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<td>Li, YL; Wang, D; Phillips, DL</td>
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Time-resolved resonance Raman spectroscopy and density functional theory investigation of the CH$_2$I–I isomer and CH$_2$I$_2$···I molecular complex products produced from ultraviolet photolysis of CH$_2$I$_2$ in the solution phase: Comparison of the structure and chemical reactivity of polyhalomethane isomers and polyhalomethane–halogen atom molecular complexes

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(Received 10 July 2002; accepted 14 August 2002)

Time-resolved resonance Raman spectra are reported for different concentrations of CH$_2$I$_2$ in cyclohexane solution. The CH$_2$I–I species is observed at low concentrations and it decays on the order of tens of nanoseconds to almost no signal at 100 ns and no other signal is observed up to 15 microseconds. Two species are observed at high concentrations. The first species CH$_2$I–I spectra and lifetime are about the same as that found at low concentration of CH$_2$I$_2$ parent molecule and the second species is a CH$_2$I$_2$···I molecular complex observed on the nanosecond to microsecond time scale and formed from bimolecular reaction of iodine atoms with CH$_2$I$_2$ molecules. The chemical reactivity of the CH$_2$I–I species and the CH$_2$I$_2$···I molecular complex towards carbon double bonds were investigated using density functional theory calculations. The structure and properties of the CH$_2$I–I species and the CH$_2$I$_2$···I molecular complex and their reaction towards ethylene were compared. The CH$_2$I–I species and the CH$_2$I$_2$···I both have weak I–I bonds that are the chromophores responsible for similar intense transient absorption bands. However, the geometry of the I–I bond relative to the C–I bond is noticeably different for these two species and this leads to distinctly different chemical reactivity toward carbon double bonds. The CH$_2$I–I isomer readily reacts with ethylene to produce a cyclopropane product and I$_2$ leaving group via a single step and low barrier to reaction while the CH$_2$I$_2$···I molecular complex reacts with ethylene to form an ethylene/I intermediate and a CH$_2$I$_2$ leaving group. Probable ramifications for other related molecule–halogen atom complexes are briefly discussed. © 2002 American Institute of Physics.

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I. INTRODUCTION

The photochemistry and chemistry of polyhalomethane molecules have long been an active subject of investigation from several viewpoints. A number of polyhalomethane molecules such as CH$_2$I$_2$, CH$_3$Br$_2$, CH$_2$C$_1$I, CH$_3$BrI, CHBr$_3$, and others have been observed in the troposphere and are thought to be important sources of reactive halogens in the atmosphere. Some polyhalomethanes have also found utility as reagents for the cyclopropanation of olefins and diiodomethylation of carbonyl compounds in synthetic chemistry. For example, the ultraviolet photoexcitation of CH$_2$I$_2$ in the presence of olefins in room temperature solutions can be used to produce cyclopropanated products in reasonably good yields with high stereospecificity. Polyhalomethane molecules have also been useful molecules to study in order to better understand fundamental aspects of photodissociation reactions. Molecular beam anisotropy measurements indicate these reactions occur in time much less than a rotational period of the parent molecule. Time-of-flight photofragment spectroscopy experiments for several polyhalomethanes indicate that the polyatomic fragments usually receive substantial degrees of internal excitation of their rotational and/or vibrational degrees of freedom. Resonance Raman studies of a range of polyhalomethanes showed that the photodissociation reactions typically had significant multidimensional character and short-time dynamics qualitatively consistent with a semi-rigid radical description of the dissociation in both gas and solution phases.

Ultraviolet excitation of polyhalomethanes in condensed phase environments leads to production of photoproducts that have characteristic transient absorption bands in the ultraviolet and visible regions that were tentatively assigned to be due to a range of possible species such as cations, radicals, and/or isomer products. Recent femtosecond transient absorption experiments suggest these species are formed by geminate recombination of the fragments within the solvent cage. Time-resolved resonance Raman experiments in conjunction with density functional theory cal-
culations for proposed photoproduction species demonstrated that polyhalomethane isomer products (isopolyhalomethanes) were mostly responsible for the ultraviolet transient absorption bands observed on the picosecond and nanosecond time scales in liquid solutions. 64–63

Both theory and experiment were recently used to examine the chemical reactivity of isopolyhalomethanes toward olefins. 64–66 The chemical reactivity of isodiiodomethane (CH$_2$I$_2$–I), the CH$_2$I radical and the CH$_2$I$^+$ cation species toward ethylene was investigated using density functional theory calculations. 64 This study showed the CH$_2$I–I species easily reacts with ethylene to produce a cyclopropane product and I$_2$ leaving group via a one-step reaction with a barrier height of about 2.9 kcal/mol. 64 However, the CH$_2$I radical and CH$_2$I$^+$ cation species have much more difficult reactions with ethylene to make a cyclopropane product via a two step mechanism that forms relatively stable iodopropyl radical or iodopropyl cation intermediates and have much greater barriers to reaction for the rate-determining step to form cyclopropane than the CH$_2$I–I species. 64 The reaction of CH$_2$I–I with cyclohexene was directly probed using time-resolved resonance Raman spectroscopy (TR$^3$) experiments 66 under conditions similar to the original photochemical studies of Blomstrom, Herbig and Simmons 10 that found significant conversion of CH$_2$I$_2$ into the norcarane product (e.g., the cyclopropanated product of cyclohexene). 10 These TR$^3$ experiments demonstrated that CH$_2$I–I reacts with cyclohexene on the 5–10 ns time scale and then almost immediately forms a CH$_2$: cyclohexene complex. 66 This in conjunction with the results from the density functional theory calculations indicates that CH$_2$I–I is the carbenoid (or methylene transfer agent) mostly responsible for the cyclopropanation of olefins when utilizing the ultraviolet photolysis of CH$_2$I$_2$. Further experimental and theoretical work indicates that a number of isopolyhalomethanes can act as carbenoids with varying degrees of reactivity towards carbon double bonds. 55,67,68

TR$^3$ experiments indicate that the CH$_2$I–I isomer species decays fairly fast in cyclohexane solution (on the order of tens of nanoseconds and there is almost no CH$_2$I–I signal by 80–100 ns) 66 while some pulse radiolysis and laser flash photolysis experiments for a number of iodoalkanes 69–73 observed a transient absorption spectrum on the microsecond time scale that is very similar to that observed for CH$_2$I–I on the picosecond to nanosecond time scales. 51–53 In this paper, we report TR$^3$ experiments done at different concentrations of CH$_2$I$_2$ in cyclohexene solution. At low concentration we mainly observe the CH$_2$I–I species and see it decay on the order of tens of nanoseconds to almost no signal at 100 ns and nothing else is observed up to 15 microseconds. At high concentration we observe spectra from two species. The first species is CH$_2$I–I and its spectra and decay are essentially identical to that found at low concentration of CH$_2$I$_2$ parent molecule. The second species is a CH$_2$I$_2$:I$^+$ molecular complex that appears to be formed from bimolecular reaction of iodine atoms with CH$_2$I$_2$ molecules. Density functional theory computations are used to explore the chemical reactivity of the CH$_2$I–I species and the CH$_2$I$^+$:I$^+$ molecular complex. We compare the structure and properties of the CH$_2$I–I species and the CH$_2$I$^+$:I$^+$ molecular complex and their reaction towards ethylene. Our results indicate that both the CH$_2$I–I species and the CH$_2$I$^+$:I$^+$ molecular complex have loosely bound I–I bonds that give rise to similar strong transient absorption bands. However, their structures are noticeably different (especially for the geometry of the I–I bond relative to the C–I bond) and this leads to distinctly different chemical reactivity toward carbon double bonds. We briefly discuss implications for other related molecule–halogen atom complexes.

II. EXPERIMENT AND CALCULATIONS

Samples of CH$_2$I$_2$ (99%) were prepared with 0.25 M and 0.62 M concentrations in spectroscopic grade cyclohexene solvent. The nanosecond time-resolved resonance Raman (TR$^3$) experimental apparatus and methods have been detailed elsewhere 66,68 so only a brief description will be given here. The pump (266 nm) and probe (416 nm) excitation wavelengths were obtained from the fourth harmonic and the first Stokes hydrogen Raman shifted laser line of the third harmonic of two nanosecond pulsed Nd:YAG lasers (Spectra Physics GCR-150-10 and LAB-170-10). A pulse delay generator (Stanford Research Systems) was used to set and synchronize the firing of both the flashlamps and Q-switches of the two lasers in order to control the relative timing of the pump and probe laser pulses. A fast photodiode and its output displayed on a 500 MHz oscilloscope (Hewlett-Packard) was used to measure the relative timing between the two laser pulses.

The pump and probe laser beams were loosely focused onto a flowing liquid stream of sample using a near-collinear and backscattering geometry. Reflective optics were used to collect the Raman scattered light and image it through a depolarizer and entrance slit of a 0.5 meter spectograph whose grating dispersed the light onto a liquid nitrogen cooled CCD detector. The CCD collected signal for about 300 s before being readout to an interfaced PC computer and 5 to 10 of these readouts were summed to obtain a spectrum at each time delay. For each time delay, a probe only spectrum, a pump only spectrum in the probe wavelength region, and a pump–probe spectrum were obtained. A background scan was also acquired before and after each experimental trial. The known vibrational frequencies of the cyclohexene solvent Raman bands were calibrated to use the Raman shifts of the resonance Raman spectra. Probe only and pump only spectra were subtracted from the pump–probe spectra so as to remove solvent and parent Raman bands and obtain the time-resolved resonance Raman spectra.

The reactions of the CH$_2$I–I isomer species and the CH$_2$I$^+$:I$^+$ molecular complex with ethylene were investigated using density functional theory calculations. The stationary structures were fully optimized using C$_2$ symmetry and B3LYP theory 74–78 and the 6-311G** basis sets. 79–81 Analytical frequency computations were performed to confirm the optimized structure to be a minimum or first-order saddle point and to also find the zero-point energy correction. Intrinsic reaction coordinate (IRC) calculations 82 were also performed to confirm the transition states connected the related reactants and products and
to characterize the reaction coordinate. The GAUSSIAN 98W program suite was used for all of the calculations.

III. RESULTS AND DISCUSSION

A. Time-resolved resonance Raman spectra, density functional theory computational results, and assignment of CH2–I and CH2···I species to the time-resolved resonance Raman spectra

Figure 1 shows time-resolved resonance Raman spectra obtained after 266 nm photolysis of 0.25 M CH2I2 in cyclohexane solution at delay times ranging from about 0 ns to 10 µs. Figure 2 presents an expanded view of the 0 ns, 20 ns, 80 ns and 500 ns spectra of Fig. 1. The spectra observed at 0 ns, 20 ns and 80 ns in Figs. 1 and 2 are in very good agreement with those obtained in earlier studies using similar concentrations of CH2I2 in cyclohexane solvent. The Raman bands observed in Figs. 1 and 2 are mainly due to the CH2–I isomer species. The larger CH2–I isomer Raman bands include the nominal I–I stretch fundamental (ν5) at ~123 cm⁻¹ and its overtones (2ν5 and 3ν5), the nominal C–I stretch fundamental (ν3) at ~698 cm⁻¹, and the nominal CH2 wag fundamental (ν4) at ~620 cm⁻¹. Table I presents selected optimized geometry parameters for the CH2–I isomer product.

Figure 3 presents time-resolved resonance Raman spectra obtained after 266 nm photolysis of 0.62 M CH2I2 in cyclohexane solution at delay times ranging from about 0 ns to 15 µs. Figure 4 gives an enlarged view of the 0, 10, 20, and 80 ns, and 15 µs spectra of Fig. 3. Comparison of the spectra shown in Figs. 3 and 4 to those in Figs. 1 and 2 shows that there are clearly two species seen after photolysis of higher CH2I2 concentrations in Figs. 3 and 4. The first species observed in the 0, 10, and 20 ns spectra of Figs. 3 and 4 are clearly the CH2–I isomer species that are also seen in the lower concentration spectra of Figs. 1 and 2 at the same delay times. The appearance of the second species has a very strong dependence on the concentration of CH2I2 used in the experiments and the second species has a significantly longer lifetime on the order of microseconds. This suggests the second species may be formed from a bimolecular reaction and not from a geminate recombination process as was mostly the case for the CH2–I species. Several previous laser flash photolysis and pulse radiolysis studies of iodoalkanes have observed transient absorption spectra on the nanosecond to microsecond time scale with an absorption maximum around 390 nm similar to that observed for the CH2–I species on the picosecond to nanosecond time scales. These longer lived transient absorption bands were assigned to iodoalkane–iodine molecular complexes like the CH3I···I species for the case of photolysis of CH3I in solutions. These iodoalkane–iodine molecular complexes were thought to be formed from bimolecular reaction of I atoms (that escape the solvent cage associated with the initially produced CH3 and I fragments) with an iodoalkane molecule. Thus, we suspect that the second species observed in Figs. 3 and 4 is the analogous CH2I2···I molecular complex. We have done density functional theory calculations for this species to estimate its structure and vibrational frequen-
cies (shown in Tables I and II, respectively). The second species time resolved vibrational frequencies in Figs. 3 and 4 are in excellent agreement with those predicted by the B3LYP computed values shown in Table II. This indicates the second species is most likely indeed the CH$_2$I$_2$ molecule and its Raman band vibrational frequencies can be assigned as follows: the strong band at 118 cm$^{-1}$ is assigned to the nominal I–C–I bend mode ($v_9$) that is computed to be at 118 cm$^{-1}$; the Raman band at 487 cm$^{-1}$ is assigned to the nominal I–C–I symmetric stretch ($v_8$) computed to be at 582 cm$^{-1}$.

**B. Comparison of the structures of CH$_2$I–I and CH$_2$I$_2$ species and their chemical reactivity toward ethylene**

Figure 5 displays schematic diagram of the computed optimized geometry determined from the B3LYP/6-311G**

**TABLE I.** Parameters for the optimized geometry computed from the B3LYP density functional theory computations for the CH$_2$I–I isomer and the CH$_2$I$_2$–I molecular complex proposed as photoproduct species formed following ultraviolet excitation of CH$_2$I$_2$ in cyclohexane solution. Bond lengths are in Å and bond angles are in degrees.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CH$_2$I–I isomer</th>
<th>CH$_2$I$_2$–I molecular complex</th>
</tr>
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<tr>
<td>B3LYP Calc.</td>
<td>B3LYP Calc.</td>
<td>B3LYP Calc.</td>
</tr>
<tr>
<td>C–I</td>
<td>1.957</td>
<td>C–I$_2$</td>
</tr>
<tr>
<td>I–I</td>
<td>3.042</td>
<td>C–I$_2$</td>
</tr>
<tr>
<td>C–H</td>
<td>1.091</td>
<td>I$_1$–I$_2$</td>
</tr>
<tr>
<td>C–I–I</td>
<td>118.2</td>
<td>C–I$_1$</td>
</tr>
<tr>
<td>I–C–H</td>
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<td>I$_1$–C–I$_2$</td>
</tr>
<tr>
<td>D(H–C–I–I)</td>
<td>90</td>
<td>D(I$_1$–C–I$_2$–I$_3$)</td>
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</table>

$^a$Values from Ref. 56.

$^b$Values from Ref. 64.

**TABLE II.** Comparison of experimental vibrational frequencies (in cm$^{-1}$) found for the two species observed in the time-resolved resonance Raman (TR$^3$) spectra of Figs. 1–4 to the B3LYP calculated vibrational frequencies for the species whose optimized geometry is given in Table I.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>B3LYP Calc.</th>
<th>TR$^3$ spectra</th>
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<td>CH$_2$I–I isomer</td>
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<tr>
<td>Possible assignment</td>
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<tr>
<td>$A^1v_1$, C–H sym. stretch</td>
<td>3131</td>
<td>This work</td>
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<td>$v_2$, C–H$_3$ scissor</td>
<td>1340</td>
<td>From Ref. 56</td>
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<tr>
<td>$v_3$, C–I stretch</td>
<td>755</td>
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<tr>
<td>$v_4$, CH$_2$ wag</td>
<td>619</td>
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<tr>
<td>$v_5$, I–I stretch</td>
<td>128</td>
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<td>$v_6$, C–I–I bend</td>
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<td>$A^1v_7$, C–H asym. stretch</td>
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<tr>
<td>$v_8$, CH$_2$ rock</td>
<td>865</td>
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<tr>
<td>$v_9$, CH$_2$ twist</td>
<td>447</td>
<td></td>
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<tr>
<td>CH$_2$I$_2$–I molecular complex</td>
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<td></td>
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<tr>
<td>Possible assignment</td>
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<tr>
<td>$A^1v_1$, C–H asym. stretch</td>
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<td>$v_2$, C–H sym. stretch</td>
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<td>$v_3$, H–C–H bend (in plane)</td>
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<td>$v_8$, I$_1$–C–I$_2$ sym. stretch</td>
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<td>$v_9$, I$_1$–C–I$_1$ bend (in plane)</td>
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<td>$v_{10}$, I$_2$–I$_3$ stretch</td>
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<td>$v_{11}$, I$_1$–C–I$_2$ bend (o.p.)</td>
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<td>$v_{12}$, C–I$_3$ stretch+H–C–H asym. bend</td>
<td>31</td>
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**TABLE II.** Parameters for the optimized geometry computed from the B3LYP density functional theory computations for the CH$_2$I–I isomer and the CH$_2$I$_2$–I molecular complex proposed as photoproduct species formed following ultraviolet excitation of CH$_2$I$_2$ in cyclohexane solution. Bond lengths are in Å and bond angles are in degrees.

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<td>I–C–H</td>
<td>119.1</td>
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<tr>
<td>D(H–C–I–I)</td>
<td>90</td>
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computations for the CH₂–I isomer, the CH₃ radical and CH₂I₂···I molecular complex species as well as the transition state(s) for the reaction of these species with ethylene. The Cartesian coordinates, total energies and vibrational zero-point energies for selected stationary structures given in Table I for the CH₂I–I isomer species and the CH₂I₂···I molecular complex reveals that they have some similarities as well as significant differences in their structures. Both species contain a loosely bound I–I bond that is somewhat weaker in the CH₂I₂···I molecular complex (3.357 Å) compared to the CH₂I–I isomer species (3.019 Å). This difference in the I–I bond is accompanied by significant differences in other parts of the structures. For example, the C–I–I angle is substantially different in the two species with a value of about 122° for the CH₂I–I species compared to about 83.7° for the CH₂I₂···I molecular complex. This difference in the C–I–I angle leads to a small but noticeable interaction between the C atom and the loosely bound terminal I atom (C–I distance of 3.788 Å and contributes to the low frequency mode $v_{12}$ at 31 cm⁻¹) for the CH₂I₂···I molecular complex. This interaction is essentially absent in the CH₂I–I isomer species. We note that the structures for the isomers of a range of polyhalomethanes have C–X–X or C–Y–X angles in the 115° to 150° range and this suggests that the terminal halogen atom of the halogen–halogen bond has little direct interaction with the carbon atom for isopolyhalomethanes. The C–I bond lengths are noticeably different with the CH₂I–I isomer species (1.968 Å) being noticeably stronger than those in the CH₂I₂···I molecular complex (2.161 Å and 2.144 Å) which are close to those of the parent CH₂I₂ molecule. These results suggest the C–I bonds are modestly perturbed by the I–I bonding in the CH₂I₂···I molecular complex compared to the parent CH₂I₂ molecule while the CH₂I–I isomer species experiences substantially stronger perturbation of its C–I bond due to the I–I bond formation. The I–C–H angles are in the 106.4° to 108.7° range for the CH₂I₂···I molecular complex and consistent with the C atom having $sp^3$ bonding character as in the CH₂I₂ parent molecule. However, the CH₂I–I isomer has I–C–H angles of about 118.1° and more consistent with the C atom having $sp^2$ bonding character.

The DFT calculations found the HOMO of the CH₂I₂···I molecular complex to be $0.065S(C) + 0.038P_y(P_y) - 0.128S(I_1) + 0.435P_x(P_x) + 0.038P_y(P_y) + 0.094P_z(P_z) - 0.218P_x(P_x) + 0.039S(H_4) - 0.044S(H_4) + 0.090S(I_1) + 0.552P_x(P_x) + 0.421P_y(P_y)$. The greatest contribution comes from the I₂ and I₃ atoms and is consistent with the C atom having $sp^3$ and consistent with the I₂–I₃ bond formation. There are also smaller contributions from the C atom and the I₂ atoms suggesting that there is also some modest interaction between these atoms and the I₂–I₃ bond formation. This is consistent with the C atom interaction with the I₂ atom and its contribution to the low frequency mode $v_{12}$ at 31 cm⁻¹ for the CH₂I₂···I molecular complex. The DFT computations found the HOMO of the CH₂I–I isomer species to be $-0.234S(I_2) + 0.745P_x(I_2) + 0.069S(H_2) - 0.042S(H_2)$ and this is consistent with the I–I bond formation.

The I–I bond formation leads to little changes in the C–I bond lengths and I–C–H bond angles in the CH₂I₂···I molecular complex compared to the parent CH₂I₂ molecule. This suggests the charge distribution and chemical reactivity of the CH₂I₂···I molecular complex will be close to that of a

**Fig. 3.** Overview of 416 nm time-resolved resonance Raman spectra obtained after 266 nm photolysis of 0.62 M CH₂I₂ in cyclohexane solution. Spectra are shown for time delays of about 0, 10, 20, 80, and 800 ns, and 1, 3, 5, 8, 10, and 15 μs. The assignments of the larger Raman bands to the CH₂I–I isomer and the CH₂I₂···I molecular complex are shown above the spectra (see text and Table II). The assignments for the CH₂I₂···I molecular complex are shown in parentheses. The asterisks mark regions where solvent/parent subtraction artifacts are present and the daggers label stray light or ambient light artifacts.

**Fig. 4.** Expanded view of the time-resolved resonance Raman spectra of Fig. 1 for time delays of 0 ns, 10 ns, 20 ns, and 15 μs. The assignments of the larger Raman bands to the CH₂I–I isomer and the CH₂I₂···I molecular complex are shown above the spectra (see text and Table II). The assignments for the CH₂I₂···I molecular complex are shown in parentheses. The asterisks mark regions where solvent/parent subtraction artifacts are present and the daggers label stray light or ambient light artifacts.

Fig. 5 are available in the supporting information. Comparison of the structures shown in Fig. 5 and geometry parameters presented in Table I for the CH₂I–I isomer species and the CH₂I₂···I molecular complex reveals that they have some similarities as well as significant differences in their structures. Both species contain a loosely bound I–I bond that is somewhat weaker in the CH₂I₂···I molecular complex (3.357 Å) compared to the CH₂I–I isomer species (3.019 Å). This difference in the I–I bond is accompanied by significant differences in other parts of the structures. For example, the C–I–I angle is substantially different in the two species with a value of about 122° for the CH₂I–I species compared to about 83.7° for the CH₂I₂···I molecular complex. This difference in the C–I–I angle leads to a small but noticeable interaction between the C atom and the loosely bound terminal I atom (C–I distance of 3.788 Å and contributes to the low frequency mode $v_{12}$ at 31 cm⁻¹) for the CH₂I₂···I molecular complex. This interaction is essentially absent in the CH₂I–I isomer species. We note that the structures for the isomers of a range of polyhalomethanes have C–X–X or C–Y–X angles in the 115° to 150° range and this suggests that the terminal halogen atom of the halogen–halogen bond has little direct interaction with the carbon atom for isopolyhalomethanes. The C–I bond lengths are noticeably different with the CH₂I–I isomer species (1.968 Å) being noticeably stronger than those in the CH₂I₂···I molecular complex (2.161 Å and 2.144 Å) which are close to those of the parent CH₂I₂ molecule. These results suggest the C–I bonds are only modestly perturbed by the I–I bonding in the CH₂I₂···I molecular complex compared to the parent CH₂I₂ molecule while the CH₂I–I isomer species experiences substantially stronger perturbation of its C–I bond due to the I–I bond formation. The I–C–H angles are in the 106.4° to 108.7° range for the CH₂I₂···I molecular complex and consistent with the C atom having $sp^3$ bonding character as in the CH₂I₂ parent molecule. However, the CH₂I–I isomer has I–C–H angles of about 118.1° and more consistent with the C atom having $sp^2$ bonding character.
CH₂I₂ molecule with an I atom nearby. In contrast, the I–I bond formation in the CH₂I–I isomer leads to significant changes in the C–I bond compared to either the parent CH₂I₂ molecule or the CH₂I radical. The difference between the parent CH₂I₂ molecule compared to sp<sup>3</sup> bonding in the CH₂I–I isomer and the CH₂I radical have both sp<sup>2</sup> bonding but the C–I bond is still significantly shorter and stronger in the CH₂I–I isomer (1.968 Å) compared to the CH₂I radical (2.052 Å). This leads the CH₂I–I isomer to have a significantly different charge distribution than that found in the CH₂I radical and the CH₂I₂ parent molecule. The CH₂I–I species has a CH₂I<sup>−</sup>I<sup>−</sup> radical ion pair character and very different chemical reactivity towards C≡C bonds than the CH₂I radical or the CH₂I₂ molecule. Previous density functional theory calculations demonstrated that the CH₂I–I isomer readily re-

FIG. 5. Schematic diagram of the computed optimized geometry determined from the B3LYP/6-311G** computations for the CH₂I–I isomer, the CH₂I radical and CH₂I₂···I molecular complex species as well as the transition state(s) for the reaction of these species with ethylene. TS1 = transition state for reaction of CH₂I–I with ethylene. TS2 = transition state for reaction of CH₂I radical to produce an iodopropyl radical (IM). TS3 = transition state for reaction of the iodopropyl radical to form a cyclopropane product and I atom leaving group. TS4 = transition state for reaction of CH₂I₂···I molecular complex with ethylene to produce an iodopropyl radical (IM). TS5 = transition state for reaction of CH₂I₂···I molecular complex with ethylene to produce an ethylene/I species and CH₂I₂ leaving group. Selected structural parameters are shown for each species with the bond lengths in Å and the bond angles in degrees. Values for the reactions of the CH₂I–I isomer and the CH₂I radical are from Ref. 64. The values given in parentheses are those found using the Sadlej-pVTZ basis set.
acts with ethylene to give a cyclopropane product and I₂ molecule leaving group via a one step reaction with a small barrier of about 2.9 kcal/mol.\textsuperscript{64} However, the CH₂I radical reacts with ethylene via a barrier of about 5.2 kcal/mol to produce an iodopropyl radical that is difficult to produce a cyclopropane product and I atom leaving group via a large barrier of about 13.5 kcal/mol.\textsuperscript{64} Similarly the CH₂⁺ cation reacts with little or no barrier to give a relatively stable iodopropyl cation that is even more difficult to undergo ring closure to produce a cyclopropane molecule or cyclopropane cation via large barriers of 96.7 kcal/mol and 35.9 kcal/mol, respectively.\textsuperscript{64} This work and further experimental work indicates the CH₂I–I isomer is the species mainly responsible for production of cyclopropanated products from olefins when using ultraviolet photolysis of CH₂I₂ in the presence of olefins.\textsuperscript{64,66} We have done similar density functional theory calculations for the reactions of the CH₂I₂⋅⋅⋅I molecular complex with ethylene. The optimized geometry for the reactants, transition states, intermediates and products for these reactions are shown in Fig. 5 and the computed relative energies (in kcal/mol) for these reactions are shown in Fig. 6. We have also included the CH₂I–I isomer reaction with ethylene optimized geometry and relative energies from our previous work in Figs. 5 and 6 for comparison purposes.\textsuperscript{64} We note the structures, vibrational frequencies and energies are only modestly affected upon changing the basis set from the Sadlej-pVTZ to the smaller 6-311G** for the CH₂I–I isomer and its reaction with ethylene.\textsuperscript{64} Since the CH₂I₂⋅⋅⋅I molecular complex contains three I atoms and is noticeably more computationally demanding, we have used the 6-311G** basis set for the B3LYP calculations for the reaction of the CH₂I₂⋅⋅⋅I molecular complex with ethylene given in Figs. 5 and 6.

Inspection of Fig. 6 shows that the CH₂I₂⋅⋅⋅I molecular complex reaction with ethylene can break the weak CH₂–I bond to produce an ethylene/I species and an CH₂I₂ leaving group relatively easily with a small barrier to reaction of about 3.2 kcal/mol. The CH₂I₂⋅⋅⋅I molecular complex can also react with ethylene to break the stronger C–I bond to from an iodopropyl radical intermediate and an I₂ leaving group via a large barrier of about 21.4 kcal/mol. This iodopropyl radical intermediate can then proceed to produce a cyclopropane product and I atom leaving group via a barrier of about 12.1 kcal/mol. It is very hard for the CH₂I₂⋅⋅⋅I molecular complex to break a C–I bond when it reacts with ethylene to produce the iodopropyl radical intermediate or proceed to produce a cyclopropane product. This is very different than the CH₂I–I isomer species that very easily reacts with ethylene via a one step mechanism and small barrier of about 2.9 kcal/mol to make a cyclopropane product and I₂ leaving group.\textsuperscript{64} Our results indicate that the CH₂I₂⋅⋅⋅I molecular complex will mostly react with ethylene to transfer the terminal I atom to form an ethylene/I species and a CH₂I₂ leaving group. This is similar to the reaction of an I atom with ethylene and consistent with the CH₂I₂⋅⋅⋅I molecular complex structure being only modestly different from that of the CH₂I₂ parent molecule.

Comparison of TS2 and TS4 in Fig. 5 reveals some interesting similarities: the CCC angle is about the same (106.9° and 106.6°, respectively), the ethylene C=C bond length is the same (1.355 Å), the C₁–C₂ bond length is about the same (2.308 Å and 2.312 Å, respectively) and the C–I bond length is about the same (2.117 Å and 2.118 Å, respectively). This indicates the CH₂I₂⋅⋅⋅I molecular complex reaction with ethylene to form the iodopropyl radical intermediate is very similar to the reaction of the CH₂I radical with ethylene.\textsuperscript{64} This also indicates the larger barrier to reaction of about 21.4 kcal/mol for the CH₂I₂⋅⋅⋅I molecular complex compared to the lower barrier of about 5.2 kcal/mol\textsuperscript{64} for the CH₂I radical to form the iodopropyl radical intermediate is mainly due to the need to break the strong C–I bond of the CH₂I₂⋅⋅⋅I molecular complex which is lengthened to 4.567 Å in TS4 compared to about 2.179 Å in the CH₂I₂⋅⋅⋅I com-
plex. The strengthening of the I–I bond from 3.396 Å in the
CH$_2$I$_2$···I complex to about 2.736 Å in TS4 is not enough to
compensate the energy needed to break the C–I bond and
TS4 is much higher than TS2.

Comparison of the chemical reactivity of the CH$_2$I$_2$···I
molecular complex, the CH$_2$I radical and the CH$_2$I–I isomer
species with ethylene reveals that several factors contribute
to the very different and remarkable reactivity of the CH$_2$I–I iso-
mer toward C=CI bonds. First, the greater perturbation of the
C–I bond in the CH$_2$I–I isomer by the I–I bond formation
leads the CH$_2$I–I isomer to have a significantly different
charge distribution than found in the CH$_2$I radical, the CH$_2$I$_2$
parent molecule or the CH$_2$I–I···I molecular complex. This
leads to the CH$_2$I–I species having a CH$_2$I$^{+1}$ radicals ion
pair character and activates the CH$_2$I moiety (e.g., like a
CH$_2$I$^+$ cation that readily reacts with ethylene).$^{64}$ Second,
the sp$^3$ bonding character of the C atom in the CH$_2$I–I iso-
mer or the CH$_2$I radical compared to the sp$^3$ bonding char-
acter of the C atom in the CH$_2$I$_2$···I molecular complex
means that a C–I bond does not need to be almost com-
pletely broken as in TS4 for the CH$_2$I–I···I molecular com-
plex reaction with ethylene in order to have the C atom
added to the C=C bond. This leads to lower barriers for the
CH$_2$I–I isomer or the CH$_2$I radical to add to the C=C bond
of ethylene. Third, the transition state structure TS1 which
has a smaller CCC angle around 95°–97° and the radical ion
pair character for the CH$_2$I–I isomer species appear to com-
bine to give a concerted ring closure so that the CH$_2$I–I iso-
mer is a very effective methylene transfer agent (e.g., car-
benoid species). The radical ion pair character of CH$_2$I–I
appears to promote formation of two molecular products
rather than ion or radical leaving groups when forming the
cyclopropane product. However, the analogous CCC struc-
ture in TS2 for the CH$_2$I radical reaction with ethylene has
an angle near 107° (further away from ring closure). The
CH$_2$I radical also lacks the radical ion pair character of the
CH$_2$I–I isomer. Thus, addition of the CH$_2$I radical to ethyl-
ene leads to formation of the relatively stable isopropyl
radical intermediate rather than to directly give a cyclopro-
pane product.

C. Implications for other molecule–halogen
complexes and their reactions

The CH$_2$I$_2$···I molecular complex appears to be able to
relatively easily transfer its terminal I atom of the I–I bond
when it reacts with a C=C bond. We also recently observed the
CH$_2$I···I molecular complex using transient resonance
Raman spectroscopy and density functional theory calcula-
tions suggest that it has a structure similar to that of the
CH$_2$I$_2$···I molecular complex with a C–I–I angle in the
80°–90° range.$^{85}$ We note that similar haloalkane–mole-
cule complexes have been observed following pulse radioly-
sis and/or photolysis of a variety of haloalkanes and
polyhaloalkanes.$^{69–73}$ In so far as the structures and chemical
reactivity of the haloalkane–halogen atom complexes are
similar to that of the CH$_2$I$_2$···I molecular complex one may
expect that these types of complexes will transfer the termi-
nal halogen atom of the halogen–halogen bond in reactions
with other molecules but the halogen atom thus transferred
would have a different chemical reactivity than the reaction
of a free halogen atom. There is a range of evidence in the
literature to support this hypothesis.

Recent studies of free radical chlorination of alkanes in
several halogenated solvents found that the tertiary selectiv-
ity was enhanced in these types of solvents$^{86,87}$ as was pre-
viously found for reactions in aromatic and CS$_2$
solvents.$^{88–106}$ This work and other investigations suggested
that halogenated solvent–Cl atom molecular complexes were
responsible for the enhanced tertiary selectivity for chlorina-
tion of alkanes observed in these halogenated solvents.$^{86,87}$ A
similar CS$_2$/Cl complex with a characteristic transient ab-
sorption band around 370 nm was shown to be responsible
for the increased tertiary selectivity in chlorination of al-
kanes in CS$_2$ solvent.$^{106}$ We recently directly characterized
the structure of this CS$_2$/Cl complex using transient reso-
nance Raman spectroscopy in conjunction with density func-
tional theory calculations.$^{107}$ The CS$_2$/Cl complex was
found to have a structure with the Cl atom attached to the S
atom of CS$_2$ (e.g., an S=С=S···Cl molecular complex).$^{107}$

This S=С=S···Cl molecular complex has the Cl atom
loosely bound to the S atom and the CS$_2$ moiety structure
is only slightly perturbed from that of the parent CS$_2$
 molecule.$^{107}$ This is very similar to the CH$_2$I$_2$···I molecular
complex where the C–I bonds are only slightly perturbed
from that of the parent CH$_2$I$_2$ molecule. This suggests
the halogenated solvent–Cl atom molecular complexes (respon-
sible for the enhanced tertiary selectivity for chlorination of
alkanes observed in halogenated solvents) have structures
similar to the CH$_2$I$_2$···I and the S=С=S···Cl molecular
complexes. It is also very likely these halogenated solvent–Cl
atom molecular complexes have a chemical reac-
tivity similar to the S=С=S···Cl molecular complex that
leads to the enhanced tertiary chlorination selectivity of al-
kanes in halogenated alkane solvents.$^{86,87}$

The differing chemical reactivity for the CH$_2$I–I species
and the CH$_2$I$_2$···I molecular complex is consistent with the
amount of cyclopropanated product that is formed as the
concentration of alkene reactant is varied. For example,
Kropp and co-workers found that the yield of cyclopropan-
ated product increased substantially from 16% to 66% to
80% as the concentration of cyclohexene increased from
0.18 to 1.8 to 10 M, respectively, and the CH$_2$I$_2$ precursor
concentration was kept constant at 0.05 M.$^{12}$ At low cyclo-
hexene concentration the longer lifetime of the CH$_2$I$_2$···I
molecular complex and other long-lived species like the
CH$_2$I radical and I atoms would be more likely to react with
cyclohexene to produce additional products and relatively
low amounts of cyclopropanated product from reaction with
the short-lived CH$_2$I–I carbenoid species. However, the
shorter-lived but more highly reactive CH$_2$I–I carbenoid spe-
cies can better compete with the addition reactions of the
longer-lived species to produce a higher yield of cyclopro-
panated product at high cyclohexene concentrations as found
in Kropp and co-workers experiments.$^{12}$ The chemical
reactivity of the CH$_2$I$_2$···I molecular complex to mainly
transfer an I atom and not produce a cyclopropanated prod-
uct is also consistent with the chemical reactivity of related
halogenated solvent–Cl atom molecular complexes that have
been proposed for being responsible for the enhanced tertiary selectivity for chlorination of alkanes observed in these halogenated solvents.108–119

Breslow, Krogh-Jespersen and co-workers showed that the pyridine/Cl complex (responsible for enhanced tertiary selectivity in photochlorination of alkanes in pyridine solvent) is a σ-complex with three-electron–two-center N–Cl bonding.98 The Cl atom is a highly reactive species with high electronegativity and an unpaired electron in the p-orbital and can therefore easily interact with some types of solvent molecules. A number of radical cations have been shown to form 2σ1/1σ* two-center–three-electron bonds (also known as 2c–3e bonds) from the interaction of a singly occupied sulfur p orbital and lone pairs of O, N, P, or halogen atoms.108–119 These sulfur (or nitrogen, halogen atom) radical cation 2c–3e bonded radical cation complexes typically have intense, broad and structureless UV/visible absorption bands108–119 similar to transient absorption bands observed for isopolyhalomethanes and halogenated solvent–halogen atom complexes that contain the weak halogen–halogen bond as a chromophore.46,47,51–55,69–73,86,87 The isopolyhalomethanes and halogenated solvent–halogen atom complexes also exhibit weak bond formation from the p-orbital overlap of the two halogen atoms forming the halogen–halogen bond similar to the traditional 2c–3e bonded radical cation complexes.108–118 The actual structure, properties and bond strength of 2c–3e bonds (or p-orbital interactions between S, N, O, and/or halogen atoms) are expected to be influenced by the structure and properties of the radical cation or molecule that interacts with the p-orbital of a S, N, O or halogen atom (F, Cl, Br or I) as well as the solvent environment. A range of quantum mechanical calculations have been done to develop a better understanding of 2c–3e bonding.120–133 However, most experimental characterization of 2c–3e radical cation bond complexes have been indirect with the transient absorption spectra typically used as an indicator for this kind of bonding and this has made detailed comparisons between theory and experiment somewhat difficult.108–118 Recently femtosecond spectroscopy has been used to examine a 2c–3e bonded sulfur system.119 Our present comparison of the weak 1–I bond in CH2I–I isomer and CH2I2–I molecular complex using time-resolved resonance Raman spectroscopy illustrates the usefulness of time-resolved vibrational spectroscopy to directly characterize the structure and properties of p-orbital interactions similar to 2c–3e bonding in neutral species. We anticipate that similar experiments for 2c–3e bonded radical cation complexes will enable vibrational mode-specific characterization of these interesting species to be done and allow an even greater understanding of these species to be developed. It will be very interesting to compare the 2c–3e bonding in the radical cation complexes to those of the isopolyhalomethane and halogenated solvent–halogen atom complexes that are neutral species.

IV. CONCLUSION

Time-resolved resonance Raman spectra were acquired after ultraviolet photolysis of different concentrations of CH2I2 in cyclohexane solutions. At low concentrations, the CH2I–I isomer species was observed between 0 and 100 ns and no other discernible species was seen up to a 10 μs time delay. At high concentrations, the CH2I–I isomer species was observed with spectra and a lifetime almost identical to that found at lower concentrations and a second species was also observed with a much longer lifetime on the order of microseconds. The second species was assigned to be due to the CH2I2–I molecular complex formed from the bimolecular reaction of I atom with the CH2I2 molecule. Density functional theory calculations were performed to examine the chemical reactivity of the CH2I–I isomer and CH2I2–I molecular complex toward C≡C using ethylene as an example. The CH2I–I isomer reacts with ethylene to give a cyclopropane product and I2 leaving group via a one step reaction with a low barrier of about 2.9 kcal/mol. The CH2I2–I molecular complex reacts with ethylene to produce a ethylene/I intermediate and CH2I2 leaving group with a barrier to reaction of about 3.2 kcal/mol. Our results indicate that CH2I–I acts as an effective methylene transfer agent while the CH2I2–I molecular complex essentially transfers the terminal I atom of the I–I bond. This very different chemical reactivity of the CH2I–I and CH2I2–I species can be explained by their differing structures and properties. While both species contain a weak I–I bond, the geometry of the I–I bond relative to the C–I bond is substantially different and leads to greater changes in the case of the CH2I–I species. This leads the CH2I–I species to have a CH2I+·I radical ion pair character while the CH2I2–I moiety has a charge distribution similar to a CH2I+ cation and thus more easily attacks the C≡C bond.64 The sp2 bonding character of the C atom in the CH2I–I isomer compared to the sp3 bonding character of the C atom in the CH2I2–I molecular complex also makes the CH2I–I species more able to form a C–C bond between the C≡C bond and the CH2I–I species compared to the CH2I2–I molecular complex which would need to essentially break a C–I bond to do the same. The structure of the CH2I2–I molecular complex is very similar to the parent CH2I2 molecule and this is consistent with its transfer of the terminal I atom of the I–I bond in its reaction with ethylene. We compare our results for the structure and chemical reactivity of the CH2I2–I molecular complex to other halogenated solvent–halogen atom molecular complexes and discuss probable implications for photochlorination reactions of alkanes in halogenated solvents.

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