

Picosecond time-resolved resonance Raman observation of the iso-CH₂I–I photoproduct from the “photoisomerization” reaction of diiodomethane in the solution phase

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We report a preliminary picosecond Stokes and anti-Stokes time-resolved resonance Raman (267 nm pump and 400 nm probe excitation wavelengths) investigation of the initial formation and vibrational cooling of the iso-CH₂I–I photoproduct species produced after ultraviolet excitation of diiodomethane in room temperature solutions. A comparison of the picosecond resonance Raman spectra with previously reported nanosecond transient resonance Raman spectra and density functional theory computations shows that the iso-CH₂I–I photoproduct species is predominantly responsible for the ~385 nm transient absorption band observed from several picoseconds to nanoseconds after ultraviolet excitation of diiodomethane in the solution phase. Similar results were obtained in both nonpolar solution (cyclohexane solvent) and polar solution (acetonitrile) solvent. The picosecond resonance Raman spectra confirm that the iso-CH₂I–I photoproduct species is formed vibrationally hot within several picoseconds and then subsequently undergoes vibrational cooling on the 4–50 ps time scale. This is consistent with the absorption bands changes occurring over similar times in a recent femtosecond transient absorption study. We discuss a possible qualitative scenario for the formation of the iso-CH₂I–I species that is in agreement with the available gas phase experimental results for the ultraviolet photodissociation reaction of diiodomethane and gas phase collisional deactivation studies of the CH₂I radical. The proposed hypothesis is consistent with the lack of distinct resonance Raman bands in the first few picoseconds of our solution phase spectra of the iso-CH₂I–I photoproduct as well as previously reported femtosecond transient absorption bands that are broad and weak in the 300–500 nm region over the 0.3–3 ps time scale. © 2000 American Institute of Physics. [S0021-9606(00)02241-8]

I. INTRODUCTION

Diiodomethane is used as a reagent to perform cyclopropanation reactions with olefins via activation by a Zn–Cu couple in the Smith–Simmons reaction¹ or by ultraviolet excitation of diiodomethane.^{2–5} Dihalomethanes are also of interest in atmospheric chemistry for both gas and condensed phase reactions since they may be an important natural source of organoiodine and organobromine compounds emitted into the atmosphere.^{6–9} The importance of diiodomethane, dibromomethane, and bromoiodomethane as

possible sources for reactive halogens in the troposphere and in the marine boundary layer has recently been assessed.¹⁰ In addition, diiodomethane has been of interest for investigating the fundamental mechanism of direct photodissociation reactions in both the gas phase and the solution phase.^{11–36}

Ultraviolet excitation (<5 eV photon energy) of diiodomethane results in direct photodissociation to give CH₂I and I or I* fragments.^{11–13} Even though it is energetically possible to form CH₂ and I₂ fragments at wavelengths below 333 nm, this channel is symmetry forbidden^{14,15} and only starts to become noticeable at excitation energies >6.4 eV.^{16,17} Schmitt and Comes¹² found that ultraviolet excitation of gas phase diiodomethane gives rise almost entirely to the CH₂+I or I* channels. Anisotropy measurements from

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molecular beam experiments have shown that gas phase diiodomethane ultraviolet photodissociation occurs on a repulsive potential energy surface on a time scale much smaller than a rotational period of the molecule.^{11,13} Both translational photofragment spectroscopy experiments^{13,18} and infrared fluorescence experiments^{19,20} suggest that the CH₂I fragment receives a large amount of internal excitation from the photodissociation reaction.

While the ultraviolet photodissociation reaction of diiodomethane in the gas phase appears relatively well understood, the situation for its photodissociation in condensed phases remains murky with many conflicting reports. For instance, the excitation of diiodomethane in condensed phases with ultraviolet light,^{21–24} direct photoionization,²⁵ or radiolysis^{26,27} all form photoproducts that have very similar characteristic ~ 385 nm (strong) and ~ 570 nm (weak) absorption bands and these transient absorption bands have been attributed to a variety of species such as trapped electrons,²¹ the CH₂I₂ radical cation,^{25,27} and the isomer of diiodomethane (CH₂I–I).^{23,24} Recently, several research groups have examined the solution phase photodissociation reaction of diiodomethane using femtosecond transient absorption spectroscopy experiments.^{28–30} Probe wavelengths of 620,²⁸ 400,²⁹ and 290–1220 nm³⁰ were used to follow the photoproduct species formed from the ultraviolet photodissociation diiodomethane in room temperature solutions. The ultrafast transient absorption experiments^{28–30} all exhibited similar qualitative features: a fast rise of a few hundred femtoseconds attributed to C–I bond cleavage to give CH₂I and I fragments (we note that this is consistent with the gas phase experiments^{11–20} and resonance Raman investigations of both gas and solution phase diiodomethane^{31–36}) followed by a fast decay of several hundred femtoseconds and a subsequent slower rise of 7–15 ps. However, these results were given three different interpretations that varied due to their assignments of which the photoproduct species was responsible for the transient absorption being monitored during the experiment.^{28–30} The conflicting assignments for the ~ 385 nm and ~ 570 nm transient absorption bands, observed in both the photochemistry experiments^{21–27} and the femtosecond transient absorption experiments,^{28–30} prompted a nanosecond transient resonance Raman investigation of the intense ~ 385 nm transient absorption band in order to unambiguously identify the photoproduct species responsible for it.³⁷ These experimental results and a comparison to the results of density functional theory computations for several proposed photoproduct species clearly demonstrated that the iso-CH₂I–I species is mainly responsible for the ~ 385 nm transient absorption band.³⁷ These results³⁷ suggest that if the ~ 385 nm absorption band seen on the nanosecond time scale is the same as that observed on the ultrafast time scale, then the assignment and interpretation of the femtosecond transient absorption spectra, proposed by Åkesson, is likely correct in its basic features.³⁰ They indicated that ultraviolet excitation of diiodomethane in solutions first leads to C–I bond cleavage (the fast rise time of a few hundred femtoseconds) to give CH₂I and I fragments, which then interact with the solvent cage to give some recombination resulting in a hot iso-CH₂I–I photoproduct (the fast decay of several hun-

ded femtoseconds), which then vibrationally cools (a slow rise of 7–15 ps) to give the relaxed iso-CH₂I–I photoproduct observed at longer times.

In this paper we report picosecond time-resolved resonance Raman experiments that probe the initial formation of the hot iso-CH₂I–I photoproduct following ultraviolet excitation of diiodomethane in room temperature solutions. These experiments establish a connection between the ultrafast time scale and the longer nanosecond time scale observation of the iso-CH₂I–I photoproduct.³⁷ We report results for iso-CH₂I–I formation in both nonpolar (cyclohexane) and polar (acetonitrile) solvents. We examine the pattern of frequency shifts and intensity changes observed in the picosecond spectra and compare them to femtosecond transient absorption results in the solution phase. We then discuss the probable mechanism(s) of iso-CH₂I–I formation and subsequent vibrational cooling.

II. EXPERIMENT

The experiments were carried out using a TR³ apparatus based on optical parametric amplifiers described in detail elsewhere.³⁸ Briefly, a 800 nm pulse generated from a femtosecond Ti:Sapphire oscillator (Spectra Physics) is amplified to 2–3 mJ at 1 kHz in a regenerative amplifier (Spectra Physics). The output from the amplifier was frequency doubled in a 2 mm type I BBO (β -barium borate) crystal to generate the 400 nm probe pulses for TR³ spectroscopy. The 267 nm pump wavelength was the third harmonic of the regenerative amplifier. Typical pump and probe pulse energies at the sample were ~ 5 – 15 μ J with ~ 1 ps pulse duration (FWHM).

Diiodomethane (99% purity) and solvents were obtained commercially and used without further purification. Solutions were prepared at concentration 5×10^{-2} mol dm⁻³ in spectroscopic grade solvents. Both the pump and probe beams had parallel polarization and were focused to a spot size of around 100 μ m in a jet with diameter ~ 500 μ m. Scattered photons were collected at 90° using a parabolic aluminum mirror ($f^{\#} = 0.8$, $f = 4$ cm), dispersed in a triple stage spectrograph and detected by a liquid nitrogen cooled CCD.

Each spectrum presented here was subtracted from a scaled probe before pump and scaled net solvent measurements in order to eliminate solvent and diiodomethane ground state Raman peaks. Copper wires were put into the samples to absorb the photoproduct iodine and the samples exhibited less than a few percent degradation, as indicated by the UV absorption spectra recorded before and after the TR³ measurement. Solvent Raman bands were used to calibrate the spectra with an estimated accuracy of ± 10 cm⁻¹ in absolute frequency. The total acquisition time for the spectrum of each time delay was about 200 s.

III. RESULTS AND DISCUSSION

Figure 1 shows the ultraviolet absorption spectrum of diiodomethane in cyclohexane and acetonitrile solutions with the pump (267 nm) and probe (400 nm) excitation wavelengths for the picosecond resonance Raman experiments in-

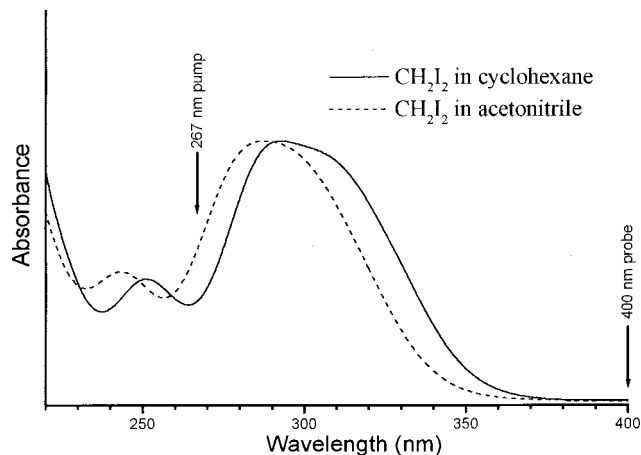


FIG. 1. Absorption spectrum of diiodomethane in cyclohexane solution (solid line) and acetonitrile solution (dashed line) with the pump and probe excitation wavelengths (in nm) for the picosecond time-resolved resonance Raman experiments shown above the spectrum.

indicated above the spectra. The picosecond time-resolved resonance Raman spectra obtained for photoproducts produced from ultraviolet excitation of diiodomethane are shown in Fig. 2 (Stokes spectra) and Fig. 3 (anti-Stokes

spectra) for experiments carried out in a cyclohexane solution and in Fig. 4 (Stokes spectra) and Fig. 5 (anti-Stokes spectra) for experiments in an acetonitrile solution. Figure 6 compares a nanosecond Stokes resonance Raman spectrum of iso-diiodomethane in cyclohexane solution (obtained with 309 nm pump and 416 nm probe excitation wavelengths)³⁷ to the picosecond time-resolved resonance Raman spectra with 30 and 500 ps pump-probe time delays in cyclohexane solution and 15 and 100 ps pump-probe time delays in acetonitrile solution. Table I presents the Raman shifts for the major Raman bands observed for the five spectra shown in Fig. 6. Inspection of Fig. 6 and Table I shows that the resonance Raman spectra are all similar to one another and suggests that the same photoproduct species is observed in the nanosecond transient resonance Raman spectrum and the picosecond time-resolved resonance Raman spectra. Table II compares the experimental fundamental vibrational frequencies (nanosecond resonance Raman spectrum, the picosecond time-resolved resonance Raman spectra of Fig. 6 and previously reported infrared spectra^{23,24}) to the density functional theory computations done for several species (iso-CH₂I-I, CH₂I₂⁺ radical cation or CH₂I radical) proposed to be the photoproduct responsible for the ~385 nm transient absorption observed after ultraviolet photoexcitation of di-

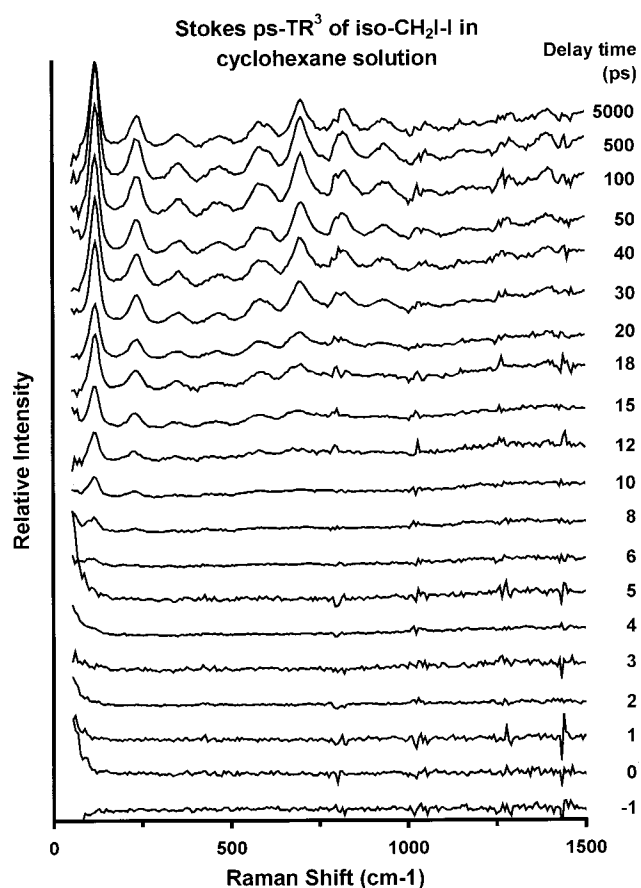


FIG. 2. Stokes picosecond time-resolved resonance Raman spectra of the iso-CH₂I-I photoproduct produced from ultraviolet excitation of diiodomethane in cyclohexane solution. Spectra were obtained at varying pump (267 nm) and probe (400 nm) time delays, which are indicated near each spectrum.

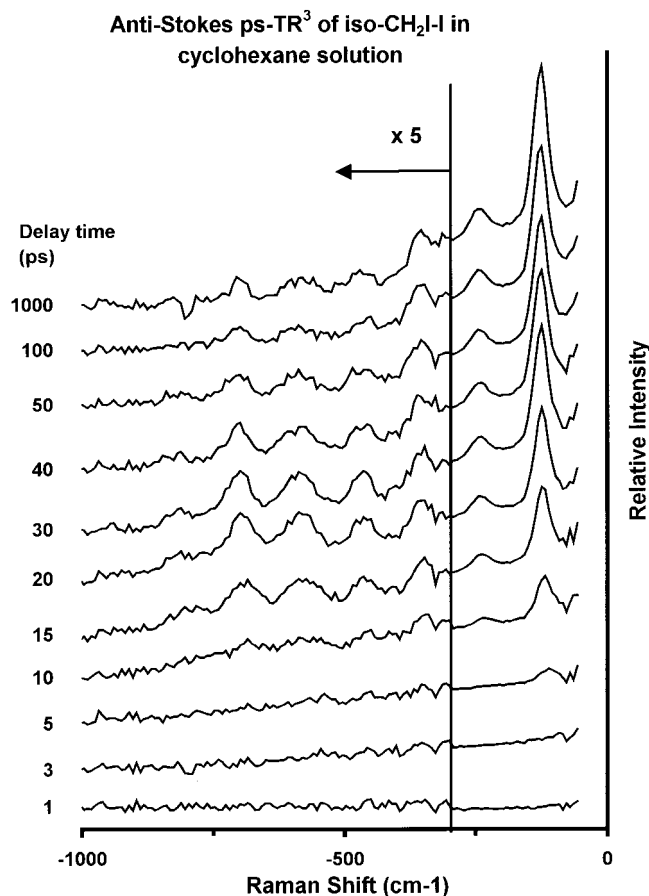


FIG. 3. Anti-Stokes picosecond time-resolved resonance Raman spectra of the iso-CH₂I-I photoproduct produced from ultraviolet excitation of diiodomethane in cyclohexane solution. Spectra were obtained at varying pump (267 nm) and probe (400 nm) time delays, which are indicated near each spectrum.

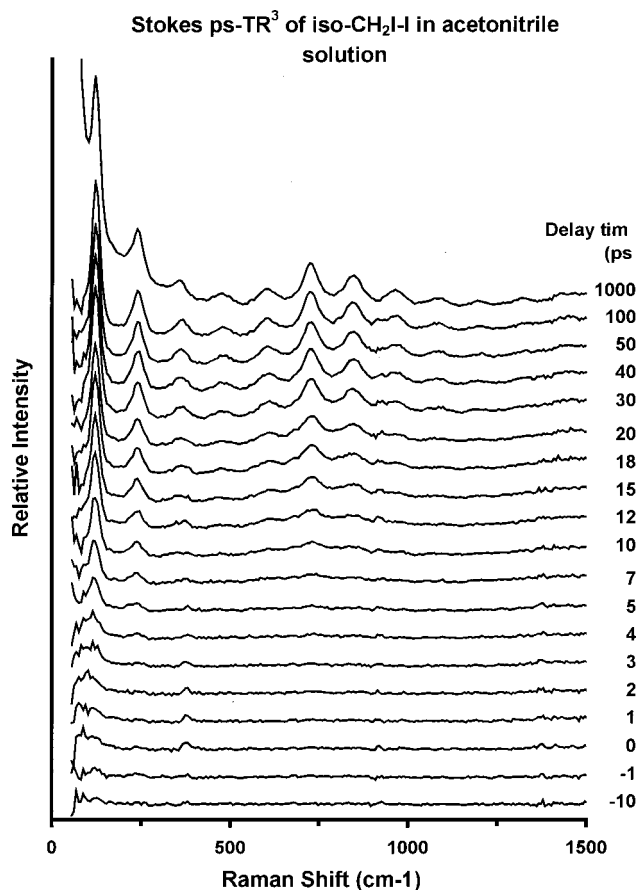


FIG. 4. Stokes picosecond time-resolved resonance Raman spectra of the iso-CH₂I-I photoproduct produced from ultraviolet excitation of diiodomethane in acetonitrile solution. Spectra were obtained at varying pump (267 nm) and probe (400 nm) time delays, which are indicated near each spectrum.

iodomethane in the condensed phase.³⁷ Inspection of Table II shows that the fundamental vibrational bands of the resonance Raman and infrared spectra have values that agree well with those computed for the iso-CH₂I-I species but not with either of the other proposed species (the CH₂I₂⁺ radical cation and the CH₂I radical). The CH₂I radical does not have any low-frequency A₁ vibrational mode in the 100–130 cm⁻¹ region that is clearly due to the photoproduct species observed in all of the resonance Raman spectra. Similarly, the CH₂I₂⁺ radical cation species has only one A₁ mode in the 500–750 cm⁻¹ region while the photoproduct species has two modes, ~700 cm⁻¹ and ~610 cm⁻¹, that have strong combination bands with the lower-frequency ~120 cm⁻¹ mode. We also note the experimental Raman bands assigned to the nominal C–I stretch (ν_3) and CH₂ wag (ν_4) fundamental of the photoproduct species exhibit very good agreement with the infrared bands observed for iso-CH₂I₂ in low-temperature solid matrices.^{23,24} Isotopic shift data from nanosecond resonance Raman spectra³⁷ and infrared spectra^{23,24} as well as density functional theory computed electronic absorption transition energies and oscillator strengths³⁷ are all consistent with the assignment of the photoproduct to the iso-CH₂I-I species. Therefore, the resonance Raman spectra in conjunction with results from den-

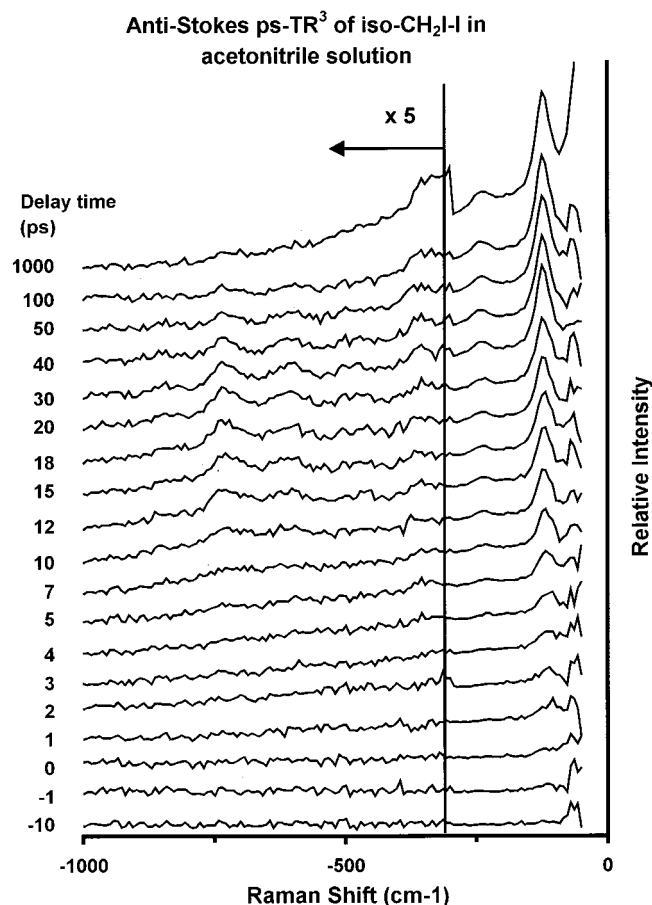


FIG. 5. Anti-Stokes picosecond time-resolved resonance Raman spectra of the iso-CH₂I-I photoproduct produced from ultraviolet excitation of diiodomethane in acetonitrile solution. Spectra were obtained at varying pump (267 nm) and probe (400 nm) time delays, which are indicated near each spectrum.

sity functional theory computations³⁷ unequivocally indicate that the iso-CH₂I-I species is predominantly responsible for the picosecond to nanosecond ~385 nm transient absorption band in solution. A comparison of the resonance Raman spectra shown in Figs. 2–6 indicates that this is true for ultraviolet excitation of diiodomethane in nonpolar solvents like cyclohexane as well as in polar solvents such as acetonitrile.

Examination of the picosecond time-resolved spectra in Figs. 2–5 indicates that Raman bands attributable to the iso-CH₂I-I photoproduct begin to appear within several picoseconds (~8 ps in cyclohexane solution and ~5 ps in acetonitrile solution) after ultraviolet excitation of diiodomethane in the solution phase. These resonance Raman bands grow in intensity as time increases and appear to shift somewhat to higher vibrational frequencies. Table III lists some of the Stokes and anti-Stokes Raman band vibrational frequencies as a function of time for the picosecond data observed in Figs. 2–5. Examination of Table III and Figs. 2–5 shows that the resonance Raman bands tend to shift from lower to higher vibrational frequency and become more intense as the iso-diiodomethane Raman bands appear in the 4–20 ps time scale. The vibrational frequency shifts are only readily

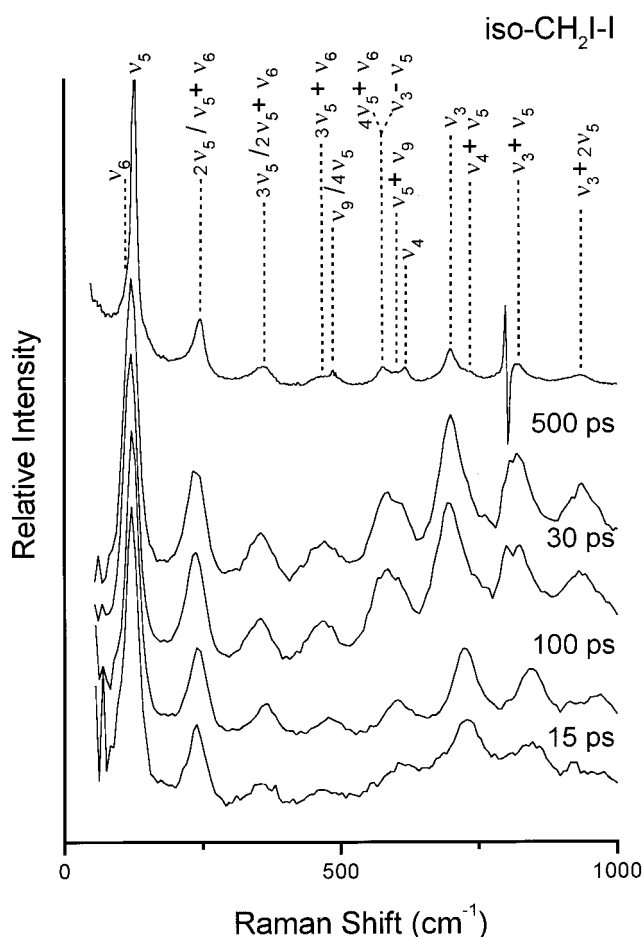


FIG. 6. A nanosecond Stokes resonance Raman spectrum of iso-diiodomethane in cyclohexane solution obtained with 309 nm pump and 416 nm probe excitation wavelengths (top) is compared to selected picosecond time-resolved resonance Raman spectra. Shown are the picosecond resonance Raman spectra with 30 and 500 ps pump-probe time delays in cyclohexane solution and 15 and 100 ps pump-probe time delays in acetonitrile solution and the time delays, which are indicated near each spectrum.

apparent at times between 4 and 18 ps in both cyclohexane and acetonitrile solvents, although the changes seem to occur somewhat faster in acetonitrile. Our picosecond time-resolved resonance Raman results show a good correlation with changes found in the femtosecond transient absorption spectra observed by Akesson and co-workers³⁰ in acetonitrile solvent at times between 3 and 50 ps that they tentatively ascribe to vibrational cooling of the hot iso-diiodomethane photoproduct. Their transient absorption spectra between 3 and 50 ps show absorption in the range of 350–500 nm that is relatively flat, broad, and weak at 3 ps that begins to sharpen and becomes more intense from 3 to 50 ps with most of this change occurring between 3 and 20 ps [see Fig. 1(c) of Ref. 30]. This behavior is very similar to what we observe in our picosecond resonance Raman spectra with most of the vibrational frequency shifts and intensity changes occurring in the first 20 ps or so with some additional sharpening of the Raman bands and an increase of intensity at longer times. Our picosecond time-resolved resonance Raman results confirm that the iso-diiodomethane photoproduct is formed vibrationally hot within several picoseconds and then undergoes subsequent vibrational cooling between 4 and 50 ps. Examination of the anti-Stokes spectral changes as a function of time in cyclohexane solvent (Fig. 3) and acetonitrile solvent (Fig. 5) provides additional support for this interpretation. Between 5 and 100 ps in the anti-Stokes resonance Raman spectra obtained in cyclohexane solvent, the ν_3 , $\nu_3 + \nu_5$, $4\nu_5 + \nu_6/\nu_3 - \nu_5$, $4\nu_5$, and $3\nu_5$ first grow in intensity and then decrease in intensity until they are similar to that observed at 1000 ps. This behavior also indicates a highly excited iso-CH₂I-I species that is vibrationally cooling between 5 and 50 ps. The anti-Stokes resonance Raman spectra in acetonitrile solvent (Fig. 5) also exhibit similar behavior.

The results presented provoke some interesting questions. How is the vibrationally hot iso-CH₂I-I species formed in the first few picoseconds after ultraviolet photoex-

TABLE I. Stokes resonance Raman band vibrational frequencies (in cm⁻¹) observed for the nanosecond resonance Raman spectrum and picosecond resonance Raman spectra shown in Fig. 6.

Tentative Vibrational	Ns ^b	30 ps	500 ps	150 ps	100 ps
Assignment (iso-CH ₂ I-I) ^a	in C ₆ H ₁₂	in C ₆ H ₁₂	in C ₆ H ₁₂	in CH ₃ CN	in CH ₃ CN
ν_6 (sinh of ν_5)	~110?				
ν_5	128	121	121	122	122
$2\nu_5/\nu_5 + \nu_6$	245	239	233	239	239
$3\nu_5/2\nu_5 + \nu_6$	359	356	356	362	362
$3\nu_5 + \nu_6$	472	472	472		
$\nu_9/4\nu_5$	487				
$\nu_3 - \nu_5/4\nu_5 + \nu_6$	579	587	587	604	604
$\nu_5 + \nu_9$	602			604	604
ν_4	619	606	612	604	604
ν_3	701	694	700	729	723
$\nu_4 + \nu_5$	736				
$\nu_3 + \nu_5$	821	826	819	847	848
$\nu_3 + 2\nu_5$	934	931	937		970

^aThe vibrational assignment descriptions are given in Ref. 37.

^bThe values shown are those for the nanosecond transient resonance Raman spectrum at the top of Fig. 2 in Ref. 37.

TABLE II. A comparison of the experimental fundamental vibrational frequencies (in cm^{-1}) found from the transient nanosecond (Ref. 37) and picosecond (this work) resonance Raman spectra and infrared absorption spectra (Refs. 23 and 24) to the calculated B3LYP density functional theory vibrational frequencies from Ref. 37. The corresponding vibrational frequencies for deuterated iso-diiodomethane are given in parentheses. Here str.=stretch; sym.=symmetric; asym.=asymmetric; def.=deformation.

Vibrational mode	B3LYP/ Sadlej TZVP	ns RR in C_6H_{12} (from Ref. 37)	IR in low T solid (Refs. 23 and 24)	30 ps RR in C_6H_{12}	500 ps RR in C_6H_{12}	15 ps RR in CH_3CN	100 ps RR in CH_3CN
$\text{CH}_2\text{I}-(\text{CD}_2\text{I}-\text{I})$							
A' ν_1 , CH_2 sym. str.	3131 (2260)	...	3028 (2213)				
ν_2 , CH_2 scissor	1340 (1011)	...	1373 (1041–1033)				
ν_3 , C–I stretch	755 (645)	701 (640)	714/705 (645)	694	700	729	723
ν_4 , CH_2 wag	619 (746)	619 (496)	622–611 (498–486)	606	612	604	604
ν_5 , I–I stretch	128 (128)	128 (128)	...	121	121	122	122
ν_6 , C–I–I bend	99 (93)	? (~110)	...				
A'' ν_7 , CH_2 asym. str.	3281 (2451)	...	3151 (2378)				
ν_8 , CH_2 rock	865 (697)				
ν_9 , CH_2 twist	447 (318)	487 ?(352.?)	...				
CH_2I_2^+							
A_1 ν_1 , CH sym. str.	3103 (2246)						
ν_2 , CH_2 def.	1365 (1003)						
ν_3 , CI sym. str.	551 (522)						
ν_4 , ICI bend	114 (114)						
B_1 ν_5 , CH asym. str.	3220 (2401)						
ν_6 , CH_2 rock	755 (576)						
A_2 ν_7 , CH_2 twist	983 (696)						
B_2 ν_8 , CH_2 wag	1080 (813)						
ν_9 , CI asym. str.	517 (490)						
CH_2I							
A_1 ν_1 , CH sym. str.	3126 (2252)						
ν_2 , CH_2 def.	1309 (974)						
ν_3 , C–I stretch	614 (576)						
B_1 ν_4 , CH_2 wag	234 (180)						
B_2 ν_5 , CH asym. str.	3288 (2457)						
ν_6 , CH_2 rock	832 (619)						

CH_2I and I photofragments are formed and then examine their interaction with the solvent cage. Molecular beam experiments have shown that ultraviolet excitation of diiodomethane results in a direct photodissociation to CH_2I and I or I^* fragments in a time much less than a rotational period of the diiodomethane molecule.^{11,13} For 266 nm excitation, about 80%–90% of the available photodissociation

energy goes into internal (rovibrational) excitation of the CH_2I fragment and a rough analysis of the data indicates about 40% of this internal excitation goes into rotational degrees of freedom and 60% goes into vibrational degrees of freedom.¹³ Infrared fluorescence experiments^{19,20} also indicate that ultraviolet (248 and 308 nm) photodissociation of diiodomethane results in very highly excited CH_2I radicals.

TABLE III. Selected Stokes and anti-Stokes resonance Raman band frequencies (in cm^{-1}) as a function of delay time (before 30 ps) between the pump and probe excitation pulses (data shown in Figs. 2–5).

Resonance Raman band	In cyclohexane solution							
	Raman shift in cm^{-1}							
	5 ps	10 ps	12 ps	15 ps	18 ps	20 ps	30 ps	
$-\nu_5$	-110	-118	...	-124	...	-124	-124	
$-\nu_3$...	-685	...	-699	...	-699	-699	
ν_5		108	114	121	121	121	121	
$2\nu_5$			226	232	239	239	239	
ν_3				700	700	700	694	
Resonance Raman band	In acetonitrile solution							
	Raman shift in cm^{-1}							
	4 ps	7 ps	10 ps	12 ps	15 ps	18 ps	20 ps	30 ps
$-\nu_5$	-104	-117	-124	-117	-117	-124	-124	-124
$-\nu_3$...	-728	-721	-729	-729	-736	-736	-736
ν_5	115	115	122	122	122	122	122	122
$2\nu_5$	239	233	239	245	239	239	239	239
ν_3			730	724	730	730	730	730

Excitation of diiodomethane with 248 nm light formed CH₂I radicals that produce strong infrared emission throughout the 590–4100 cm⁻¹ region (2.5–17 μm wavelengths) and this indicates a very high degree of vibrational excitation of the CH₂I radical consistent with the results of the molecular beam experiments.¹³ The infrared emission of the CH₂I radical had pronounced broad features in the C–H stretch (~3000 cm⁻¹), CH₂ bend (~1332 cm⁻¹) and C–I stretch (~611 cm⁻¹) regions superimposed on a broad quasicontinuum emission.²⁰ Since the initially formed CH₂I radical receives 80%–90% of the available energy into its internal degrees of freedom,¹³ this suggests that the CH₂I radical is excited into a region with a high density of states (many states per cm⁻¹). For example, Baughcum and Leone²⁰ used a simple harmonic model to estimate that with ~22 000 cm⁻¹ of energy available from the photodissociation could lead to the density of states for the CH₂I radical to be as high as 49 states per cm⁻¹. Therefore, a very large amount of rovibrational states with a very broad energy distribution is likely to be found for the initially formed CH₂I radicals.

The collisional deactivation of the CH₂I radical in the gas phase was also examined by Baughcum and Leone.²⁰ Both randomization of the energy by intramolecular relaxation and by molecular collisions as well as the depletion of the CH₂I radical vibrational energy via vibrational to vibrational (*V*→*V*) and vibrational to translational or rotational (*V*→*T,R*) energy transfer processes during these molecular collisions will be important in determining the energy partitioning and flow during the solvent cage interaction and recombination of the CH₂I and I fragments to form the iso-CH₂I-I photoproduct. Baughcum and Leone²⁰ found that collisional deactivation occurs very fast for the CH₂I radicals in CH₂I₂ (on the order of five to ten hard sphere collisions and removing about 1250–1900 cm⁻¹ energy per collision) probably by efficient *V*–*V* energy transfer mechanisms. However, collisional deactivation of the CH₂I radical occurred more slowly in argon gas (about 70–140 hard sphere collisions and removing about 90–140 cm⁻¹ of energy per collision).²⁰ This indicates that the type of solvent molecule significantly influences the rate of energy loss by the CH₂I radical to its solution phase environment. It is very interesting to note that two femtosecond transient absorption studies on ultraviolet photodissociation of diiodomethane in the solutions phase suggested that recombination of the CH₂I and I fragments in the solution phase occurs mostly via single-collision geminate recombination.^{28,30} Harris and co-workers²⁸ estimated that the single collision geminate recombination of the CH₂I and I fragment occurs on the 300–500 fs time scale in room temperature CCl₄ solutions. Similarly, the recent study by Åkesson and co-workers³⁰ for the ultraviolet photodissociation of diiodomethane in room temperature acetonitrile solution observed the appearance of a 350 nm subband at 500 fs in their transient absorption spectrum tentatively ascribed to the CH₂I radical, which was then followed by the appearance of the “product-like” spectra in ~1 ps. Both of these studies indicate that recombination of the initially produced CH₂I and I fragments in the solution phase occurs around 500–1000 fs after one (or a few) solvent collisions(s). This strongly suggests that the initially

formed iso-CH₂I-I product species is formed with a very high degree of internal excitation and likely to house enough energy to have a broad quasicontinuum of populated vibrational states. Therefore, one could expect that there is not much initial population in any particular vibrational energy level and the resonance Raman cross sections would also tend to be fairly low for higher-energy vibrational states. The very broad femtosecond transient absorption between 300 and 500 nm and low oscillator strength of these absorption bands in the 300 fs to 3 ps range³⁰ are consistent with this hypothesis.

With the initial internal excitation of the iso-CH₂I-I product spread over a broad quasicontinuum of states of which any particular state has relatively little of the overall population and the high-energy levels populated also having low resonance Raman cross sections, the initial iso-CH₂I-I product resonance Raman spectra during the first few picoseconds may appear as a weak broad quasicontinuum with little discernible features until the iso-CH₂I-I product undergoes enough consolidation via intramolecular relaxation and molecular collisions so that it has a fewer number of populated vibrational states at lower energy with larger resonance Raman cross sections. This behavior is similar to what we observe in our picosecond resonance Raman spectra probing the initial formation of the iso-CH₂I-I photoproduct at 400 nm following 267 nm excitation of diiodomethane in either cyclohexane or acetonitrile solutions (see the first few ps spectra in Figs. 2–5).

We note the caveat that our present results for probing the initial formation of the iso-CH₂I-I photoproduct species following ultraviolet excitation of diiodomethane in the solution phase are preliminary in nature. Further experimental and theoretical work is needed to better elucidate how the iso-CH₂I-I species is formed in the solution phase, particularly from 100 fs to 5 ps after photoexcitation. Several types of experiments should prove useful in probing the initial formation of the iso-CH₂I-I species. For example, using pump excitation wavelengths closer to the threshold for dissociation would make less energy available to partitioning into internal excitation of the CH₂I radical (and then to the iso-CH₂I-I product). This would lower the density of states populated and the initial internal excitation would also be shifted to lower energy. This may allow discernible vibrational features of the initially formed iso-CH₂I-I photoproduct species to be seen at earlier delay times. Similarly, one could also change the probe excitation wavelength to be more in resonance with the higher-energy vibrationally excited iso-CH₂I-I species and better examine the shorter delay times associated with the vibrationally hot iso-CH₂I-I species. We plan to attempt these types of experiments with ~1 ps resolution. These ~1 ps resolution experiments will enable us to gain a better idea of what experimental conditions are best suitable to resolving the initial 100 fs to 1 ps of the photodissociation process, leading to the formation of the iso-CH₂I-I photoproduct species. At that time, further experiments using ~100–200 fs time-resolved resonance Raman experiments may also prove helpful to better understand how the solvent cage induces formation of the iso-CH₂I-I species.

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