signal from the transient vibrational levels exhibits a very strong resonance enhancement, whereas the thermally populated levels do not. In fact, Figure 3.1 shows that the transient signal at 106 cm\(^{-1}\) is about ten times the magnitude of the entire I\(_2\) ground state band. These considerations indicate that the transient bleach of the I\(_2\) ground state band should be more than 100 times weaker compared to the transient signal at 106 cm\(^{-1}\). This small magnitude of signal is not observed with the present signal-to-noise.

In contrast, the 266nm spectra shown in Figures 3.3 and 3.4 exhibit depletion of ground state iodine. In this case, the lower thermally populated levels in the \(X\) state have a small resonance enhancement resulting in a stronger Raman signal. A small change in the \(X\) state signal from the \(v=0,1,2,3\) levels can be detected at 266nm resulting in the observation of depletion.
Pure transient Raman difference spectra of I$_2$ in cyclohexane using probe wavelength of 354.7nm. Optical delay between pump(532nm) and probe(354.7nm) lasers is given in each frame. The arrows indicate the transient X state peak positions at various time delays. The band at 106 cm$^{-1}$ is due to the A' excited state.$^{(56)}$ The dashed lines in frames A and D are an 2.5x(A) and 8x(D) enlargement of the original curve. Concentration is 2mM. Frequency units are in cm$^{-1}$. Quantum numbers are calculated from the gas phase RKR potential.$^{(57)}$
Figure 3.3: Pure transient Raman difference spectra of I$_2$ in cyclohexane. Optical delays between pump(532nm) and probe(266nm) are indicated in each frame. Spectra are normalized to the one color I$_2$ ground state band and represent the true dynamical intensity variations. The dashed insert in the 200ps frame is a 6x enlargement of the original spectra. Concentration is 2mM. Frequency units are in cm$^{-1}$. Quantum numbers are calculated from the gas phase RKR potential.$^{(57)}$ The apparent depletion of the $X$ state signal at -5ps is believed to be due to the finite width of the pump and probe laser pulses. The band labeled $A/A'$ is due to the $A'$ excited state.
Figure 3.3

VIBRATIONAL QUANTUM NUMBERS
60  40  20  10  0

Relative Intensity

RAMAN FREQUENCY
VIBRATIONAL QUANTUM NUMBERS
60  40  20  10  0

Relative Intensity

RAMAN FREQUENCY
In principle, the Raman spectra should be corrected for the resonance Raman enhancement which is clearly dependent on the originating vibrational level. Unfortunately, this quantity is difficult to calculate for probe wavelengths at 354.7nm because the Raman enhancement arises from a resonance between the \( X \) state and higher energy contact charge transfer states\(^{(58-59)} \). These states are poorly characterized making Franck-Condon calculations of the vibrational dependence of the Raman enhancement difficult. For this reason we believe that it is much more meaningful to compare the time-dependent intensity and shape of the hot \( X \) state vibrational envelope using the singlet \( D \leftarrow X \) transition\(^{(60)} \) detected at 266nm. This resonance is shown in Figure 1.2.

### 3.2.2 Raman Detection at 266nm

Figure 3.3 shows vibrational cooling on the \( X \) state using a probe wavelength of 266nm. The spectra in Figure 3.3 are normalized with respect to each other to reflect the true relative intensity of the transient signal. The vibrational quantum number calculated from the gas phase \( X \) state RKR potential\(^{(57)} \) is indicated on the top x axis. Figure 3.3 shows that the \( X \) state vibrational envelope at time zero is peaked near 155 cm\(^{-1} \). This feature continues to shift during the first 25ps settling on a value of 187 cm\(^{-1} \) in the 25ps spectrum shown in Figure 3.3.

In the 25ps frame shown in Figure 3.4 there appears to be an asymmetry in the band. Figure 3.5 shows two different sets of data which demonstrate the repeatability typical of our apparatus. This asymmetry is reproducible and is interpreted as a sudden increase in the resonance Raman enhancement. The increase occurs in the
iodine $X$ state Raman spectrum near 180 cm$^{-1}$ for vibrational levels near $\nu = 25$. Calculations of the resonance Raman enhancement (see below and Appendix A) qualitatively support this interpretation. In addition the spectrum obtained using a probe wavelength of 354.7nm shown in Figure 3.2B indicates that at 30ps a symmetric population distribution exists which is peaked near $\nu = 25$. This result also suggests that the asymmetry in the 266nm probe spectra (Figure 3.3) is the result of the vibrational level dependence of the resonance Raman enhancement.

### 3.2.3 Resonance Raman Enhancement

The $X$ state vibrational level dependence of the resonance enhancement for fixed frequency Raman excitation at 266nm has been calculated and the results are shown in Figure 3.6. It is assumed that the only resonant transition involved is $D \leftarrow X$. The details of the calculation are given in Appendix A. The calculated resonance enhancement in Figure 3.6 is broad and flat from $\nu = 35$ to $\nu = 70$. It peaks sharply at $\nu = 30$ and falls off steeply by $\nu = 20$.

The sharp peak in the resonance enhancement qualitatively accounts for the asymmetry observed in the transient Raman spectrum near $\nu = 25$ vibrational levels. However, the calculation predicts a maximum enhancement for higher levels near $\nu = 30$. This discrepancy could be the result of solvent shifts in the potentials. In the calculation shown in Figure 3.6, the potentials have been shifted to account for the estimated solvent shifts. However, these estimates are uncertain.

Nevertheless, it is believed that the general trends observed for the $X$ state dynamics are not affected by resonance enhancement. Both the 354.7nm and 266nm
Figure 3.4: Pure transient Raman difference spectra of I$_2$ in d$_{12}$-cyclohexane.

All curves are normalized in the same manner as Figure 3.3 and represent the true dynamical intensity variations. The arrows indicate the peak position of the transient $X$ state signal. The dashed inserts in the -5ps and 200ps frame are 8x and 6x enlargements of the original curve. The apparent depletion of the $X$ state signal at -5ps is believed to be due to the finite width of the pump and probe laser pulses. Other conditions are the same as in Figure 3.3.
Figure 3.4

VIBRATIONAL QUANTUM NUMBERS
60  40  20  10  0

t= 200 ps

Relative Intensity

Raman Frequency

VIBRATIONAL QUANTUM NUMBERS
60  40  20  10  0

t= 150 ps

A/A'

100 150 200 250

Relative Intensity

Raman Frequency
Multiple scans of 25ps $X$ state dynamics in cyclohexane to establish reproducibility. Conditions are the same as in Figure 3.3.
Figure 3.6

Resonance Raman enhancement for $X$ state vibrational levels detected at 266nm. Enhancement is plotted on a relative scale starting from zero. Calculation is described in Appendix A.
transient Raman spectra are in agreement regarding the dynamics of the shape of the population distribution and its position in the $X$ state well. In both sets of data there is a smooth temporal evolution of the population distribution. That is, the peak of the population distribution shifts smoothly in time to lower vibrational levels with only minor asymmetries observed.

There is one major difference between the transient Raman spectrum obtained with a 354.7nm probe laser (Figure 3.2) and the spectrum obtained with 266nm probe laser (Figure 3.3). In Figure 3.2 there is a strong $A'$ state band\(^{56}\) at 106 cm\(^{-1}\) which is much weaker in Figure 3.3. Apparently, the resonance Raman enhancement for the $A'$ state band is significantly reduced at 266nm.

### 3.2.4 Effect of $A'$ State Dynamics on $X$ State Dynamics

It should not escape the attention of the reader that there is an important relationship between the $A'$ state and $X$ state dynamics shown in Figure 3.2—that is, the $X$ state vibrational band envelope appears to shift in frequency independently of the dynamics of the $A'$ state band. The Raman spectra can separately measure both $A'$ and $X$ dynamics by identifying each component in the frequency domain.

In the Raman data there is no apparent second distribution of vibrational population resulting from $A' \rightarrow X$ state intersystem crossing. This is a curious result since the effect of a bimodal population was clearly observed in the transient absorption studies of Harris et al.\(^{24}\) in chlorinated methane solvents. We interpret *

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* The quantum yields for recombination onto various electronic states have not yet been measured.
these observations to indicate that the fraction of recombined iodine population in the \( A' \) state is very small compared to the \( X \) state in alkane solvents. In this event, \( A' \to X \) state intersystem crossing has little effect on the \( X \) state dynamics. There is further support for this claim.

The lifetimes of the \( A' \) state Raman band at 106 cm\(^{-1} \) have been reported in our previous work\(^{(56)} \). The lifetimes are 95, 112, 252, 521, 1500, and 2843 ps in n-hexane, cyclohexane, \( \text{d}_{12}\)-cyclohexane \( \text{CH}_2\text{Cl}_2 \text{ CHCl}_3 \) and \( \text{CCl}_4 \) respectively. If the \( A' \) dynamics greatly affected the \( X \) state dynamics, the data for \( \text{d}_{12}\)-cyclohexane should exhibit a second growth rate of 250 ps. This is not observed. In fact, the vibrational dynamics on the \( X \) state in Figure 3.7 are virtually identical for cyclohexane and \( \text{d}_{12}\)-cyclohexane even though the \( A' \) state lifetimes differ by a factor of 2.25. Note also that in the 200 ps frame of Figure 3.4 the \( X \) state signal has decayed to the baseline while the \( A' \) state band is still clearly visible. Clearly, there is no evidence in this data for \( X \) state signal resulting from \( A' \) state to \( X \) state intersystem crossing. Apparently, the \( X \) state vibrational dynamics are not affected by the \( A' \) state electronic relaxation.

Further support for this argument exists in the intensities of the \( A' \) and \( X \) vibrational spectrum. In alkane solvents the \( A' \) state vibrational spectrum is weak while in chlorinated methane solvents the spectrum is very strong. In contrast the \( X \) state bands are strong in alkane solvents but are not observed at all in chlorinated solvents\(^{(52)} \). This observation supports the conclusion that the \( A' \) state is formed in small yields in alkane solvents. The transient absorption experiments of Harris
Overlay of \( \chi \) state dynamics in cyclohexane (solid curve) and \( \text{d}_{12}\)-cyclohexane (dashed curve) from Figures 3.3 and 3.4. Pure transient Raman difference spectra. The thick vertical line at 183 cm\(^{-1}\) (\( v = 23 \)) indicates the maximum V-V efficiency predicted for \( \text{d}_{12}\)-cyclohexane as shown in Figure 3.9.
and co-workers\textsuperscript{(24)} suggests that the $A'$ state is formed with a yield $10^3$ times less in alkane solvents compared to chlorinated solvents.

The important conclusion from these considerations is that the $X$ state vibrational dynamics we observe in alkane solvents is not affected by the electronic relaxation of the $A'$ state. As a result, the solvent dependence of the $X$ state VER dynamics in various alkane solvents can be directly interpreted. The solvent dependence of VER has been studied and the results are presented in Figure 3.3, Figure 3.4, Figure 3.8 for the solvents cyclohexane, d$_{12}$-cyclohexane, and n-hexane/neo-hexane respectively.

A final concern in the interpretation of $X$ vibrational dynamics is the possible contribution from overtones of the $A'$ state band. In the 200ps frame of Figure 3.4 where the $X$ signal has decayed to zero, it is clearly seen that there is no evidence for appreciable $A'$ state overtone signal. When I$_2$ is probed at 266nm, it is expected that this same result is also true for the other alkane solvents discussed in this chapter.

3.2.5 Fast Relaxation in the Upper Regions of the Potential

In the time zero spectrum\textsuperscript{*} shown in Figure 3.3 vibrational levels are populated with energy gaps ranging from $\approx 130 \text{ cm}^{-1}$ to $\approx 180 \text{ cm}^{-1}$. These levels correspond to quantum states from $\nu = 52$ to $\nu = 25$, respectively. We attribute this broad population distribution to three contributing factors: (1) The finite time for $B^3\Pi_{0+u}$

\textsuperscript{*} Time zero corresponds to temporal overlap of the pump and probe laser pulses. The Raman spectrum represents the dynamics integrated over the 7ps laser pulse width.
Figure 3.8: Pure transient Raman difference spectra of I$_2$ in n-Hexane (dashed curve) and neo-hexane (solid curve). Optical delays between pump(532nm) and probe(266nm) are indicated in each frame. The intensity of each curve is normalized to the ground state I$_2$ band so that the spectra represent the true dynamical intensity variations. Frequency units are in wavenumbers. Quantum numbers are calculated from the gas phase RKR potential.$^{57}$ Concentration is 3mM.
Figure 3.8

VIBRATIONAL QUANTUM NUMBERS

$60 \ 40 \ 20 \ 10 \ 0$

$\delta t = 200 \text{ps}$

$\delta t = 100 \text{ps}$

$A/A'$

$\delta t = 50 \text{ps}$

$\delta t = 25 \text{ps}$

$\delta t = 10 \text{ps}$

$\delta t = 0 \text{ps}$

RAMAN FREQUENCY
state predissociation and geminate recombination. (2) Fast VER for the upper vibrational levels, and (3) The 8ps experimental pulse resolution of the laser which produces a temporal distribution of $X$ state species.

The existence of a broad range of populated vibrational levels qualitatively agrees with the Nesbitt and Hynes\(^{11-12}\) predictions for the upper regions of the $X$ state. Their trajectory studies indicate that the efficiency of V-T collisional energy transfer does not monotonically depend on vibrational quantum number. Instead the efficiency peaks at very high vibrational levels. The position of the maximum is calculated\(^*\) to be near $I_2$ vibrational levels at $v=80$ for argon and $v=90$ for $\text{CCl}_4$. For each solvent the efficiency falls off rapidly on both sides of the maximum value.

In the region of maximum efficiency the amount of energy exchanged in a single collision is large\(^{11-12}\) (on the order of $1.2k_bT$). As vibrational cooling takes place, levels with larger energy gaps become populated and the amount of energy transferred per collision drops to a small fraction of $k_bT$. As a result, a broad distribution of levels is populated in the region where energy transfer is the most efficient.

The experimental results shown in the early time spectra in Figure 3.2 and Figure 3.3 for 354.7nm and 266nm probe wavelengths do not show evidence for an initially broad distribution which narrows as slower relaxing vibrational levels become populated. The population distribution appears to maintain approximately

\(^*\) The quantum numbers calculated by Nesbitt and Hynes\(^{11-12}\) are for the $I_2\ X$ state vibrational levels assuming a Morse potential. These values differ slightly from the RKR values quoted throughout the rest of this chapter.
the same width throughout the entire range of observed levels. Apparently, the vibrational levels which we observe relax inefficiently, transferring only a small fraction of $k_b T$ per collision. This inefficient transfer results in a narrow population distribution. The broader distribution predicted by Nesbitt and Hynes\textsuperscript{(11-12)} is expected to occur for higher vibrational levels than those observed in the present experiment. The observation of inefficient energy transfer for levels $\leq v=52$ is consistent with this prediction.\textsuperscript{(11-12)}

It is interesting to compare the quantitative predictions for VER in the upper regions of the potential with the experimental results. The Nesbitt and Hynes\textsuperscript{(12)} calculation for the solvent CCl$_4$ predicted that 40% of the vibrational energy was lost during the first 10ps. For the lighter cyclohexane solvent, relaxation is expected to be even more complete, as lighter solvent molecules give rise to more efficient V-T (and V-R) energy transfer.\textsuperscript{(11-12)} The early time spectra in Figure 3.2 and Figure 3.3 show that the maximum of the vibrational population distribution is positioned at energy gaps (Raman shifts) of 155 cm$^{-1}$ in the time zero spectrum. In the gas phase this corresponds to levels near $v=38$. In other words, within the 8ps experimental time resolution the combined processes of $B$ state predissociation, geminate recombination, and vibrational cooling are complete to the extent that the vibrational population is peaked near levels containing 7200 cm$^{-1}$ of total energy. This energy is already 42% of the way down the $X$ state well and is more than

\textsuperscript{1} The $X$ state population distribution appears to become slightly broader in the 10ps spectrum compared to the 0ps frame of Figure 3.3. We attribute this to the growth of the resonance Raman enhancement for vibrational levels near $v=20$. See calculation in Appendix A and Figure 3.6.
25k_bT below dissociation. This result is in excellent agreement with theoretical predictions.*

As time progresses during the first 50ps the vibrational distribution shifts towards the lower quantum levels. The cooling rate appears to stagnate when the vibrational energy gap reaches 190-200 cm\(^{-1}\) (levels near \(v=20\)). This result is consistent with the predictions for V-T collisional energy relaxation but does not preclude additional relaxation mechanisms. The fact remains that vibrational cooling becomes much less efficient near \(v=20\). In cyclohexane the final relaxation from \(v=20\) to \(v=0\) requires several hundred picoseconds, as shown in Figure 3.3.

During the first few picoseconds, VER may be affected by heating of the local solvent cage. In fact, we have observed evidence for transient heating in the solvent cage resulting from the energy released upon photodissociation of iodine.\(^{61}\) A pulse width limited (15ps) decay dynamics was observed.\(^{61}\) Molecular dynamics calculations\(^{62}\) of iodine photodissociation in Xe indicate that the local solvent environment returns to equilibrium within 1-2ps. It is therefore expected that local solvent heating does not affect dynamics after the first 1-2ps.

* The Nesbitt and Hynes\(^{(12)}\) prediction of a distribution peaked at \(v=40\) in CCl\(_4\) at a time 10ps following dissociation may have slightly overestimated the VER rate. The present experiment finds a distribution peaked at \(v=40\) where the solvent is cyclohexane. In this solvent it is expected that the relaxation rate is faster than that in CCl\(_4\) since V-T (and V-R) energy transfer is more efficient in the lighter solvent. If this expectation is correct, then relaxation would be less complete in CCl\(_4\) compared to cyclohexane which indicates that the theoretical rate is somewhat too fast. We have tried without success to find the Raman scattering from hot vibrational levels of I\(_2\)(X) in CCl\(_4\).
3.2.6 VER in Complex Solvents

The possible role of V-V energy decay pathways has been discussed by several groups for the specific case of iodine X state relaxation. The low-frequency normal modes for various solvents are summarized in Table 3.1. It is assumed that the exchange of vibrational energy with the solvent takes place with a propensity for a change in quantum state of \( \Delta \nu = \pm 1 \). For cyclohexane the lowest frequency vibrational mode is 248 cm\(^{-1}\), which is far from resonance with the iodine 210 cm\(^{-1}\) vibration. In cyclohexane the contribution of V-V relaxation is therefore expected to be minimal. As shown below, calculations indicate that this is indeed the case. The deuterated analog, however, has a 203 cm\(^{-1}\) mode which is in resonance with iodine vibrational levels near \( \nu = 10 \). The X state dynamics in \( \text{d}_{12} \)-cyclohexane are shown in Figure 3.4. For the purpose of comparison the data for cyclohexane and \( \text{d}_{12} \)-cyclohexane are plotted together in Figure 3.7.

The data in Figures 3.3 and 3.4 indicate that VER is slightly slower in the deuterated solvent during the first 10 ps when relaxation is occurring in the upper regions of the X state potential. This point is illustrated further in the overlay of the cyclohexane and \( \text{d}_{12} \)-cyclohexane spectra plotted in Figure 3.7. We attribute the slower rate of VER in \( \text{d}_{12} \)-cyclohexane to less efficient V-T energy relaxation due to the larger mass of \( \text{d}_{12} \)-cyclohexane compared to cyclohexane. It has been previously suggested that V-R effects are also important in the vibrational decay of iodine. While V-R effects may be important near the bottom of the well, they are
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Vibrational Frequencies cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>383 248</td>
</tr>
<tr>
<td>d$_{12}$-cyclohexane</td>
<td>298 203</td>
</tr>
<tr>
<td>n-hexane</td>
<td>216 208 139 125 94 61</td>
</tr>
<tr>
<td>neo-hexane</td>
<td>232 201 197 197 193 76</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>282</td>
</tr>
</tbody>
</table>

Low frequency solvent modes which can potentially contribute to V-V energy relaxation.
not expected to be important in the upper regions of the potential. Nevertheless, we do not rule out the possible contribution of the V-R process to VER.

The important result of the d_{12}-cyclohexane data shown in Figure 3.4 is that VER is not significantly faster near the bottom of the potential where the iodine vibrational energy gap (near \( v=10 \)) comes into resonance with the 203 cm\(^{-1} \) solvent vibration. This result clearly demonstrates the low efficiency of V-V energy relaxation channels.

More complicated alkane solvents such as n-hexane and neo-hexane have many more low frequency vibrations (see Table 3.1 which can enhance V-V energy transfer. This possibility was first discussed by Wilson et al.\(^{19} \) and later by Harris et al.\(^{24} \) The transient Raman data for iodine relaxation in these solvents is shown in Figures 3.8 for n-hexane and neo-hexane respectively. In general both of these solvents exhibit much faster relaxation than either cyclohexane or d_{12}-cyclohexane. However, it is not clear that this acceleration in the VER rate can be entirely related to V-V relaxation. A better understanding of the importance of V-V processes can be realized by comparing the results for the entire range of \( X \) state vibrational levels with what is expected theoretically. These considerations are discussed immediately below.

3.3 Discussion

The dynamics of the Raman data presented above provide direct information about the rate of VER at specific I\(_2\) vibrational energy gaps. These data can be
analyzed to determine how specific vibrational resonances in the solvent molecules enhance the rate of VER.

We now consider the question of whether the faster VER rates in the lower region of the potential in n-hexane and neo-hexane are entirely related to the existence of V-V relaxation channels. The efficiency of V-V transfer has been considered by Nesbitt and Hynes\(^ {12} \) for iodine in CCl\(_4 \). It was noted that in order to describe V-V energy relaxation over the entire range of \( X \) state levels, it is necessary to account for large differences between the frequency of the iodine oscillator and the solvent resonance. This is a result of the fact that the \( X \) state vibrational energy gaps range from 0 to 210 cm\(^{-1} \). As vibrational cooling occurs, the local iodine energy gap will “tune” into and then out of resonance with the solvent vibrations. There are several models of V-V energy exchange, however most describe resonant or near-resonant energy transfer.\(^ {66} \) The Rapp\(^ {67-69} \) model was developed to provide estimates of V-V efficiencies between non-resonant levels and is expected to be accurate\(^ {66} \) for resonance defects up to 350 cm\(^{-1} \). This is the approach\(^ {69} \) used by Nesbitt and Hynes.\(^ {12} \)

We have extended this model to the more complicated solvents discussed in this chapter. The approximate form\(^ {69} \) of the Rapp model is used, where the integration over the distribution of collision velocities is replaced by the mean velocity \( v^* = (3k_BT/\mu)^{1/2} \). This gives the following result for the V-V relaxation probability
\[ \langle P \rangle = \frac{2\mu k_b T j (k + 1)}{L^2 \omega_1 \omega_2} \left( \frac{CD}{(B + C)(A + D)AB} \right) \times \text{sech}^2 \left[ 2L\Delta \omega \left( \frac{\mu}{3k_b T} \right)^{1/2} \right] \exp \left( \frac{\hbar \Delta \omega}{2k_b T} \right) \]

In this equation, \( \mu \) is the collision reduced mass. The quantum numbers for the excited iodine vibration and solvent accepting mode are given by \( j \) and \( k \) respectively. Vibrational frequencies in this equation are angular frequencies \( (\omega = 2\pi c \times \text{frequency in cm}^{-1}) \). The subscripts 1 and 2 denote the iodine and solvent frequencies and \( \Delta \omega \) the energy defect. \( L \) is a parameter which measures the steepness of the interaction potential. This parameter is not easily obtained but typically ranges from 0.2\( \AA \) for \( \text{H}_2-\text{H}_2 \) collisions to 0.38\( \AA \) for \( \text{I}_2-\text{I}_2 \) collisions.\(^{67}\) We adopt the value used by Nesbitt and Hynes (.263\( \AA \)) for the \( \text{I}_2-\text{CCl}_4 \) collision.\(^{12}\) It is likely that this value overestimates \( L \) since in a hydrocarbon solvent an I-H interaction might be expected to be more repulsive than I-Cl. In this event, the true V-V efficiency curves will peak at somewhat lower \( \text{I}_2 \) vibrational energy gap but should not affect the relative efficiencies calculated for different hydrocarbon solvents. The Rapp model considers a collision between two diatomic molecules \( \text{A-B and C-D} \) consisting of atoms with mass \( \text{A,B,C, or D} \). We have ignored these terms in the prefactor since we are interested only in the relative dependence of the V-V efficiency on quantum number, energy defect, and reduced mass of the collision.

Figure 3.9 shows the results of this model for \( \text{d}_{12}\)-cyclohexane and cyclohexane. Figures 3.10 and 3.11 show the results for \( \text{n-hexane and neo-hexane} \), respectively. The y-axis of all three figures has been normalized to that of \( \text{n-hexane} \) (Figure 3.10).
There are two important features which should be pointed out. First, the peaks of the V-V efficiency curves reach a maximum for iodine energy gaps which are lower than the frequency of the solvent resonance due to the fact that the efficiency increases with the iodine vibrational quantum number \( j \). (Higher iodine quantum number corresponds to lower iodine energy gaps and therefore more efficient V-V energy transfer at a lower frequency than the solvent resonance.) The second feature to note in these calculations is the increase in efficiency at higher quantum numbers. This is also the result of the \( j \) dependence of the V-V energy transfer efficiency. In Figures 3.10 and 3.11 the V-V contribution from each solvent resonance is plotted as a dashed line and the overall efficiency, which is simply the sum of all V-V channels as a solid line.

In cyclohexane the lowest vibrational mode has a frequency of 248 cm\(^{-1}\). Poor V-V energy transfer efficiency is predicted as shown by the solid curve in Figure 3.9. Experimentally it is found that VER begins to stagnate at vibrational energy gaps near 190 cm\(^{-1}\) (Figure 3.3,3.4). The point on the potential where stagnation occurs is presumably a measure of the decreasing efficiency of V-T (and possibly V-R) energy transfer mechanisms.\(^{11-12}\)

For \( \text{d}_{12} \)-cyclohexane Figure 3.9 shows that the expected V-V efficiency peaks in the vicinity where VER is found to stagnate in cyclohexane. It should be noted that the higher V-V efficiency predicted by equation 1 for \( \text{d}_{12} \)-cyclohexane compared to cyclohexane arises from the fact that higher iodine quantum numbers are involved when the iodine oscillator is in resonance with the 203 cm\(^{-1}\) \( \text{d}_{12} \)-cyclohexane mode.
Efficiency for V-V energy transfer in d$_{12}$-cyclohexane (dashed-dotted curve) and cyclohexane (solid curve) calculated from equation 3.1. See text for details. The d$_{12}$-cyclohexane curve is the sum of the efficiency for the 298 cm$^{-1}$ and 203 cm$^{-1}$ mode. The 298 cm$^{-1}$ mode contributes less than 1% to the intensity of the data. The efficiencies of both curves are normalized to the results in Figures 3.10 and 3.11. (Note the scale change between this figure and Figures 3.10 and 3.11.) Energy gaps are calculated from the gas phase RKR potential.$^{(57)}$
Figure 3.10

Calculated efficiency for V-V energy transfer in n-hexane. The efficiency is normalized to be on the same scale as the results in Figures 3.9 and 3.11. The dashed curves are the individual components from each solvent vibration not including the degeneracy of the vibration. The solid line is the sum of all components including degeneracy. See text for details. Energy gaps are calculated from the gas phase RKR potential.(57)
Calculated efficiency for V-V energy transfer in neo-hexane. The efficiency is relative and is normalized to be on the same scale as the results in Figures 3.9 and 3.10. The dashed curves are the individual components from each solvent vibration not including the degeneracy of the vibration. The solid line is the sum of all components including degeneracy. See text for details. Energy gaps are calculated from the gas phase RKR potential.\textsuperscript{(57)}
As discussed above relaxation in d_{12}-cyclohexane is slower compared to cyclohexane (Figure 3.7). The thick vertical line at 183 cm\(^{-1}\) in Figure 3.7 indicates the maximum calculated V-V efficiency in d_{12}-cyclohexane. The lack of an increase of VER rate in the 183 cm\(^{-1}\) region observed for d_{12}-cyclohexane indicates that the V-V relaxation channel is not as important as predicted by this simple model.\(^{(12)}\)

For n-hexane and neo-hexane the interpretation is not as straightforward. Figure 3.10 shows that in n-hexane there are many V-V resonances\(^{(70)}\) which can enhance relaxation from every vibrational level in the I\(_2\) X state. Figure 3.10 indicates that the expected efficiency peaks in the region where the iodine vibrational energy gap is in the range 50 to 150 cm\(^{-1}\). This might account for the much faster relaxation in n-hexane in the upper regions of the I\(_2\) X state potential. However, it is important to note that in this region of the X state potential relaxation is complete in all solvents within the first 10ps as a result of efficient V-T and V-R relaxation. As a result, in n-hexane the highest populated iodine vibrational levels have “tuned” out of resonance with most of the efficient V-V channels within the first 10ps following recombination.

Neo-hexane has several vibrational modes\(^{(71)}\) which can facilitate V-V transfer for lower levels in the X potential. Figure 3.11 shows the expected efficiency of the V-V processes in this solvent. There are five vibrations which combine to raise the overall efficiency to a maximum near iodine energy gaps of 185 cm\(^{-1}\). It is important to note that: (1) The calculated efficiency peaks in the region where the rate of VER stagnates in cyclohexane. and (2) The expected overall efficiency of
V-V transfer is higher in the V-T stagnation region than that for n-hexane. However, the experimental data shown in Figure 3.8 indicate that the relaxation rate is slower in neo-hexane compared to n-hexane for relaxation from vibrational levels with energy spacings in the vicinity of 185 cm\(^{-1}\). This is an important result. Apparently, despite the existence of five possible V-V relaxation pathways in neo-hexane the rate of relaxation is slower than in n-hexane. Slower relaxation is particularly evident in neo-hexane in the 170-200 cm\(^{-1}\) region, which is precisely where the neo-hexane solvent resonances are expected to accelerate relaxation.

This result suggests that VER through V-V channels is more complicated than accounted for by the Rapp model.\(^{(69)}\) This is not surprising, since the Rapp model is very approximate and was developed for gas phase collisions between simple diatomic molecules. It is apparent from the data presented here that V-V transfer must involve additional considerations. In particular, coupling to the solvent coordinate is likely to be mode specific. For example, in neo-hexane the important solvent resonances are associated with the cooperative motions involving many atoms about the tertiary carbon atom.\(^{(71)}\) These modes might be less strongly coupled to the solute than the torsional motions in the straight chain section of neo-hexane. If torsional modes are more efficient V-V acceptors, the larger number of low-frequency torsional modes in n-hexane\(^{(70)}\) might prove to be more effective in quenching the iodine vibrational energy. The apparent difference in VER rate between neo-hexane and n-hexane could therefore be the result of more efficient coupling to the solvent resonances in n-hexane.
3.3.1 The Role of V-V Energy Relaxation

The overall kinetics for repopulation of the ground \((v=0)\) vibrational level can be studied by measuring the recovery of the ground state \(I_2\) Raman band. In previous experiments using transient absorption spectroscopy, additional signals have been found arising from the \(A'\) state as well as iodine atom contact charge-transfer absorption. Raman spectroscopy, however, is a direct measure of the ground state recovery and does not suffer from artifacts observed when the recovery of a transient absorption signal is measured. Figure 3.12 shows the ground state recovery for iodine in cyclohexane and n-hexane. These data illustrate that the overall time required to re-populate the \(v=0\) level is significantly longer in cyclohexane compared to n-hexane. This result agrees qualitatively with the dynamics near \(v = 20\) discussed above. The fact that the decay in n-hexane is faster than that in cyclohexane over the entire range of energy levels is believed to be due in part to V-V decay to resonances in n-hexane.

It was shown above by comparing the dynamics in n-hexane and neo-hexane that it is not a simple matter to predict the efficiency of V-V decay in complex solvents. This point is made even clearer by comparing the overall cooling rate in n-hexane and \(CH_2Cl_2\) as shown in Figure 3.13. Apparently, despite the existence of many possible V-V decay pathways in n-hexane, the overall decay rate in this solvent is no faster than that in \(CH_2Cl_2\), which has no accessible solvent resonances.

Harris et al.\(^{(24)}\) have studied iodine relaxation in chlorinated-methane solvents in detail. They found that relaxation in \(CH_2Cl_2\) was a factor of three faster than
The recovery dynamics of $I_2 \ X$ state $v=0$ Raman band at 210 cm$^{-1}$ using 532nm as both pump and probe beams. The dashed line is the dynamics of $I_2$ in $n$-Hexane. The solid line shows the dynamics of $I_2$ in cyclohexane.
Figure 3.13

The recovery dynamics of I₂ X state ν=0 Raman band at 210 cm⁻¹ using 532nm as both pump and probe beams. The dotted line shows dynamics of I₂ in n-Hexane. The dashed line shows dynamics of I₂ in dichloromethane solution.
in CCl$_4$. Harris et al.\textsuperscript{(24)} attributed the fast decay in CH$_2$Cl$_2$ to V-T and possibly V-R decay, which was previously un-recognized as an efficient decay channel in the condensed phase. It is also possible that the nature of the collision is entirely responsible for the observed difference in the rate of VER. In this example the collision frequency alone is approximately a factor of 2.0 higher in CH$_2$Cl$_2$ compared to CCl$_4$. An approximate formula\textsuperscript{(72)} for collision frequency in the condensed phase is $Z(R) = 4\pi R^2 (N/V)(k_b T/m)^{1/2}g(R)$ which represents a simple density scaling of the gas phase collision frequency. The radial distribution function $g(R)$ should be similar for CH$_2$Cl$_2$ and CCl$_4$. However, the factor $(N/V)(1/m)^{1/2}$ is a factor of 2.0 higher for CH$_2$Cl$_2$ compared to CCl$_4$.

In long-chain alkane solvents, estimates of the collision frequency are even less accurate than in chlorinated-methane solvents. However, in comparing relaxation rates in different solvents collision frequency is clearly an important consideration. For V-V relaxation pathways the results discussed in this work indicate that the efficiency is very solvent dependent. The point we are making is that the solvent dependence of V-V transfer may reflect the solute-solvent vibrational coupling as well as the detailed nature of the collision potential, which is difficult to characterize in alkane solvents.
4. DYNAMICS OF IODINE A'

4.1 Introduction

Electronic curve crossing processes in solution have long been recognized as an important aspect of condensed phase chemical reaction dynamics.\(^{73-76}\) In this chapter I present a transient Raman investigation of three major aspects of the condensed phase geminate recombination reaction of I\(_2\) onto the excited electronic states illustrated in Figure 1.2. In particular, this chapter concentrates on the solvent dependence of geminate recombination, vibrational energy relaxation (VER), and electronic relaxation. By obtaining detailed information about reaction dynamics on potential energy surfaces of intrinsically different shapes it should be possible to develop a comprehensive understanding of condensed phase reactivity.

The exchange of energy between vibrations in a reacting molecule can greatly influence the reaction rate and product branching ratios. In recent years, there has been great interest\(^{76}\) in testing the fundamental RRKM assumption of complete energy randomization for reactions in solution. In fact, non-RRKM behavior has been predicted\(^{76-77}\) in some cases. In the gas phase, VER has been widely studied. However, in solution it is still not well understood due to experimental difficulties. Condensed phase VER has been considered theoretically\(^{11-12,78-80}\) and a number of predictions now exist for the rate as a function of vibrational energy gap, energy of the oscillator, and the form of the potential between the molecule and the solvent environment. The experiments presented in this work are unique in the respect that VER is studied for I\(_2\) in an excited electronic state and the results directly
compared to the VER in $X$ state studied in Chapter 3 where the potential energy well supports a different frequency oscillator. These experiments are also relevant to recent studies of geminate recombination for $I_2^-$ in CO$_2$ clusters\(^{(81)}\) since the ground electronic state of $I_2^-$ and the excited electronic states in I$_2$ are quite similar.

Geminate recombination of I$_2$ on excited electronic states was first discovered by Flynn in rare gas matrices.\(^{(55)}\) In solution, Kelly\(^{(20)}\) has applied picosecond transient absorption spectroscopy to study the dynamics of iodine photodissociation and found that recombination also occurs on the excited electronic states in room temperature fluids. An interesting result was obtained in subsequent studies by Harris $et$ $al.$\(^{(25)}\) who discovered that the rise time of the transient absorption signal assigned to the recombined excited state iodine was $\geq 10$ps in chlorinated methane solvents. No attempt was made to rationalize this observation. Preliminary studies\(^{(20,24)}\) of the large solvent dependence of the electronic relaxation rate have been made, however, there is no conclusive experimental data which provide a complete understanding of the decay mechanism. This is not surprising in view of the fact that electronic decay mechanisms are not well understood even for gas phase collisions between electronically excited atoms and molecular quenchers.

Photoexcitation into the $B^3 \Pi_{\pi+\pi}$ electronic state at 532nm results in rapid predissociation. Geminate recombination and VER on the excited electronic state is directly observed in the transient Raman spectrum as shifts in the anharmonic frequencies of the "local" excited vibrational levels (vibrational energy gaps). The solvent dependence of VER is compared to that in $X$ state described in Chapter 3.
Slow geminate recombination is observed suggesting a new interpretation for the formation mechanism of the excited state. The last section describes experiments which probe the solvent dependence of electronic relaxation using knowledge about the excited state potential in combination with dynamics and solvent isotope effects. New interpretations for the electronic decay mechanism are suggested from these results.

4.2 Identity of the Transient

The Raman spectrum of iodine in CCl$_4$ is shown in Figure 2.2. Three Raman bands are observed. The band position for first Raman band is at 106 cm$^{-1}$. The other two bands are at 204 and 299 cm$^{-1}$. These two bands have two features of overtone. First, the band intensity and vibrational frequency spacings decrease in progression. Second, the bandwidth increases in progression. Therefore we assign these two bands as overtones of band at 106 cm$^{-1}$.

There are many possible transient species which can be formed from photoexcitation of iodine in solution. The obvious possibilities are I$_2$(X$^1\Sigma_g^+$), I$_2$(A$^3\Pi_{2u}$), I$_2$(A$^3\Pi_{1u}$), I$_2$(B$^3\Pi_{0+u}$), I$_2^-$, I$_2^+$, (I$_2$)$_n$, and I-Solvent. The transient shown in Figure 2.2 is assigned to the A$^3\Pi_{2u}$ state based on dynamic and spectroscopic arguments. The I$_2$(B$^3\Pi_{0+u}$) and I$_2$(X$^1\Sigma_g^+$) have gas phase$^{(32)}$ vibrational frequencies of 124 and 213 cm$^{-1}$ respectively (These values are for the energy gap $\omega_e - 2\omega_e x_e$). The data shown here were obtained at an optical delay of 500ps which is long compared to the known lifetimes$^{(82)}$ of the I$_2$(B$^3\Pi_{0+u}$) and vibrationally hot$^{(22-25,52,83)}$
$I_2(X^1\Sigma^+_g)$ in solution. It is therefore unlikely that these electronic states are responsible for the transient observed in Figure 2.2. The lifetime of the transient vibrational spectrum shown in Figure 2.2 is similar to the species which was tentatively assigned\(^{(20,24)}\) to the $I_2(A^3\Pi_{1u})$ and $I_2(A'\,^3\Pi_{2u})$ states detected in earlier picosecond absorption studies. The v=0-1 vibrational spacings for these states are known in the gas phase to be 90.1 and 104.3 cm\(^{-1}\) respectively.\(^{(53,84)}\) Since only small frequency shifts are expected for the condensed phase analog the most likely assignment of the transient shown in Figure 2.2 is the $A'$ state. This result is consistent with the expectation of facile electronic curve crossing processes in solution. If the $A^3\Pi_{1u}$ state was initially formed, internal conversion should result in the fast production of the $A'$ state—as is observed.

It might seem curious at first that there is no dip in signal near 214 cm\(^{-1}\) in Figures 2.2 and 4.1 due to the depletion of the $I_2$ ground state band. The absence of population bleaching in the spectrum is simply due to the magnitude of the transient Raman spectrum compared to the fraction of population removed by the pump laser. Under the laser conditions used in these experiments about 1% of the $I_2$ is photodissociated. The magnitude of the bleach should therefore be on this order. However, the Raman signal from the transient exhibits a very strong resonance enhancement whereas the ground $X$ state $I_2$ band does not. In fact, Figure 2.2C shows that the transient signal at 106 cm\(^{-1}\) is about five times the magnitude of the entire $I_2$ ground state band. (The iodine ground state band makes up about 2-3% of the intensity of the CCl\(_4\) solvent band at 217 cm\(^{-1}\).) These considerations
indicate that the transient bleach of the $I_2$ ground state band should be about 500 times weaker compared to the transient signal at 106 cm$^{-1}$. This small magnitude of signal is not observed. The pure transient Raman spectra become somewhat noisier in the region where solvent bands have been subtracted out. However, the sensitivity of the measurement does not change in this region of the spectrum.

There are several additional species which might account for the transient shown in Figures 2.2 and 4.1. The possibility of transient signals from $I_2^-$, $I_3^-$, and $(I_2)_n$ can be ruled out for the following reasons. The intensity of the transient is observed to be roughly linear in concentration from 0.5mM to 11mM, whereas the number of oligomers is expected to increase at higher concentrations. The stable anionic species $I_3^-$ can be formed by the addition of KI to the iodine solution. At a concentration of $10^{-4}$mM of KI in isopropanol the near UV absorption spectrum of $I_3^-$ at 360nm was found to be very intense indicating an $I_3^-$ concentration of $3 \times 10^{-5}$mM.\(^{(85-86)}\) However, no effect was observed on the intensity of the transient shown in Figure 2.2. It is therefore unlikely that the species we have assigned to the $A'$ state results from $I_3^-$. In addition, since $I_2^-$ is known to be produced photochemically\(^{(85-86)}\) from $I_3^-$ it can also be eliminated as a possibility for the transient observed in Figure 2.2.

4.3 Vibrational Energy Relaxation

Population relaxation from higher vibrational states is observed as a change in the Raman band which shifts at later times to higher frequencies due to the anharmonicity of the potential. In principle, rates of vibrational relaxation can be
extracted from the time dependence of the Raman spectrum. For an excited vibrational level at any given energy in the potential, the Raman frequencies correspond directly to the quanta of energy that must be lost to depopulate the level. However, this analysis is somewhat complicated by the fact that the spectrum from a single vibrational level is overlapped with the spectra from nearby levels. For a fundamental vibrational frequency of 106 cm$^{-1}$, with the $A'$ state anharmonicity, the thermal population will be 43%, 26%, 16%, 10%, ... for the $v=0,1,2,3,...$ levels. The anharmonicity of the lower levels determined in this work is such that the Raman scattering from adjacent levels is only shifted by an average of 6 cm$^{-1}$. The relative populations and small anharmonicity combine to give a resulting Raman spectrum which is characteristic of an ensemble of levels.

Figures 4.1 and 4.2 show the Stokes and anti-Stokes spectra at various time delays following photodissociation of I$_2$. The Raman bands in the Stokes spectrum appear to shift in frequency during the first 25ps. This is a result of the relaxation of the vibrational population distribution into the lowest vibrational levels of the $A'$ electronic state. The anti-Stokes spectrum does not appear to exhibit the same large frequency shift during the first 25ps. This is exactly what is expected for the vibrational spacings determined from the overtone spectrum shown in Figure 4.3. The vibrational spacings (energy gaps) for the first three vibrational gaps are 106, 94, and 92 cm$^{-1}$ for $v=0$-1, 1-2, and 2-3 levels respectively. Anti-Stokes scattering can only originate from vibrational states where $v \geq 1$. Stokes scattering can
originate from any vibrational level. Apparently, the vibrational population distribution detected* at time zero is centered at \( v=1 \). As a result, when the maximum of the vibrational population distribution cools into \( v=0 \) during the first 25ps, the fundamental of the Stokes Raman spectrum appears to change in frequency from 96 to 105 cm\(^{-1}\). This is very close to the observed vibrational energy gaps.\(^{\text{I}}\) The anti-Stokes spectrum does not exhibit the same magnitude of frequency change simply because the anti-Stokes Raman scattering takes place predominantly from \( v=1 \) at all times. The observed anti-Stokes frequency of 102 cm\(^{-1}\) closely matches the experimental \( v=0-1 \) energy gap determined from the overtone spectrum. This result increases the confidence of the interpretation that the observed dynamics can be attributed to vibrational energy relaxation. It should be pointed out that there are additional effects which might result in the frequency changes observed in Figure 4.1. These include \( A \rightarrow A' \) electronic state relaxation, solvent complex formation, or solvent reorganization. However, if these processes are important similar frequency changes would be expected in the dynamics of the anti-Stokes spectrum. The fact that only the Stokes spectrum appears to change in frequency, is a strong indication that the interpretation of vibrational energy relaxation is correct.

It might seem curious that only vibrational levels near the bottom of the potential are observed in the transient Raman spectrum. We believe that this is the

* The band detected in a resonance Raman experiment has an intensity which is a combined effect of population and resonance enhancement.
\(^{\text{I}}\) The frequency position of the band does not have to be exactly the same as the energy gap obtained from the Stokes spectrum because the resonance Raman enhancement can be different for the Stokes and anti-Stokes spectrum. As a result a different intensity distribution can be observed for each resulting in slightly different frequency positions.
Pure transient difference Stokes Raman spectra in n-hexane. Optical delay between pump (532nm) and probe (354.7nm) lasers is given in each frame. The dashed line indicates the final frequency position of the band assigned to the $A'$ state fundamental vibration at later times (100ps). Spectra are normalized to the *one color* $I_2$ ground state band (not shown) and reflect the true dynamical intensity variations. Frequency units are in cm$^{-1}$.
Figure 4.2

Pure transient difference anti-Stokes Raman spectra in n-hexane. Optical delay between pump(532nm) and probe(354.7nm) lasers is given in each frame. The dashed line indicates the final frequency position of the band assigned to the $A'$ state fundamental vibration at later times (100ps). Spectra are normalized to the one color $I_2$ ground state band (not shown) and reflect the true dynamical intensity variations. Frequency units are in cm$^{-1}$. 
Pure transient difference spectrum in n-hexane. Bands assigned to the $A'$ state fundamental and overtone vibrations are indicated with solid lines. Quantum numbers are given to indicate the initial and final levels involved in the Raman transition. (Note that the quantum numbers refer only to transitions originating from $v=0$ and do not include hot band transitions which contribute a minority component to the Raman band intensity.) Optical delay between pump(532nm) and probe(354.7nm) lasers is 200ps. Frequency units are in cm$^{-1}$. 
result of the strong vibrational level dependence of the resonance Raman enhancement. In other words, the 354.7nm probe wavelength provides a “window” which allows vibrational levels near the bottom of the potential to be observed. It may also be difficult to observe higher vibrational levels simply because they have such a short lifetime. As the I₂ molecule relaxes on the A' state the wavelength dependent enhancement makes it difficult to characterize the time dependent vibrational population distribution. However, it should be possible to determine the dynamics of the peak of the population distribution as it passes through the “observation window” consisting of the lower lying vibrational levels.

The approximate rate of VER can be obtained by dynamically measuring the ratio of the intensity of the anti-Stokes to Stokes Raman signal. Figures 4.4A and 4.4B illustrate the dynamics of the Raman spectrum obtained from the Stokes and anti-Stokes scattering at the frequency of the fundamental vibration in the A' electronic state. The anti-Stokes spectrum in Figure 4.4A rises faster than the Stokes spectrum in Figure 4.4B. Figure 4.4C is the anti-Stokes/Stokes ratio which is the computed point-by-point ratio of Figure 4.4 frame A/B. These spectra probe the vibrational population in the excited levels near the bottom of the potential well where the energy gap is ≈100cm⁻¹. The ratio in frame C qualitatively illustrates the dynamics of the vibrational population which rises to a maximum in 15ps and decays to an equilibrium value in 25ps. The dynamics of the anti-Stokes/Stokes ratio in other solvents has been obtained and the results are shown in Figure 4.5. These data illustrate the general trend in population relaxation. In CCl₄ and CHCl₃
there is clear evidence of a rise and fall in the anti-Stokes/Stokes ratio as shown in Figure 4.5C and B respectively. For CH$_2$Cl$_2$ in Figure 4.5A there is a prompt rise to a steady state value. The existence of a slow rise and fall in CCl$_4$ compared to a fast rise in CH$_2$Cl$_2$ can only be interpreted as faster VER in CH$_2$Cl$_2$. The data in Figure 4.5 therefore indicate that the trend in VER rate decreases in the order $k_{\text{VER}}$(CH$_2$Cl$_2$) > $k_{\text{VER}}$(CHCl$_3$) > $k_{\text{VER}}$(CCl$_4$).

In order to extract approximate rates of VER from these data the following analysis was performed. It is assumed that the 354.7nm probe wavelength provides an observation window which allows levels near the bottom of the potential to be observed. A three level system is assumed consisting of the following. (1) an upper level $U$ which is not observed in the Raman spectrum. Note that $U$ contains excited vibrational levels from approximately $v=5$ and upwards, iodine which has not yet geminately recombined, and recombined I$_2$ trapped in higher excited electronic states. (2) A middle level $H$ which represents an ensemble of hot excited vibrations near $v=1$ to 3. (3) The cold thermally equilibrated ground state vibrations $C$ which primarily represent $v=0$. These three levels are assumed to obey the following kinetics.

$$U \xrightarrow{k} H$$

$$H \xrightarrow{k_{\text{VER}}} C$$

The rate constants $k$ and $k_{\text{VER}}$ represent the rates of formation and VER respectively. (Note that $k$ also contains VER in the upper regions of the $A'$ state potential. $k_{\text{VER}}$ is for the lower levels observed in the Raman spectrum.) As thermal equilibrium is approached the population in $H$ reaches a steady state value. The
Dynamics of transient Raman spectrum of the \( A' \) state band at 106 cm\(^{-1}\). Anti-Stokes spectrum is shown in frame A), Stokes spectrum in frame B), and the point-by-point ratio frame A/B is shown in frame C). Concentration is 11mM in n-hexane. Laser pulse width is 7ps. Pump wavelength 532nm, probe wavelength is 354.7nm.
Dynamics of the anti-Stokes/Stokes ratio for the $A'$ state fundamental band at 106 cm$^{-1}$ in: A) CH$_2$Cl$_2$ B) CHCl$_3$ C) CCl$_4$. Concentration is 11mM. Laser pulse width is 7ps. Pump wavelength 532nm, probe wavelength is 354.7nm.
anti-Stokes signal at this later time therefore represents Raman scattering from thermalized vibrational levels which have the dynamics represented by $C$. These rate constants can be extracted from the dynamics of the Stokes and anti-Stokes data if it is assumed that the spectra represent the kinetics described by the following equations:

$$\text{anti-Stokes}(t) = H(t) + \text{factor} \times C(t)$$

$$\text{Stokes}(t) = C(t)$$

The $\text{factor}$ is obtained from the data at long times where $H(t) = 0$. The data in various solvents have been interpreted in this way and the results are shown in Figure 4.6 and Figure 4.7. These data represent the rate of formation and decay of the hot excited vibrational states $H$. The curve shown as the solid line is a fit to the kinetics representing the solution to the coupled differential equations for $H$ which is given by the equation $H(t) = \exp(-kt) - \exp(-k_{\text{ver}}t)$. Figure 4.6 clearly shows that the rate of VER in alkylhalide solvents is fastest in $\text{CH}_2\text{Cl}_2$ and slowest in $\text{CHBr}_3$. This is the same qualitative trend determined from the data representing the anti-Stokes/Stokes ratios shown in Figure 4.5. For the alkane solvents shown in Figure 4.7 the rate of VER is faster for n-hexane compared to cyclohexane. Approximate rate constants extracted from these data are summarized in Table 4.1.

4.4 Geminate Recombination

The appearance time of the $A'$ Stokes spectrum is delayed in all solvents as summarized in Table 4.1. Figure 4.8 shows the risetimes of the $A'$ Stokes signal in several solvents with the dye autocorrelation as reference. The question is—can
Dynamics of transient Raman spectrum $A'$ state fundamental band at 106 cm$^{-1}$. The data have been manipulated according to the model described in the text and represent the dynamics of the hot vibrational states. $H(t) = \text{anti-Stokes}(t) - \text{factor} \times \text{Stokes}(t)$. The smooth curve through the data points represents a fit to the model $H(t) = \exp(-kt) - \exp(-k_{\text{vib}}t)$. The frames are arranged in the order A) CH$_2$Cl$_2$, B) CHCl$_3$, C) CCl$_4$, D) CHBr$_3$. 
Dynamics of transient Raman spectrum $A'$ state fundamental band at 106 cm$^{-1}$. The data have been manipulated according to the model described in the text and represent the dynamics of the hot vibrational states. $H(t) = \text{anti-Stokes}(t) - \text{factor} \times \text{Stokes}(t)$. The smooth curve through the data points represents a fit to the model $H(t) = \exp(-kt) - \exp(-k_{\text{VER}}t)$. The frames are arranged in the order A) n-hexane, B) cyclohexane.
Rates of formation and decay of the hot vibrational states detected in the anti-Stokes and Stokes spectra. These values come from the data in Figs. 4.6 and 4.7 which has been fit to the equation \( I = I_0[\exp(-t \cdot k_r) - \exp(-t \cdot k_{VER})] \). The results of the fits are also shown in Figs. 4.6 and 4.7. Numbers are in picoseconds.

### Table 4.1

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Risetime (ps)</th>
<th>VER Decay Time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>9.</td>
<td>7.</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>16.</td>
<td>9.</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>22.</td>
<td>5.</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>17.</td>
<td>9.</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>11.</td>
<td>9.</td>
</tr>
<tr>
<td>CHBr(_3)</td>
<td>25.</td>
<td>14.</td>
</tr>
</tbody>
</table>
VER alone account for the appearance time of the cold vibrational levels? Appar­
tenly, the rate of formation decreases in the order: n-hexane > CCl₄ > cyclohexane
> CHCl₃ > CH₂Cl₂ > CHBr₃. This trend cannot be explained on the basis of VER alone. In other words, the rate of VER is fastest in CH₂Cl₂ and yet the appearance time is one of the slowest observed. The risetime of the Stokes Raman signal in CH₂Cl₂ is taken as evidence of slow geminate recombination, where this term is loosely meant to imply all processes, excluding VER, which lead to formation of the A' state.

Before discussing alternative mechanisms leading to slow geminate recombination on the A' state, we must consider if it is possible in CH₂Cl₂ that there is a bottleneck to VER at some energy in the A' potential. Since it is believed that the Raman experiment only probes the lowest levels in the potential, the existence of a bottleneck to VER would give the appearance of a slow rate of geminate recombination. This bottleneck behavior has been predicted¹¹⁻¹² for the X state. Following geminate recombination on the X state the vibrational energy gap varies over the entire range of frequencies from 0 to 212 cm⁻¹ as population relaxation occurs from the energy of dissociation to the zero point in the potential. The bottleneck was predicted to arise from the wide variation in energy gap which causes VER by the V-T mechanism to become less efficient for energy gaps greater than 100 cm⁻¹. At lower energies, when the vibrational energy gap becomes nearly resonant with the intramolecular vibrations of the solvent it is possible for the rate of VER to increase by V-V energy transfer. This bottleneck behavior has never been
Dynamics of the Stokes Raman signal for the $A'$ fundamental vibration in various solvents. The dye response function is plotted as the thick solid line. Dynamics in the solvents n-hexane, CCl$_4$, and CH$_2$Cl$_2$ are denoted by the symbols X, O, and ▼ respectively.
observed\(^{(24)}\) for the \(X\) state. Furthermore, for the \(A'\) state bottlenecks would not be expected since there are no V-V channels accessible in the solvent (with the exception of n-hexane). There are two obvious ways in which VER might be enhanced in the \(A'\) state. These include energy transfer to solvent phonon modes and V-R energy transfer. There has been some recent theoretical development\(^{(64)}\) in understanding the importance of these mechanisms. However, it is not clear how these considerations could lead to bottlenecks to VER. Given these expectations for the \(A'\) state, the rate of VER should decrease monotonically as the vibrational energy gap increases. The slow risetime of the Stokes Raman signal in CH\(_2\)Cl\(_2\) therefore suggests that either our understanding of VER is not adequate or that the risetime is dominated by the geminate recombination time on the \(A'\) state which is greater than 10ps in this solvent.

There has been some disagreement regarding the geminate recombination time of iodine on the \(X\) state. Kelly et al. have argued\(^{(87)}\) that a substantial fraction of the \(X\) state recombination occurs on a slow 50-100ps timescale. Recent experiments by Harris and co-workers\(^{(22,25)}\) strongly support the conclusion that recombination occurs in \(\leq 2\)ps. This interpretation is based on the similarity of transient absorption spectra following initial excitation into either the predissociative \(B^3\Pi_{0+u}\) state or repulsive \(1\Pi_u\) state. However, it might be argued that the only true measure of the recombination time is the risetime of the 1000nm absorption data which probes about halfway down the \(X\) state potential.\(^{(24)}\) (This is the highest point observed by Harris et al. in the \(X\) state potential.\(^{(24)}\)) The absorption risetimes vary
from between 4ps and 16ps but always scale directly with the rate of VER—that is, the fast risetimes occur in the solvents with the fast VER rates. Harris argues\(^{(22,25)}\) that the risetimes are therefore largely determined by the rate of VER and are not dominated by the geminate recombination time. In this work we found that the risetimes of geminate recombination on the \(A'\) state scale in the opposite direction of the VER rates. Evidently, VER alone cannot account for the appearance time of the \(A'\) state. This experimental observation is fundamentally different from that previously reported\(^{(22,24-25,87)}\) for the \(X\) state where VER is thought to completely dominate the risetime. The \(A'\) state result is the first information about the solvent dependence of geminate recombination in iodine.

We can only speculate as to the nature of the formation mechanisms which would cause the appearance of slow geminate recombination for the \(A'\) state. They include: (1) initial recombination onto the higher energy weakly bound \(A^3\Pi_0^-u\) and \(A^3\Pi_1u\) states followed by slow electronic relaxation into the \(A'\) state, (2) slow \(B^3\Pi_0^+u\) predissociation, and (3) complex formation (I + I\(\bullet\)Solvent \(\rightarrow\) I\(_2\)(\(A'\))\(\bullet\)Solvent). The first two mechanisms involve electronic curve crossing processes which are thought to be dependent on the nature of the collision between I\(_2\) and solvent.\(^{(88-89)}\) Recent simulations\(^{(89)}\) have shown that the rate of electronic relaxation is viscosity dependent with faster rates in the lower viscous media. In this case, it might be expected that electronic relaxation would be fastest in CH\(_2\)Cl\(_2\) (\(\eta = .412\text{cP}\))\(^{(90)}\) and slowest in CCl\(_4\) (\(\eta = .969\text{cP}\))\(^{(90)}\) due to the lower viscosity of
CH₂Cl₂. However, the opposite trend is observed suggesting that iodine atom solvent complexes might also be important in the formation of the A' state. It should be noted that electronic relaxation processes are not yet well understood in solution so it is difficult to make a definitive statement at this time. However, it is interesting to note that the observed geminate recombination time directly correlates with the strength of the I•Solvent interaction. If the rate of geminate recombination is limited by the time required to break the bond between the iodine atom and the solvent then the rates should scale as n-hexane > CCl₄ > CHCl₃ > CH₂Cl₂. The chlorinated solvents rank in this order due to the strong electron withdrawing capabilities of the other chlorine atoms in the molecule. The electron withdrawing power of three chlorines in CCl₄ has the effect of reducing the strength of the interaction between the remaining chlorine complexed to the iodine atom. This trend in reactivity correlates exactly with the experimentally observed geminate recombination times.

Experimental evidence⁹¹ for Br atom solvent complexes has been recently obtained using transient absorption spectroscopy following formation of Br atoms by pulse radiolysis. Complexes with dibromomethane, bromoform, and carbon tetra-bromide were observed.⁹¹ The stabilities of the complexes decreased as the number of bromine atoms in the solvent molecule increased. It was suggested⁹¹ that complexes of halogen atoms with alkylhalide solvents form three electron bonds as opposed to the charge transfer interactions typically observed for halogen atoms.
with aromatic molecules. This result would appear to support the suggested bonding strengths of \( \text{I} \cdot \text{Solvent} \) complexes and further substantiates the possibility that these complexes are important in geminate recombination on the \( A' \) state.

### 4.5 Electronic Decay

The solvent dependence of the \( A' \) state lifetime was initially investigated by Kelly \textit{et al.}\textsuperscript{(20)} using transient absorption spectroscopy. They determined\textsuperscript{(20)} that the lifetime was strongly solvent dependent ranging from 100ps in hydrocarbon solvents to 2700ps in chlorinated hydrocarbon solvents. In order to explain this observation, Kelly postulated that the decay mechanism of the \( A' \) state is thermally activated dissociation and subsequent geminate recombination on the \( X \) state. Furthermore, in order to explain the large solvent dependence of the decay rate it was proposed that the well depth was significantly perturbed by the solvent. In the experiments described below, we have investigated these dynamics in more detail using transient vibrational spectroscopy. With this method, it is possible to obtain direct spectroscopic information about the \( A' \) potential. Using this knowledge in tandem with additional measurements of the dependence of the \( A' \) state lifetime on temperature and solvent, we propose a more detailed mechanism of electronic relaxation.

The barrier height to dissociation can be investigated by evaluating the solvent dependence of the vibrational frequency \( (\omega_e) \) and anharmonicity \( (\omega_e^2 x_e) \). Assuming that the \( A' \) state can be approximated as a Morse potential, the dissociation energy is given by \( D_e = \omega_e^2 / 4 \omega_e x_e \). For electronic states dissociating into ground
state atoms this equation will generally give a $D_e$ which is an upper limit to the actual value. The reason for this is that the Morse potential is not very accurate near dissociation and generally overestimates the dissociation limit.\textsuperscript{(32)} Of course, as the number of known vibrational levels becomes an appreciable amount of the total number in the potential, the accuracy with which the dissociation limit can be obtained increases. For example, the gas phase $A'$ state dissociation limit can be obtained within 14% by considering only the first overtone and 9% by considering the first two overtones. The dissociation energies quoted here have been obtained by using a Birge-Sponer extrapolation\textsuperscript{(32)} from the second and third overtones. In the arguments made below it is important to establish the lower limit of the dissociation energy. Since the spectroscopic values can be high\textsuperscript{(32)} by as much as 25% we have taken 75% of the experimental values as the lower limit in the dissociation energy.

For the solvents discussed in this work the largest range in $A'$ state lifetimes is between n-hexane and CCl$_4$ where the lifetime changes from 95ps to 2843ps respectively. If the solvent dependence on the lifetime is largely due to changes in the well depth of the potential, the effect on the spectroscopic constants will be most clearly observed for these two solvents. The Raman spectrum for n-hexane and CCl$_4$ is shown in Figure 4.3 and Figure 4.9 respectively. The positions of the overtones are indicated in the figures. The dissociation energies obtained from these data are 2143 and 1482 cm$^{-1}$ for n-hexane and CCl$_4$ respectively. Apparently, the solvent perturbation on the $A'$ state potential is relatively small. It is important to note that
the experimental $A'$ state dissociation energy is *larger* in n-hexane than CCl$_4$ and yet the lifetime is *shorter* for n-hexane compared to CCl$_4$. The conclusion from this result is that the decay mechanism responsible for $A'$ state electronic relaxation is *not* dominated by thermal dissociation.

There is additional experimental information which supports this conclusion. If thermally activated dissociation was the primary decay mechanism then the temperature dependence of the lifetime should be approximately determined by an Arrhenius-like equation. The temperature dependence of the $A'$ electronic state lifetime is shown in Figures 4.10 and 4.11 in n-hexane and CCl$_4$ respectively. The temperature dependence of the lifetime does not fit the behavior predicted by the Arrhenius equation. Using the higher temperature data, the expected lifetime at the lower temperature is plotted assuming Arrhenius behavior. This model was calculated using the well depths estimated from the Raman spectroscopic data. Figure 4.11 illustrates that while the CCl$_4$ data almost follows Arrhenius behavior, the n-hexane data in Figure 4.10 clearly does not. It is important to point out again that the barrier heights used in this calculation (75% of the spectroscopic values) are lower limits to the true dissociation energy. If the well depth were actually deeper, then the calculated temperature dependence of the lifetime would deviate *even more* from the experimental data.

Sceats *et al.*\(^{(89)}\) have considered the temperature dependence of the $A'$ state lifetime theoretically assuming thermal dissociation decay pathway. They have found that the viscosity of the solution is also important in determining the lifetime
Pure transient difference spectrum of I$_2$ in CCl$_4$. Bands assigned to the $A'$ state fundamental and overtone vibrations are indicated with solid lines. Quantum numbers are given to indicate the initial and final levels involved in the Raman transition. (Note that the quantum numbers refer only to transitions originating from $v=0$ and do not include hot band transitions which contribute a minority component to the Raman band intensity.) Optical delay between pump(532nm) and probe(354.7nm) lasers is 500ps. Frequency units are in cm$^{-1}$. 
Temperature dependence of the dynamics of the Stokes Raman band for the $A'$ state at 106 cm$^{-1}$ in n-hexane. Data points are plotted for the temperature 40°C. The dashed line running through the data is the fit. The fit to the 4°C data is plotted as a solid line. However, the data at 4°C is not plotted. The dotted line is the expected Arrhenius behavior at 4°C assuming the well depth determined spectroscopically. The dashed-dotted line is the Arrhenius behavior expected when corrected for the temperature dependence of the viscosity.
Temperature dependence of the dynamics of the Stokes Raman band for the $A'$ state at 106 cm$^{-1}$ in CCl$_4$. Data points are plotted for the temperature 40°C. The dashed line running through the data is the fit. The fit to the 4°C data is plotted as a solid line. However, the data at 4°C is not plotted. The dotted line is the expected Arrhenius behavior at 4°C assuming the well depth determined spectroscopically. The dashed-dotted line is the Arrhenius behavior expected when corrected for the temperature dependence of the viscosity.
due to its effect on the nature of the collision and mass transport to the dissociation limit. Taking these considerations into effect they have determined that a thermally activated dissociation process would be described by an Arrhenius equation modified by the viscosity ($\eta$).

$$k = \left(\frac{A}{\eta}\right) \exp\left(-\frac{E_a}{RT}\right)$$

This result is also plotted in Figures 4.10 and 4.11 using temperature dependent viscosities for n-hexane and CCl$_4$. The agreement with the experimental data is even worse when viscosity effects are considered. In fact, to account for the weak temperature dependence observed for n-hexane, the barrier height to dissociation would have to be $\approx 377$ cm$^{-1}$ which is extremely low compared to the spectroscopic estimate. It is hard to imagine that tunneling to the $X$ state from $v=3$ in the $A'$ state occurs at an appreciable rate. Therefore, the temperature dependence of the lifetime strongly supports the conclusion that the $A'$ state decay in n-hexane is not dominated by thermally activated dissociation.

The temperature dependence of the $A'$ state lifetime is not meant to be a critical test of the Dawes and Sceats model.$^{(89)}$ We have used this model only to consider the possible side effects of viscosity on the temperature dependence of the $A'$ state lifetime. Admittedly, this is a crude calculation. In fact, it has been shown that high frequency frictional effects are often much less than those expected from zero frequency viscosity.$^{(92)}$ It is therefore likely that the Dawes and Sceats model$^{(89)}$ provides an estimate of the maximum viscosity effect possible on the $A'$ state lifetime. The point we are making is that the effects of viscosity do not contradict the
conclusion made from the temperature dependent lifetimes—namely, that the decay channel in n-hexane is not thermally activated dissociation over a 2143 cm\(^{-1}\) barrier.

Additional experiments have been performed to investigate alternative mechanisms for the \(A'\) state decay. Two alternatives have been considered. The first is \(A' 3\Pi\sub{2u} \rightarrow X'\Sigma^+\) intersystem crossing. The second alternative is electronic relaxation through I\(_2\)•Solvent complexes—a solvent quenching mechanism.

In principle, the solvent can influence the rate of intersystem crossing to the \(X\) state by increasing the spin-orbit coupling (the external heavy atom effect) or by shifting the relative positions of the electronic states in a way that changes the Franck-Condon factor connecting the initial and final states. Potential shifts can occur for both the \(A'\) state and the upper regions of the \(X\) state as discussed by Bruskin and Berne.\(^{(93)}\) We have investigated the former possibility by calculating the Franck-Condon factors between \(A'\) and \(X\) state vibrational levels. It is assumed that the energy defect between levels can be ignored as far as the rate constant is concerned. In other words it is assumed that the rate can be predicted by a typical Fermi golden rule expression and is directly related to the Franck-Condon factor. This is a reasonable approximation for iodine since the density of vibrational levels is small compared to the magnitude of the coupling between the \(A'\) and \(X\) states. For each vibrational level near the bottom of the \(A'\) state well, the Franck-Condon factor is calculated by averaging over all \(X\) vibrational levels within the energy range
The gas phase RKR potential is used for the \( X \) state and a modified Lennard-Jones potential is used for the \( A' \) state. The Lennard-Jones potential was fit to the gas phase RKR \( A' \) state potential. In this way the solvent dependence of the \( A' \) potential and dissociation energy (which was determined from the Raman spectrum) could be simulated by adjusting the attractive term of the Lennard-Jones potential.

The details of the calculation are given in the Appendix B. Figure 4.12 shows the relative positions of the electronic states used in the calculations. It is found that the calculated Franck-Condon factors are exceeding small \( \approx 10^{-10} \) for all positions of the \( A' \) potential as it is shifted from the gas phase position through the limiting values determined spectroscopically in n-hexane and CCI\(_4\). This result is easy to visualize intuitively. The wavefunctions for the \( A' \) state are peaked near the center of the potential, while those of the \( X \) state have most of the amplitude at the classical turning points. This result suggests that it is difficult to rationalize the factor of 30 change in \( A' \) lifetime from solvent shifts in the position of the \( A' \) potential. Again, it is important to note that the potentials used in this calculation are only approximate. However, these experimentally determined potentials are believed to be the “worst cases” possible.

The considerations discussed thus far do not account for the solvent dependence of the \( A' \) state lifetime. We now consider the possibility of solvent quenching. Figure 4.13 shows a Stern-Volmer plot of the inverse lifetime as a function of cyclohexane in CCI\(_4\). These data support a solvent quenching mechanism for \( A' \) state deactivation. The straight line portion of the curve represents a fit to the
Potentials used in the Franck-Condon calculation of the vibrational overlaps between the $A'$ and $X$ state. The $A'$ potentials which are plotted with dashed lines indicate the worst case limit obtained from the spectroscopic analysis in the text. Potentials plotted as solid lines are the RKR potentials for the $A'$ and $X$ electronic states. Energy is in units of cm$^{-1}$; Internuclear separation is in units of Å.
equation \( k_{\text{obs}} = k_0 + k_q [\text{cyclohexane}] \) with a slope equal to the quenching rate constant \( k_q = 1.4 \times 10^9 \text{M}^{-1} \text{s}^{-1} \) and \( k_0 \) the rate constant in neat \( \text{CCl}_4 \). This result is interpreted as diffusion limited kinetics which reduces to a saturated non-diffusion limited process at higher cyclohexane concentrations.* These data indicate that the quenching of the \( A' \) state lifetime can occur by diffusion of a single cyclohexane molecule which forms a solvent exciplex. This interpretation is in contrast to the previous understanding that the lifetime was determined by the average local solvent environment.

The solvent complex mechanism is further exemplified by the lifetimes of the deuterated solvents listed in Table 4.2. For cyclohexane there is a factor of 2.25 increase in lifetime on deuteration. In \( \text{CHCl}_3 \) there is a factor of 1.6 increase in lifetime for the deuterated analog. This result strongly supports the solvent complex decay mechanism and suggests that the detailed nature of the solvent normal coordinate is important in determining the relaxation rate. According to radiationless transition theory\(^{(95)}\) the accepting modes in the product state will be high frequency vibrations since these modes minimize the change in quantum number necessary in making the transition to the product state. The overall trend in the \( A' \) state lifetime \( \text{CCl}_4 > \text{CDCl}_3 > \text{CHCl}_3 \approx \text{CHBr}_3 > \text{CH}_2\text{Cl}_2 > \text{D}_{12}\text{-cyclohexane} > \text{cyclohexane} > n\text{-hexane} \), can now be viewed in a simple manner. As the normal

\* The rate constant for diffusion of an iodine molecule and cyclohexane molecule cannot be precisely calculated without knowledge of the hydrodynamic radius. It is reasonable to assume that the experimental rate constant of \( k_q = 1.4 \times 10^9 \text{M}^{-1} \text{s}^{-1} \) is diffusion limited by comparison to measured diffusion constants for molecules of similar size. For example \( k_d \) for two ethyl radicals in \( \text{H}_2\text{O} \) is \( 2.4 \times 10^9 \text{M}^{-1} \text{s}^{-1} \), B. Hickel, J. Phys. Chem. 79, 1054 (1975).
Stern-Volmer plot of 1/lifetime of the $A'$ state versus concentration of cyclohexane in CCl$_4$. The dashed line is the result of a least squares fit to the first four data points. The rate constant obtained from the slope of this line is $1.4 \times 10^6 M^{-1}s^{-1}$. The intercept is $(2033 ps)^{-1}$ which represents the lifetime in pure CCl$_4$ at an I$_2$ concentration of 11mM. Under these conditions the $A'$ lifetime is quenched$^{(94)}$ through interactions with other I$_2$ molecules.
mode structure of the solvent complex is replaced by higher frequency vibrations the decay process becomes more efficient and the lifetime decreases.

4.6 Discussion

In this section we compare the $A'$ state dynamics to experimental measurements for I$_2$ in other potential states and to the predictions of current theoretical models.

4.6.1 VER in Different Electronic States

It is interesting to compare the rates of VER observed for the $A'$ state with those of the $X$ state to determine how the detailed nature of the potential influences the decay process. In Chapter 3 we have shown that the $X$ state cools very quickly in the upper regions of the potential resulting in a population distribution which is peaked at levels which have a characteristic energy gap of 150 cm$^{-1}$ within the first 8 ps following recombination. In fact, those studies observed\cite{52,83} no population at all in vibrational levels with an energy gap near 106 cm$^{-1}$ which is characteristic of the $A'$ state frequency. It would appear that the $X$ and $A'$ electronic states have enormously different rates of VER.

This disparity in the decay rate can be explained by the theoretical model of Nesbitt and Hynes.\cite{11,12} The dominant mechanism of VER is predicted to be V-T energy transfer when the energy gap is small $\approx$100 cm$^{-1}$. Under these conditions, the decay rate is a function of the energy gap and the phase averaged kinetic energy
**Table 4.2**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Lifetime (4°C)</th>
<th>Lifetime (22°C)</th>
<th>Lifetime (40°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>107</td>
<td>95</td>
<td>83</td>
</tr>
<tr>
<td>cyclohexane</td>
<td></td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>D_{12}-cyclohexane</td>
<td>252</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td></td>
<td>521</td>
<td></td>
</tr>
<tr>
<td>CHCl₃</td>
<td></td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>CDCl₃</td>
<td></td>
<td>2370</td>
<td></td>
</tr>
<tr>
<td>CHBr₃</td>
<td></td>
<td>1243†</td>
<td></td>
</tr>
<tr>
<td>CCl₄</td>
<td>3356</td>
<td>2843</td>
<td>2237</td>
</tr>
</tbody>
</table>

Lifetime of the I₂(A') state in picoseconds determined by measuring the intensity of the Stokes Raman band at 106 cm⁻¹ as a function of the optical delay between pump and probe lasers. The values reported in this work are longer than those reported previously due to the lower I₂ concentrations used in the present work. Higher concentrations lead to lifetime shortening as a result of quenching by ground state I₂ molecules.
in the oscillator. A simple formula was proposed\(^{(11-12)}\) which relates energy transfer \(\Delta E\) to the frequency \(\omega(E)\) of the oscillator and the quantum number \(v\).

\[-\Delta E \propto \omega(E) \frac{1}{2}(v + 1/2)\]

This equation is valid for any form of the potential and should apply to both the \(X\) and the \(A'\) states. The energy transfer efficiency predicted by this equation for both electronic states has been plotted in Figure 4.14 as a function of the "local" oscillator frequency which describes the vibrational energy gap. The energy levels were obtained from the gas phase RKR potentials. Figure 4.14 illustrates why the decay rates for a common "local" oscillator frequency are so different in these two electronic states. In the \(A'\) state the vibrational energy gap is 106 cm\(^{-1}\) for the lowest two vibrational levels. In the \(X\) state the local vibrational frequency decreases to 106 cm\(^{-1}\) near \(v=64\). There is much more kinetic energy associated with this \(X\) state oscillator compared to similar frequency oscillators in the \(A'\) state. This results in much faster rates of decay for the \(X\) state vibrations simply because the \(X\) state oscillator has more energy to give up and interacts more strongly with the solvent as a result of the larger amplitude vibration.

Recent experimental\(^{(24)}\) and theoretical\(^{(50)}\) considerations of VER in the \(I_2(X)\) state suggest that V-R energy transfer is also an important energy exchange mechanism. It is not clear to what extent V-R relaxation contributes to VER on the \(A'\) state and we do not suggest that V-T alone is responsible for \(A'\) state relaxation. In comparing the rate of VER between the \(X\) and \(A'\) state it is reasonable to expect
Predicted efficiency of kinetic energy transfer to solvent as a function of the local vibrational energy gap for the $X$ and $A'$ electronic states. The curves are normalized to represent the relative efficiencies for energy transfer in these two electronic states.
that both V-T and V-R relaxation mechanisms increase with the quantum number of the I\(_2\) vibration.

There is another interesting aspect of this data which must be considered. The VER rates in the \(A'\) state were found to be extremely solvent dependent. Except for n-hexane, there are no intramolecular solvent vibrations which can contribute to energy transfer by a V-V mechanism. It was shown in various solvents that the rate of VER decreased in the order CH\(_2\)Cl\(_2\) > n-hexane > cyclohexane \(\sim\) CHCl\(_3\) \(\sim\) CCl\(_4\) > CHBr\(_3\). The general aspects of this trend appear to be accounted for by a mass dependence. For V-T (and V-R) energy transfer the lighter and faster moving solvent molecules are more efficient in converting the I\(_2\) vibrational quanta into translational energy. In addition, the collision potential between I-H is likely to be more repulsive than between I-Cl. As a result, the higher frequency components in the force for the I-H interaction cause VER to be more efficient in CH\(_2\)Cl\(_2\) compared to CCl\(_4\). For n-hexane the rate of VER is considerably faster than that in cyclohexane as shown in Figure 4.7. This may indicate the importance of V-V energy transfer to the 101 cm\(^{-1}\) vibration in n-hexane.\(^{(56)}\) This general conclusion concerning V-T (and V-R) transfer has also been reached\(^{(50)}\) for the solvent dependence of \(X\) state VER in the chlorinated hydrocarbons. On the \(X\) state additional effects due to V-V energy transfer to the 217 cm\(^{-1}\) vibration in CCl\(_4\) are possible. However, this is not likely to be important for the \(A'\) state due to the large energy mismatch with the 106 cm\(^{-1}\) fundamental vibration.
It is interesting to compare the VER relaxation results for the $A'$ state with those of Lineberger et al. for $I_2^-$ in CO$_2$ clusters.$^{(81)}$ In rare gas matrices this anion has a ground electronic state with a fundamental frequency$^{(97)}$ of about 114 cm$^{-1}$ and is therefore similar to the $I_2(A')$ potential. Lineberger has determined$^{(81)}$ that following geminate recombination, the appearance time of the cold $I_2^-$ ground vibrational levels is on the order of 10 ps for $I_2^-(CO_2)_{16}$. The appearance time is much faster than that observed for the appearance time of the vibrationally cold neutral $I_2(X)$ state in solution.$^{(22-25,52,83)}$ This result was interpreted as a combination of two mechanisms: the large amount of energy lost from CO$_2$ ejection and faster VER in the anion compared to the neutral. Although it is possible for the dynamics of the anion to be greatly influenced by the existence of the negative charge,$^{(81,98)}$ it is also possible for the shape of the potential to affect the dynamics. The observed 10 ps appearance time$^{(81)}$ for the anion is quite similar to that observed here for the neutral $I_2(A')$ state. The result suggests an alternative explanation for the dynamics observed for the anion. That is, the fast appearance time represents the combined geminate recombination and VER dynamics which apparently are more influenced by the nature of the potential than the existence of the charge.

### 4.6.2 Electronic Relaxation

The temperature and solvent quenching measurements of electronic relaxation have shown that the decay mechanism is not dominated by an activated dissociation process. Franck-Condon density calculations were performed to determine if a shift of the $A'$ state potential energy surface within the limits imposed by the
spectroscopic measurements could account for the observed electronic decay. These calculations indicate that this mechanism alone cannot explain the observed relaxation rates.

Another mechanism which must be considered is solvent effects on the upper region of the X state potential which shifts the X state in a manner that increases the interaction with the A' state. Although the gas phase potentials do not appear to exhibit much sensitivity to solvation in the lower regions of the potential, they may be extremely sensitive to solvation in the upper regions of the potential near the dissociation point. There is no available spectroscopic information on the X state in solution at 10,000 cm\(^{-1}\) above the zero point that can be utilized to directly address this concern. However, there is kinetic information in the isotope results which can be used to investigate this possibility. It is reasonable to assume that isotopic substitution in the solvent should not strongly affect the I\(_2\)(X) solvent interaction. As a result, isotopic substitution in the solvent would not be expected to have a major effect on the A' state lifetime if the decay mechanism was dominated by solvent effects on the attractive wall of the X state potential. The fact that large isotope effects (factor of 2) on the lifetime were observed strongly argues against this possibility. The collective experimental results therefore suggest that the A' state decays through formation of solvent exciplexes.

Experimental evidence\(^{(99)}\) for the complex quenching mechanism on the I\(_2\)(A') electronic state has been obtained in the gas phase. Relatively inert gases such as He, Ar, and N\(_2\) quench the A' state by thermal deactivation. However, more
strongly interacting colliders such as SF₆ and I₂ show a very weak temperature dependence suggesting⁹⁹ that deactivation is through dissociation of I₂•SF₆ complexes.

Theoretical predictions of collisional effects on E→V electronic relaxation are difficult to make¹⁰⁰-¹⁰¹ because the rate constant critically depends on the curvature of the potential and the interaction strength in the region where the curves cross. However, for electronically excited atoms a general trend has been observed¹⁰¹ in the quenching rate with molecules as the quenching species. The rate is strongly correlated¹⁰¹ to the change in vibrational quantum number and therefore the vibrational frequency of the oscillator receiving the energy. This result indicates that higher frequency oscillators are better quenchers. The same trend is predicted theoretically,¹⁰²-¹¹³ although there is not complete agreement on the details of the mechanism.

For the I₂(A′) state the solvent dependence of electronic relaxation is also strongly correlated to the normal mode frequencies in the solvent. This result suggests that the relaxation mechanism may be similar to that of atoms where a "collision" or exciplex between I₂(A′) and the solvent is formed. During electronic relaxation the most efficient channels are those that involve high frequency modes in the solvent.

It is interesting to note that the barrier height estimated from the temperature dependence of the electronic decay rate agrees with what is expected for the E-V relaxation mechanism suggested in this work. One way to picture the E-V relaxation
pathway is to consider the $A'$ state to be lowered in energy (with respect to $X$) by one quanta of the solvent accepting mode. It is reasonable to presume that curve crossing from the $A'$ to $X$ state takes place at the outer turning point. According to this picture, in the $I_2$ solvent complex the barrier height between the bottom of the $A'$ state and the crossing point between the $A'$ and $X$ states is approximately $425 \text{ cm}^{-1}$ for the C-H stretch in n-hexane. The barrier height suggested from the temperature dependence is $430 \text{ cm}^{-1}$ which is in reasonable agreement with the $(425 \text{ cm}^{-1})$ barrier expected for the E-V relaxation. It is important to realize that this result is only suggestive since the temperature dependence may be a combination of an activation factor and a probability for transfer in the activated region. In addition, we have considered only one quanta transitions involving solvent vibrations. This simplification would cause the calculated barrier for E-V relaxation to be higher than actual. For $\text{CCl}_4$ the barrier height for $A'$ state decay in the solvent complex is $1404 \text{ cm}^{-1}$ and the experimental value from the temperature dependence $680 \text{ cm}^{-1}$. Here again, the temperature dependence is consistent with the proposed E-V relaxation mechanism if multiple transitions in the solvent vibration are considered.
5. GEMINATE RECOMBINATION OF I+I$_2$

5.1 Introduction

Chapter 3 and 4 discuss transient Raman studies of geminate recombination of iodine on both $X$ and $A'$ states. This recombination process refers to the recombination of two iodine radicals. We found that the rate of geminate recombination of two radicals is very fast ($\leq$10ps). How does the geminate recombination of a polyatomic molecule differ from that of diatomic molecule? This is the question we try to answer in this chapter.

The study of geminate recombination in polyatomic molecular systems is much more difficult than for diatomic molecules. In transient absorption experiments, correct interpretation relies on the knowledge of Franck-Condon factors between different electronic states. Without calculating Franck-Condon factors it is almost impossible to separate the geminate recombination from vibrational energy relaxation in a transient absorption spectrum. Unlike the diatomic molecule case in which the Franck-Condon factors can be calculated from the well known potentials, it is often difficult to obtain similar information in a polyatomic molecule since very little information is available about the polyatomic potential surfaces. In order to get the information of geminate recombination in a polyatomic molecular system, it is necessary to separate geminate recombination from vibrational energy relaxation without knowing Franck-Condon factors. As shown in Chapter 3 and 4 only transient vibrational spectroscopy is capable of doing this.
Using picosecond transient Raman spectroscopy we have directly observed the geminate recombination of \( I + I_2 \rightarrow I_3 \) by photodissociating \( I_4 \) into two iodine atoms and one iodine molecule. The formation of \( I_3 \) is directly detected in the Raman spectrum. The confirmation of geminate recombination of \( I + I_2 \) is achieved by measuring both the Stokes and anti-Stokes transient Raman spectra after the photodissociation of \( I_4 \) using a 532nm photon.

There is some indirect evidence for the formation of \( I_3 \) by recombination of \( I \) and \( I_2 \). The first theoretical calculation\(^{114}\) to infer the stability of \( I_3 \) dated back to 1930's. Using a simple London equation it was estimated that the \( I \) and \( I_2 \) reaction has an activation barrier of \( \approx 600 \text{ cm}^{-1} \) and the formation enthalpy of \( I_3 \) is \( \approx 600 \text{ cm}^{-1} \). Since then there have been several theoretical attempts\(^{115-117}\) to calculate the activation barrier for atomic-exchange reaction \( I + I_2 \rightarrow I_2 + I \) where \( I_3 \) is proposed as the intermediate species of this reaction. Experimentally\(^{118}\) \( I_3 \) was suspected to be the intermediate of iodine recombination reaction which is catalyzed by iodine molecule in the gas phase. In solution phase\(^{20}\) \( I_3 \) was also suggested to be responsible for some of the observed dynamics in the picosecond transient absorption measurement. Using transient Raman spectroscopy we have directly detected \( I_3 \) as a result of geminate recombination of \( I + I_2 \). The dynamics of geminate recombination are obtained and the solvent dependence of geminate recombination is also studied in detail.

5.2 Results
5.2.1 Experimental Evidence for the Existence of \( I_3 \)

In this section experimental evidence will be presented for the existence of \( I_3 \) following photodissociation of \( I_4 \) in a concentrated solution. We assign the transient species observed in concentrated solution as \( I_3 \) based on the concentration dependence of the transient Raman spectrum, energetic consideration of transient species, Raman frequency of the transient and the dynamics for the transient. The details of the assignment are given immediately below.

The concentration dependence of the transient Raman spectra are plotted in Figure 5.1. The Raman spectra are obtained in different concentrations at the same time delay of 100ps. It is very clear that the transient vibrational frequency in 2mM solution is at 111 cm\(^{-1}\) and this band shifts to 122 cm\(^{-1}\) in 4mM solution and stays in that position when the concentration is increased up to 20mM. This transient band cannot be assigned to the \( A' \) state, since the \( A' \) state vibrational frequency is at 106 cm\(^{-1}\). Therefore this transient comes from photodissociation of certain species in the concentrated solution.

It is well known\(^{(119-124)}\) that there is a high percentage of dimer existing in concentrated iodine solutions. In 2mM iodine solution the concentration of \( I_4 \) is about .5mM. In 20mM iodine solution the concentration of \( I_4 \) is about 11mM.* Photoexcitation of concentrated iodine solution will dissociate both iodine monomer and iodine dimer. The photochemistry of iodine molecule has been extensively

* The concentrations of \( I_4 \) are calculated based on the equilibrium constants deduced in Refs. 120 and 121. The equilibrium constant was given in a range from 0.5 to 0.05. The concentrations presented here are the averages of two extreme cases.
Concentration dependence of transient Raman spectrum in n-hexane. The concentration of each solution is indicated in each frame. All three spectra are measured at same time delay of 100ps. The arrow in bottom frame indicates the Raman band position in 2mM solution. The dashed vertical line indicates Raman band position at concentrations higher than 4mM. Raman frequency units are in cm\(^{-1}\).
studied\(^{(22-25,56,83)}\) and discussed in Chapter 3 and 4. However, there are very few studies on the photoexcitation of iodine dimer. In the gas phase\(^{(125)}\) it is found that excitation of iodine dimer above the dissociation limit of iodine molecule will result in the formation of one iodine in the ground \(\textit{X}\) state and the other iodine molecule in rotational and vibrational excited \(\textit{B}\) state (an excited electronic state). In the condensed phase it is well known that \(\textit{B}\) state predissociation occurs fairly rapidly\(^{(22,25,83)}\) (less than 2ps) if the initial exciting vibrational levels are above the crossing point of the repulsive curve with the \(\textit{B}\) state potential curve. This \(\textit{B}\) state predissociation will result in the generation of two ground state atoms. Energetically, excitation with 532nm photon will populate the \(v = 31\) vibrational level of the \(\textit{B}\) state. The iodine dimer dissociation energy is about 500 cm\(^{-1}\).\(^{(120)}\) Considering the energy loss due to dissociation of dimer, it will populate \(v = 25\) vibrational levels of \(\textit{B}\) state. This level is far above the estimated crossing point of the repulsive curve which is \(v < 6\) vibrational level.\(^{(39)}\) Although we do not know the amount of energy lost in the translation of dissociated iodine molecule, we can estimate the energy lost from the gas phase experiment. Van den Bergh \textit{et al.}\(^{(125)}\) found that excitation above the dissociation limit of iodine will result in larger amount of energy lost to translational mode as compared to those excitations below the \(\textit{B}\) state dissociation limit. Excitation of 532nm is below the dissociation limit of iodine molecule. We thus use the energy lost in van den Bergh's experiment which excites iodine dimer above the dissociation limit as the upper limit energy loss in our experiment. Such consideration will populate one of the iodine to \(v \approx 12\) level of the \(\textit{B}\) state. Under
this condition the initially populated \textit{B} state will undergo rapid predissociation in less than 2ps in the solution phase. Therefore the first step after photoexcitation of \textit{I}_4 is

\[ \textit{I}_4 \rightarrow \textit{I}_2(\textit{X}) + \textit{I}_2(\textit{B}) \rightarrow \textit{I}_2(\textit{X}) + \textit{I} + \textit{I}. \]

Two processes could occur after photodissociation. First, the two nascent iodine radicals can recombine to form an iodine molecule which is vibrationally hot in the ground \textit{X} state. This subject has been well studied\textsuperscript{(22-23,25,56,83)} The second possibility is that one iodine radical recombine with the iodine molecule to form \textit{I}_3. The formation enthalpy\textsuperscript{(114-118)} of \textit{I}_3 is a negative number, which indicates that \textit{I}_3 is an energetically favorable transient species.

The fact that the vibrational frequency of this transient is at 122 cm\textsuperscript{-1} indicates that there are only two possible assignments for this transient. One possibility is \textit{I}_3 and the other is \textit{I}_2 \textit{B} state. For \textit{I}_3, only the total symmetric vibration (\(\nu_1\)) is Raman active assuming that \textit{I}_3 molecule is symmetric. The calculated \(\nu_1\) vibrational frequency is about 120 cm\textsuperscript{-1}\textsuperscript{(115)} For \textit{I}_2 \textit{B} state, the vibrational frequency in the gas phase is 124 cm\textsuperscript{-1}\textsuperscript{(32)} However, since rapid (< 1ps) predissociation of the \textit{B} state is expected, we believe that the transient we observe in concentrated solution which has a vibrational frequency of 122 cm\textsuperscript{-1} is \textit{I}_3.

There are also some experimental data which support the arguments why the observed transient cannot be \textit{I}_2 \textit{B} state. First, the formation time of this transient is much longer than the expected formation time of \textit{B} state. The formation of \textit{B} state should occur at the dissociation rate of \textit{I}_4, which we believe to be short
(< 2ps). In the transient Raman spectra we should observe a transient forming within our pulsewidth 8ps. However, the transient we observe takes at least 50ps to rise in the cyclohexane solution. (The formation time of I₃ is determined to be 50–100ps in cyclohexane solution in next section.) This fact argues against the assignment as B state. Second, it is possible that the 50–100ps is the time required for vibrational cooling after the formation of B state. To separate vibrational relaxation from formation dynamics, we measured the transient Raman spectra in both Stokes and anti-Stokes regions. There are two characteristic features of vibrational cooling in the time-dependent Raman spectra. First, the Raman band frequency continuously shifts to higher wavenumbers with time in both Stokes and anti-Stokes regions. At early time, the band maximum in anti-Stokes is at higher vibrational frequency than in the Stokes region for a small oscillator (such as A' band described in Chapter 4). Second, because the Stokes Raman scattering occurs from lower vibrational levels and anti-Stokes Raman scattering occurs from higher vibrational levels, the intensity change with time will reflect the population change in different vibrational levels. In other words, the intensity of the Raman band will increase with time in the Stokes region and decrease with time in the anti-Stokes region if vibrational relaxation occurs. On the other hand, if a new species forms, the Raman band position should shift the same amount similarly for both Stokes and anti-Stokes regions and the band intensity should increase in both Stokes and anti-Stokes regions.
Figure 5.2 shows the transient Raman spectra of both Stokes and anti-Stokes at 25ps and 100ps in 20mM iodine solution in n-hexane. Note that at the same time delays overlay of both Stokes and anti-Stokes Raman spectra show that the vibrational frequency of the species at ≈ 122 cm⁻¹ are exactly the same in both Stokes and anti-Stokes regions. This argues against the assignment of vibrational relaxation of iodine B state. For Stokes spectra at different time delays, the intensities are normalized to the ground state iodine bands. The normalized intensity increases from 25ps to 100ps. In the anti-Stokes region, the normalized intensity of the Raman band for the new species also increases from 25ps to 100ps. This is opposite to what is expected for vibrational cooling.

In addition we have plotted the energy diagram for each transient species possibly generated after photoexcitation in Figure 5.3. As indicated in Figure 5.3 the energy position of I₃ is lower than vibrationally hot iodine B state. Therefore the transient we observe is more likely to be I₃ than I₂ B state energetically.

Combining all the facts together, we assign the transient observed in the concentrated solution as I₃ from the geminate recombination of I radical and iodine molecule. The detailed dynamics of geminate recombination will be given in the next section.

5.2.2 Geminate Recombination of I + I₂

The rate of geminate recombination of I+I₂ → I₃ can be deduced from the transient Raman spectra at different time delays. Both intensity and vibrational frequency position of the Raman band are analyzed to obtain the formation time
Stokes and anti-Stokes Raman spectra in n-hexane at time delays of 25ps and 100ps. The concentration of solution is 20mM. Solid curves are plots of Stokes spectra. Dashed curves are plots of anti-Stokes spectra. The vertical dashed and dotted line indicates Raman band position for I$_3$ at 25ps. The intensities in Stokes spectra are normalized to the ground state Raman I$_2$ band and represent true dynamical intensity variations. Anti-Stokes intensities are normalized in the same manner. Frequency units are in cm$^{-1}$. 

Figure 5.2
Energy diagram for possible transients generated following photoexcitation of iodine dimer with a 532nm photon. Arrows indicate possible photochemical processes. I$_4^*$ represents excited I$_4$ molecule. I$_2$(B(v=n)) represents vibrational hot I$_2$ B state.
of $I_3$. In order to correctly estimate the formation time of $I_3$, the effect of the $A'$ state must be evaluated. The $A'$ state has a vibrational frequency of $106 \text{ cm}^{-1}$ and an electronic relaxation lifetime of $\tau = 95 \text{ ps}$ in cyclohexane as shown in Chapter 4. Since the vibrational frequency of $A'$ is so close to that of $I_3$, the existence of the $A'$ state will strongly affect the observed transient band shape, position and intensity at time delays less than 100ps. Specifically, a strong $A'$ state band will broaden the Raman bandwidth and shift the Raman maximum to lower vibrational frequency.

Figure 5.4 is a stack of transient Raman spectra at different time delays of iodine in cyclohexane in 12mM solution. It appears that the band intensity for the new species which we assign as $I_3$ increases about a factor of 2 from $t=5\text{ps}$ to $t=100\text{ps}$ and increases only slightly after 100ps. The big intensity change in first 100ps is due to the formation of $I_3$. We can make the determination of formation time of $I_3$ more definitive by examining the intensity of the Raman band of the newly formed transient. In Frame 5.4C at time delay of 50ps, the intensity of the transient band is much stronger than it should be if this band is entirely from $A'$ state. The true intensity of $A'$ state can be obtained from the transient Raman spectra in more dilute solution where the concentration of iodine dimer is really low. We can approximately normalize the intensity of the $A'$ state to the transient $X$ state at the same time delay. Such comparison indicates that this transient band intensity at 50ps is at least a factor of 2 stronger than the normal $A'$ state band. Therefore at 50ps spectrum the observed transient comprises both the $A'$ state and $I_3$. From this information, the formation time of $I_3$ is determined to be about 50–100ps.
Transient Raman spectra of I$_3$ in 12mM cyclohexane solution at various time delays. Optical delays between pump (532nm) and probe (266nm) are indicated in each frame. Spectra are normalized to the one color I$_2$ ground state band and represent the true dynamical intensity variations. The dash and dotted vertical line indicates transient band position at 200ps time delay. The arrow in Frame D indicates the band position at 5ps. Frequency units are in cm$^{-1}$. 
Another piece of evidence which supports this formation time of $I_3$ is the Raman band position of this new species. Theoretically the formation of new species is indicated by the intensity change only. The vibrational frequencies should be the same at all time delays. However, it appears that in Figure 5.4 the Raman band position is continuously shifted from 5ps to 100ps. This is due to the existence of $I_2 A'$ state band, since the $A'$ state is at 106 cm$^{-1}$. The continuous shift of vibrational frequency results from mixing of $A'$ state and $I_3$ band. In Figure 5.4 at time delay of 5ps, the transient Raman band is at 108 cm$^{-1}$ which is very close to the $A'$ state vibrationless frequency of 106 cm$^{-1}$. Therefore at 5ps the transient is entirely dominated by $A'$ state. In Frame 5.4B at 100ps the transient band is shifted to 118 cm$^{-1}$. The effect from the $A'$ state is very small at this time delay. We believe that the Raman band at 100ps is dominated by $I_3$ from the geminate recombination of $I + I_2$. At 50ps time delay the Raman band vibrational frequency is in between the band positions of $A'$ state and $I_3$. This spectrum comprises both $A'$ state and $I_3$. Therefore, from both intensity and frequency considerations, the geminate recombination time of $I + I_2$ is about 50–100ps in cyclohexane solution.

It may be argued that the 50–100ps could be the time taken for vibrational cooling of $I_3$ assuming $I_3$ forms much faster. This possibility can be excluded from the data for time-dependent Stokes and anti-Stokes transient Raman spectra. In Figure 5.2 of the last section it was shown that the Raman frequency change and intensity change in both Stokes and anti-Stokes regions argue against the assignment
of vibrational relaxation. Therefore 50–100ps is the time taken for the formation of I₃. The vibrational relaxation should occur much faster.

### 5.2.3 Solvent Dependence of Geminate Recombination for I + I₂

The transient Raman spectra have been measured in four solvents: cyclohex- ane, n-hexane, neo-hexane and deuterated cyclohexane. The formation times of I₃ can be extracted in the same manner as in the last section.

In n-hexane the normalized intensities at various time delays indicate that the intensity increases a factor of 1.5 from 10ps to 25ps, a factor of 1.8 from 10ps to 100ps and increases very slightly after 100ps (spectra not shown). From this intensity variation it seems that a formation time from 25ps to 100ps is plausible.

The intensity of this new transient band at 25ps time delay is carefully examined by comparing this band with the A' state band in the low concentration solution. Figure 5.5 shows a comparison of transient Raman spectra in two different concentrations 2mM and 20mM at 25ps time delay. The intensity of the new transient band increases by a factor of 3 in 20mM solution if we normalize it to the X state transient band. In 2mM spectrum the transient Raman band is mainly from the A' state. The increase in intensity for the new species Raman band originates entirely from the formation of I₃. The band in 20mM solution at 25ps is dominated by the band of I₃. Therefore the intensity analysis indicates that I₃ forms in 25ps in n-hexane solution.
Transient Raman spectra of I$_3$ in n-hexane in different concentrations at same time delay of 25ps. The concentrations are indicated in each frame. The vertical dash and dotted line indicates transient band position in 20mM solution. The arrow indicates band position in 2mM solution. Frequency units are in cm$^{-1}$. 
Frequency considerations also give the same result. In Figure 5.5 the Raman band of the new species is already at 120 cm⁻¹ at 25ps in 20mM solution. This indicates that this Raman band is mainly from I₃. Therefore, from the intensity increase and the band position of the new species in 20mM solution at 25ps, the formation time of I₃ from I+I₂ in n-hexane is determined to be less than 25ps. In cyclohexane solution I₃ does not form until 50ps. Therefore the geminate recombination of I + I₂ is faster in n-hexane than in cyclohexane.

Figure 5.6 is a plot of time-dependent transient Raman spectra in 12mM neo-hexane solution. In neo-hexane, the intensity for the species at ≈ 120 cm⁻¹ increases about a factor of 2 from t=10ps to t= 100ps and very slightly after 100ps. These intensity variations are similar to those in cyclohexane solution. However, the band position of the transient is at higher vibrational frequency than the band in cyclohexane at 50ps time delay. That means the band at 50ps contains more contributions from I₃ Raman band. This indicates that the geminate recombination in neo-hexane of I+I₂ has similar rate as in the cyclohexane or slightly faster.

Figure 5.7 is a plot of time-dependent transient Raman spectra in 11mM deuterated cyclohexane solution. The intensities for transient bands are not normalized with respect to each other. The information about the formation time of I₃ in this solvent can be obtained by comparing the intensity of the new species band with the A' state band in the dilute iodine solution. In Frame 5.7C at 45ps time delay the intensity of the new transient relative to the intensity of X state is similar to that in the 2mM deuterated cyclohexane solution (spectrum is shown in Chapter 4).
Figure 5.6

Transient Raman spectra of I$_3$ in 12mM neo-hexane solution at various time delays. Optical delays between pump (532nm) and probe (266nm) are indicated in each frame. Spectra are normalized to the one color I$_2$ ground state band and represent the true dynamical intensity variations. The dash and dotted vertical line indicates transient band position at 200ps time delay. The arrow indicates band position at 10ps. Frequency units are in cm$^{-1}$.
where no $I_3$ is detected. Therefore the band at 45ps is dominated by the $A'$ state band. It appears that $I_3$ forms after 50ps.

In deuterated cyclohexane the actual band positions of $I_3$ at all time delays are complicated by the existence of strong $A'$ state. Compared to the $A'$ state in cyclohexane solvent, the $A'$ state in deuterated cyclohexane has stronger intensity and longer lifetime (in Chapter 4). The $A'$ state of deuterated cyclohexane has an electronic relaxation time constant of $\tau \approx 200 \text{ps}.^{(56)}$ The apparent band positions of $I_3$ are at lower vibrational frequency at all time delays under the influence of the $A'$ state. This is why at 200ps delay the Raman band of transient only shifts to 118 cm$^{-1}$. At 45ps time delay, the transient Raman band position appears to be at 112 cm$^{-1}$ within the signal-to-noise ratio given by the data. This frequency is much higher than the pure $A'$ state band. Therefore, the transient band at 45ps comprises both $A'$ state and $I_3$. $I_3$ forms in about 50–100ps from such analysis.

In the intensity analysis, we did not see any $I_3$ band at 45ps. This is probably because that the intensity of the $A'$ state is close to the intensity of the $I_3$ band at 45ps. Only a frequency shift is apparent. In the other three solvents we discussed, the intensities of the $I_3$ band at time delay $\geq 25$ps are much stronger than the $A'$ state band. In these cases, intensity analysis can give reliable formation times. Nonetheless we conclude that the rates of geminate recombination of $I+I_2$ are similar in deuterated cyclohexane and cyclohexane within the signal-to-noise ratio of our data.
Transient Raman spectra of I₃ in 11mM deuterated cyclohexane solution at various time delays. Optical delays between pump (532nm) and probe (266nm) are indicated in each frame. The dash and dotted vertical line indicates transient band position at 200ps time delay. The arrow indicates the band position at 10ps. Frequency units are in cm⁻¹.
Summarizing all the formation times of $I_3$ in different solvents, the formation rates of $I_3$ from $I+I_2$ can be arranged as $n$-hexane > neo-hexane ≥ deuterated cyclohexane ≈ cyclohexane.

5.3 Discussion

5.3.1 Activation Barrier for Recombination of $I+I_2$

The geminate recombination of $I+I_2$ requires much longer time than that for two iodine radicals. The geminate recombination rate of two iodine radicals has been measured using transient Raman spectroscopy\textsuperscript{(56,83)} as discussed in Chapter 3 and 4. The two geminate iodine atoms recombine in less than 2ps on the $X$ state and ≈ 5ps on the $A'$ state in cyclohexane. However, the geminate recombination for $I+I_2$ takes about 50–100ps in cyclohexane. This difference in rate can be understood from the activation barrier heights for these two reactions. The activation barrier for the radical recombination is zero which gives rise to fast geminate recombination for two iodine atoms. The slow geminate recombination rate of $I+I_2$ indicates that there is an activation barrier for this reaction. There are several theoretical and experimental attempts\textsuperscript{(115-117)} to obtain the activation barrier for this recombination reaction. Most calculations indicate that there is an activation barrier for the reaction $I+I_2$. The activation barrier is estimated to be from 700 cm\textsuperscript{-1} to 1700 cm\textsuperscript{-1} in different calculations. However, even the existence of the activation barrier for this reaction is questioned\textsuperscript{(127)} theoretically. Our experimental
results provide direct evidence for the existence of an activation barrier for the geminate recombination of $I + I_2$.

5.3.2 Formation of $I_3$ Solvent Complex

In Figure 5.4 the $I_3$ Raman band appears to be slightly shifted to higher frequency from 100ps to 200ps and continues shifting up to 500ps. The intensity is only slightly increased from 100ps to 500ps. This fact is probably due to the formation of $I_3$ solvent complex. At 100ps the effect of the $A'$ state is reasonably small, since the $A'$ state of iodine in cyclohexane has an electronic relaxation time of $\tau = 95$ps. At time delays $\geq 100$ps, the effect of $A'$ state can be evaluated from two aspects. First, at 100ps the intensity of the $A'$ state has decayed to less than $1/3$ of the maximum intensity. Second, the resonance Raman enhancement for $A'$ state at 266nm is much smaller than $I_3$. This point can be made clearer by comparing the intensity of $A'$ state and $I_3$ at 100ps time delay in Figure 5.1. In the 2mM solution at 100ps, the $A'$ state has about the same intensity as the $X$ state. In the 20mM solution at 100ps the intensity of $I_3$ is so strong that neither the $X$ state nor the $A'$ state could be observed. Therefore the dynamics observed at time delays $\geq 100$ps are purely from $I_3$.

The transient Raman spectra of iodine in n-hexane in 20mM solution in both Stokes and anti-Stokes regions have been measured from time delay of 10ps to 200ps. The frequency of both Stokes and anti-Stokes shifts to higher vibrational frequency with time. The intensities in both Stokes and anti-Stokes regions increase with time. These data indicate that the frequency shift after 100ps originates from
a structural change of I$_3$ other than vibrational cooling. We thus attribute this frequency shift to the formation of I$_3$ solvent complex. The slight frequency shift after 100ps is found in all four solvents we measured. It appears that the formation of I$_3$ solvent complex takes several hundreds of picoseconds in all four solvents. The slight increase in the intensity after 100ps is probably due to the slight increasing resonance Raman enhancement of I$_3$ solvent complex at 266nm. Such increase of the resonance enhancement could result from the formation of I$_3$ solvent complex, as the effect of solvent could give more favorable Franck-Condon overlaps.

5.3.3 The Lifetime of Transient I$_3$

The stability of I$_3$ has been discussed in several theoretical attempts. The formation enthalpy of I$_3$ has been estimated to be from 700 cm$^{-1}$ to 1700 cm$^{-1}$. Experimentally this energy is also estimated in the gas phase. The study of iodine recombination$^{(118)}$ in the gas phase measured the temperature dependence of the recombination reaction of two iodine atoms in the presence of iodine molecule. It was believed that iodine molecule accelerates the recombination reaction by forming I$_3$ with one of the iodine radical as the first reaction step. Such measurement gives a formation enthalpy of about 1700 cm$^{-1}$ by assuming I and I$_2$ interact via a Lennard-Jones potential.

I$_3$ could exist for a certain period of time since the formation enthalpy is a negative value. However, I$_3$ could easily react with other species in the solution to convert to other products. I$_3$ could react with I radical to form vibrationally hot I$_4$
or could directly form two dissociated iodine molecules. In our transient Raman measurement we can propose a range for the lifetime of I$_3$.

The longest time delay we measured is 500ps, where it appears that the intensity of I$_3$ band is increasing with time. Therefore, the lifetime of I$_3$ is at least longer than 500ps. The repetition rate of our laser is 2kHz. If I$_3$ lives longer than 500$\mu$s, we shall observe it in the probe only Raman spectrum which is the static Raman spectrum. However, we did not observe a Raman band at around 120 cm$^{-1}$ in the probe only spectrum. Therefore the lifetime of I$_3$ should be shorter than 500$\mu$s.
6. SUMMARY AND CONCLUSIONS

In general, transient Raman spectroscopy is a superior tool in studying condensed phase reaction dynamics. We have for the first time measured the geminate recombination between two iodine atoms and iodine atom with iodine molecule. We have for the first time directly measured vibrational energy relaxation in both ground $X$ state and excited $A'$ state. I will summarize the conclusions according to the dynamics discussed in Chapter 3, 4, and 5.

6.1 Summary of $X$ State Dynamics

Direct observation of geminate recombination and vibrational decay has been observed for the $I_2 X$ state. In cyclohexane, relaxation in the upper regions of the potential is shown to be very fast. Geminate recombination is complete with a loss of 42% of the nascent vibrational energy within the 8ps laser pulse width. This experimental result is close to theoretical expectations.

The population distribution (width of the distribution of levels populated) appears to remain approximately constant throughout the range of $X$ state vibrational levels observed. This is a result of rapid geminate recombination and relatively inefficient VER.

V-V energy relaxation is not a dominant relaxation pathway in polyatomic solvents. Cyclohexane does not have any intramolecular vibrations which are low enough in frequency to act as an acceptor of one quanta of an $I_2$ vibration. When cyclohexane is deuterated, a solvent mode is shifted into resonance with the iodine oscillator. No increase in the iodine VER rate is observed in $d_{12}$-cyclohexane. In
fact, VER was found to be slightly less efficient in d_{12}-cyclohexane in the upper regions of the potential. This was interpreted as a consequence of the mass dependence of V-T (and V-R) relaxation. Heavier solvent molecules are less efficient in quenching I_2 vibrational energy. Apparently V-T (and possibly V-R) is a dominant relaxation pathway for all excited vibrational levels. The conclusion from this result is that for the highly excited vibrational states we observed, $v > 5$, V-V relaxation is not a dominant relaxation pathway in complicated polyatomic solvents.

In linear alkane solvents the rate of VER is significantly faster than that in cyclohexane. This result is believed to be partly due to V-V energy transfer pathways in the linear alkanes as suggested by Wilson\textsuperscript{(18-19)} and coworkers. It was demonstrated, however, that the rate of VER cannot be predicted purely on the availability of vibrational resonances in the solvent. In n-hexane the process of vibrational relaxation has "tuned" the I_2 vibrational levels out of resonance with the solvent vibrations within the first 10ps due to the combination of fast V-T and V-V energy exchange. In the lower regions of the I_2 $X$ state potential where VER begins to slow down, V-V relaxation pathways should become more important. In this region of the decay process, neo-hexane compared to n-hexane has more available solvent vibrations which can facilitate relaxation through V-V pathways. Despite the availability of more V-V resonances in neo-hexane, relaxation is found to be faster in n-hexane. We believe that this result indicates there is a wide range of coupling efficiencies which must be considered between I_2 and each available solvent resonance.
The rate of relaxation in n-hexane and CH$_2$Cl$_2$ was found to be very similar despite the fact that CH$_2$Cl$_2$ has no available vibrational accepting modes for single quantum transfers. We believe that this result indicates the possible role of V-R energy transfer as pointed out by Harris et al.\textsuperscript{(22,24)} Furthermore, it suggests that the detailed nature of the collision potential may also be important, particularly when comparing rates of VER in drastically different solvents.

6.2 Summary of $A'$ State Dynamics

We have investigated geminate recombination, vibrational energy decay and electronic relaxation of the iodine excited electronic state. Spectroscopic arguments were given which identify the transient vibrational spectrum as the I$_2$(A', $^3\Pi_{2u}$) state. VER was measured and found to be significantly slower than in the ground $X$ electronic state. Slow VER was attributed to the lower amplitude vibrational motion and lower kinetic energy for the $A'$ state oscillators. This result is qualitatively in agreement with the expected power law scaling of VER rate with vibrational quantum number.\textsuperscript{(11-12)}

The solvent dependence of VER was shown to be largely dependent on the mass of the solvent with slower relaxation occurring in the heavier (more viscous) solvents. This result is consistent with current expectations for relaxation by a V-T (and possibly V-R) mechanism. n-Hexane was found to be an exception to this trend and this result may indicate the importance of V-V energy transfer in that solvent.
The rate of formation of the $A'$ state was found to be inconsistent with the solvent dependence of VER. In other words, the appearance time of the cold vibrational levels of the $A'$ state is not determined by the rate of VER. This indicates that VER alone cannot account for the observed appearance time of the $A'$ state. This is an important result and suggests that the mechanism of geminate recombination on the $A'$ state may be fundamentally different than that of the $X$ state.

Two mechanisms were suggested to account for this observation. These include electronic trapping on higher lying excited electronic states and a reaction intermediate step involving $I^*$Solvent complexes. Although neither mechanism can be ruled out, the solvent dependence has the same trend as that expected for the solvent complex route. The observed trend for the rate of geminate recombination, that is $n$-hexane > $CCl_4$ > $CHCl_3$ > $CH_2Cl_2$, correlates directly with the bonding strength of the $I^*$Solvent complex.

The mechanism of electronic decay was investigated. Spectroscopic estimates of the potential well depth in tandem with temperature measurements of the $A'$ state lifetime indicate that the lifetime shortening observed in alkane solvents cannot be explained by simple thermal dissociation. Franck-Condon calculations of the overlap between $A'$ and $X$ state vibrational levels indicate that the solvent cannot shift the potentials enough to allow $A' \rightarrow X$ intersystem crossing to account for the solvent dependence of the lifetime. This calculation was performed for potentials determined by spectroscopic analysis of the vibrational overtones. Experiments were performed in mixed solvents which indicate that the excited state is
quenched by a complex with alkane solvents which proceeds at a diffusion limited rate. Further experiments in deuterated solvents proved that the lifetime was extremely sensitive to the nature of the vibrational modes in the solvent. These results suggest that electronic decay occurs through formation of exciplexes with the solvent. Furthermore, the rate of relaxation is related to the frequency of the solvent accepting mode with the more efficient energy decay pathways involving higher frequency oscillators in the solvent.

6.3 Geminate Recombination of I and I₂

We have directly observed the geminate recombination of I+I₂ → I₃ following the photoexcitation of I₄ using picosecond transient Raman spectroscopy. By measuring both the Stokes and anti-Stokes Raman spectra at various time delays, we assign the observed transient as the formation of I₃ instead of vibrational cooling. The geminate recombination time of I+I₂ is determined to be 50–100ps in cyclohexane. This process is measured in three other solvents. The geminate recombination rate is arranged as n-hexane > neo-hexane ≥ deuterated cyclohexane ≈ cyclohexane. The slow geminate recombination rate for I+I₂ provides direct experimental evidence for the existence of reaction activation barrier. The lifetime of I₃ is measured to be longer than 500ps and shorter than 500μs. The slight frequency shift after 100ps is interpreted as the formation of I₃ solvent complex in the condensed phase.
7. REFERENCES


[43.] Private communication with G.R. Fleming.


[128.] QCPE program 407, obtained from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University.


8. APPENDICES

8.1 Appendix A: Resonance Raman Enhancement Calculation

In the experiment we detected Raman scattering from $I_2(X)$ levels ranging from $v = 0$ to 52. The primary source of resonance enhancement utilizing a probe wavelength of 266nm (37,600 cm$^{-1}$ photon) is the fully allowed $D \leftarrow X$ transition. The $D^1\Sigma_u^+$ is an ion pair state with a potential minimum at 41,026 cm$^{-1}$ above the $X$ minimum and a well depth of 31,155 cm$^{-1}$.

We calculate the variation of resonance enhancement with the initial level in the $X$ state, keeping the incident laser wavelength constant. Following the general method of Sension and Strauss$^2$, we calculate the Raman polarizability tensor diagonal elements by the expression

$$|\alpha|^2 = \left| \sum_v \mu_{XD}(r_i)\mu_{XD}(r_f) \frac{\langle f | v \rangle \langle v | i \rangle}{\nu_D + \nu_v - \nu_i - \nu_L - i \Gamma_D} \right|^2,$$

where $i$ and $f$ label the initial and final vibrational levels in the $X$ state, and $v$ labels the vibrational levels of the $D$ state. $\nu_D, \nu_v, \nu_i$, and $\nu_L$ are respectively the energies in cm$^{-1}$ of the $D$ state minimum, the position within the $D$ state of the $v$th vibrational level, the position of the $i$th vibrational level in the $X$ state and the laser frequency. $\Gamma_D$ is the homogeneous width of the $D$ state. The $\mu$'s are the electronic transition moments evaluated at the r-centroid values of the $v \leftarrow i$ and $f \leftarrow v$ vibronic transitions. We do not consider r dependent variations in the transition moment function. The numerator contains the product of vibrational overlap integrals between the relevant $X$ and $D$ vibrational levels.
We are not interested in absolute Raman cross sections, thus laser polarization, geometry of the experiment and inhomogeneous broadening are not taken into account. For diatomic iodine in the nondegenerate $D^1 \Sigma_u^+$ state, only the above element of the polarizability tensor is nonzero. The $i$ dependence of this quantity gives the desired dependence of the Raman scattering on $X$ state vibrational level. The calculated dependence of the resonance enhancement on the initially populated level in $X$ is shown in Figure 3.6.

The potentials used in calculating the overlap integrals and r-centroids include both tabulated values from gas phase spectroscopic data and analytical approximations. The $X$ state curve is taken from the turning points calculated by Coxon\(^{57}\) and the $D$ state gas phase curve is a modified Rittner potential due to Tellinghuisen\(^{60}\). Some solvent effects on the $D$ curve can be identified from UV absorption spectra of I\(_2\) in relatively inert solvents. Such experiments\(^{30}\) show that the $D$ shifts down $\approx 1500 \text{ cm}^{-1}$ in n-heptane and cyclohexane solutions. With this modification taken into account, it is reasonable to use gas phase potentials in this calculation.

The vibrational wavefunctions were calculated by numerically solving the Schrödinger equation using a Fortran program implementing the Numerov-Cooley method with Richardson extrapolation.\(^{128}\) These wavefunctions are used to calculate the vibrational overlap integrals for each transition specified by the expression given above. The r-centroid for each transition is the normalized expectation value
of the radial coordinate between the vibrational wavefunctions. The resonance Raman enhancement was calculated for the $X$ initial vibrational levels $v = 0, 5, 10, \ldots, 70$. For Stokes Raman scattering from an initial vibrational level $i$, the fundamental band corresponds to scattering through a level $v$ in the $D$ state and terminating on a final level $f = i + 1$ in $X$. The result of the calculation is plotted in Figure 3.6. All interpolation and numerical integration routines were taken from Numerical Recipes$^{(129)}$. The calculations were carried out on VAX 8800 computer.
8.2 Appendix B: Franck-Condon Calculation

The potentials used in calculating Franck-Condon factors (FCFs) include both tabulated values from gas phase spectroscopic data and analytical approximations. The X state curve was taken from the turning points calculated by Coxon\(^{57}\) and the \(A'\) state gas phase curve from Tellinghuisen\(^{31}\). A cursory inspection of the gas phase potentials reveals that the FCFs for intersystem crossing from \(A'\) to X should be small; most of the probability amplitude for the upper X levels is near the classical turning points, while all of the \(A'\) vibrational amplitude lies near the center of the X well. However, solvent perturbations of the \(A'\) well could conceivably bring it into better Franck-Condon overlap with the X well.

In this work several limits were estimated for the solvent effect on the \(A'\) well. Analysis of resonance Raman overtones indicate that the \(I_2 A'\) well depths may be as shallow as 2143 cm\(^{-1}\) in n-hexane and 1482 cm\(^{-1}\) in CCl\(_4\). If the solvent attractive forces on the I atoms result in a less tightly bound excited state, a concomitant increase in internuclear separation would be expected. A limit was placed on this bond lengthening mechanism by considering an \(I_2\) potential with explicitly attractive and repulsive terms of the well-known form

\[
V(r) = \frac{a}{r^b} - \frac{c}{r^d}
\]

The parameters were first chosen to approximate the spectroscopic gas phase \(A'\) curve. Analytic expressions were derived for the well depth \(D_e\) and the equilibrium internuclear separation \(r_{eq}\) in terms of the values a, b, c, and d. Then the attractive
part of the I-I potential was reduced by lowering the value of the c parameter until
the well depth equaled the value indicated by Raman overtone analysis. Thus varying $D_e$ by reducing the attractive strength c automatically adjusted $r_{eq}$ in a physically
meaningful way.

The gas phase curve is best approximated by an 11-8 potential as shown in
Figure 4.12. Lowering the attractive part of the iodine intramolecular potential to
the worst case limit (75% of the spectroscopic value) such that $D_e = 1112 \text{cm}^{-1}$
yields $r_{eq} = 3.27 \text{Å}$, compared to the gas phase value $r_{eq} = 3.06 \text{Å}^{(31)}$. Using a 12-6
potential yields essentially the same result.

Once limits were set for solvent effects on $r_{eq}$, FCFs were calculated with
Morse potentials of the form

$$V(r) = D_e \{1 - \exp[-b(r - r_{eq})]\}^2$$

The Morse potential shape parameter b was chosen to reproduce the energy levels
obtained from picosecond Raman spectroscopy (refer to text). Parameters for the
various cases were: Case(1) $D_e = 1112 \text{cm}^{-1}$, $b=3.213$, $r_{eq}=3.06$; and Case(2) $D_e = 1112 \text{cm}^{-1}$, $b=3.213$, $r_{eq}=3.27$;

The vibrational wavefunctions were calculated by numerically solving the
Schrödinger equation with a program implementing the Numerov-Cooley method
with Richardson$^{(128)}$ extrapolation. All interpolation and numerical integration
routines were taken from Numerical Recipes$^{(129)}$. Calculations were carried out
on a DEC MicroVax II computer.
Due to the \( \approx 100 \text{ cm}^{-1} \) energy gap at the bottom of the \( A' \) well, several levels are appreciably populated at room temperature: roughly 43% in \( v=0 \), 26% in \( v=1 \), and 16% in \( v=2 \). The FCFs reported here represent averages over the FCFs for transitions between these bottom levels of the \( A' \) well and the nearby vibrational levels within \( k_b T \) in the upper region of the \( X \) well. It is well-known that individual overlap integrals depend critically upon the accuracy of the potential curves used\(^{(130)}\). In this case the choice of well depth for \( A' \) also critically affects the exact value of calculated FCF since this determines which vibrational levels in \( X \) are "near enough" in energy for crossing to take place in solution. However, by averaging over a set of transitions for nearby levels\(^{(11\text{-}12)}\), reasonable predictions can be made about Franck-Condon transition strengths between the \( X \) state and the various \( A' \) state wells considered.
9. VITA

Xiaobing Xu was born on April 4, 1965 in Baoyin, People's Republic of China. She finished her high school education in 1981 from Yangchou High school in Yangchou, China. In 1981, Xiaobing attended The University of Science and Technology of China. She got her B.S. degree in Chemistry in 1986. In 1987, Xiaobing started her Ph.D. program in the Department of Chemistry in Louisiana State University. Her research subject is to study the condensed phase reaction dynamics using picosecond transient Raman spectroscopy. Since then, Xiaobing has published ten papers in refereed journals and seven papers in conference proceedings.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate:  Xiaobing Xu

Major Field:  Chemistry (Physical)

Title of Dissertation:  Ultrafast Measurement of Chemical Dynamics in the Condensed Phase Using Transient Vibrational Spectroscopy

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:  November 6, 1991