Formation and relaxation dynamics of iso-CH₂Cl–I in cryogenic matrices

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Photolysis of chloroiodomethane (CH₂ClI) in cryogenic matrices followed by recombination of the nascent radical pair produces an isomer (CH₂Cl–I) that features a halogen-halogen (Cl–I) bond. Using ultrafast laser pulses, it is possible to follow the formation of this isomer by transient electronic absorption in low-temperature matrices of N₂, CH₄, and Ar. Frequency-domain measurements provide vibrational and electronic spectra, and electronic structure calculations give the structures of the isomers and the minimum energy path that connects them. The ultrafast experiments cleave the C–I bond with a 267-nm photolysis pulse and probe the formation of the isomer at wavelengths between 435 nm and 510 nm. The longest wavelengths preferentially interrogate vibrationally excited molecules, and their transient absorption shows that the highly vibrationally excited isomer appears within 1 to 2 ps, depending on the matrix, likely reflecting the loss of 2000 cm⁻¹ or more of energy in a strong, inelastic collision of the fragments with the matrix. The subsequent relaxation of the vibrationally excited isomer occurs in 20 to 40 ps, a time that is comparable to those observed for halomethane molecules and their isomers in liquids and in supercritical CO₂. These observations suggest that the formation and initial relaxation of the isomer in dense media do not depend strongly on the identity of the surroundings. © 2011 American Institute of Physics. [doi:10.1063/1.3633697]

I. INTRODUCTION

The photochemistry of simple halomethane derivatives continues to attract attention for reasons ranging from fundamental photochemistry and dynamics to relevance to chemistry in the environment. Chloroiodomethane, the particular halomethane derivative we study here, exists in the environment in diverse contexts. It is present in the atmosphere and in marine environments,¹⁻³ where its photochemistry influences the atmospheric iodine budget. Volcanic activity⁴, purification of drinking water,¹¹ and marine microalgae¹² are all sources of environmental chloroiodomethane.

Condensed-phase photolysis of halomethanes often generates isomers with unique bonding motifs.¹³ Maier and co-workers¹⁴, ¹⁵ first observed the iso-halomethanes, which contain a carbon-halogen-halogen linkage, in cryogenic matrices. These same isomers appear transiently in a variety of room temperature liquids and ultimately decay by thermal isomerization back to the parent molecule or by diffusive chemical reaction.¹⁶,¹⁷ Subsequent studies have shown the importance of these species as reactive intermediates in condensed phases. For example, Phillips and co-workers have shown that iso-CH₂Br₂ is the methylene transfer agent in photochemical cyclopropanation reactions in solution.¹³ In addition, isomerization of halomethanes in the gas phase is apparently an important route to molecular products.¹⁸ We have extended our ultrafast isomerization measurements to cryogenic matrices in order to study these rearrangements in a new environment and have followed the isomerization of chloroiodomethane, CH₂ClI, to iso-chloroiodomethane, CH₂Cl–I, in solid CH₄, N₂, and Ar.

Ultrafast studies of photoinduced chemical changes in the condensed phase typically use flowing, renewable liquid samples. Such measurements monitor a chemical reaction on the time scale of the period between interactions of solute and solvent molecules, and comparison to gas-phase measurements can identify the effect of interactions with the solvent. The solvent may play a minor, perturbing role or be a fundamental participant that leads to outcomes that are dramatically different from those in the corresponding gas-phase reactions. Chromophores isolated in solids typically behave in one of two ways. In one limit, they act like isolated gas-phase molecules, for example, having vibrational relaxation times of a ms or longer.¹⁹ In the other limit, interaction with the solid can open reaction pathways that are closed in the analogous gas-phase reaction.¹⁴,¹⁵,¹⁰

The rearrangement of CH₂ClI to iso-CH₂Cl–I in cryogenic matrices is a model system for observing the effect of the cold surroundings on a photoisomerization that involves large amplitude motion of a highly excited solute molecule. Our work has precedents in ultrafast studies of both isomerization and photolysis in cryogenic matrices. Hamm and co-workers have studied the infrared-driven, matrix-assisted isomerization of nitrous acid (HONO) in rare-gas matrices on the fs to μs time scale,²⁰⁻²³ and Apkarian and co-workers²⁴⁻²⁸ and Schwentner and co-workers²⁹⁻³⁲ have performed extensive analyses of ultraviolet photolysis of halogen molecules in rare-gas matrices. These results are notable in showing that strong interactions with the solvent cage mediate the transfer of energy between the chromophore and solvent.³³
We use ultrafast laser pulses to investigate several aspects of solute-solvent interactions and matrix reaction dynamics with iso-CH₂Cl—I as the reporter. Figure 1(a) is a sketch of the relevant calculated structures on the CH₂ClI potential energy surface and the minimum energy pathway that connects them. An ultraviolet photolysis pulse, \( \lambda_{\text{photolysis}} = 267 \text{ nm} \), cleaves the C–I bond of CH₂ClI, but repulsion by the solid solvent cage restricts the products to a limited portion of the potential energy surface. One possible product of photodissociation and subsequent forced recombination is iso-CH₂Cl—I, in which the cleaved I atom returns to the CH₂Cl species and bonds to the Cl atom. We monitor the formation of iso-CH₂Cl—I using its strong electronic transitions centered at 435 nm and 750 nm. As initially reported, the isomer is photolabile, and irradiating it with 440-nm light from a dye laser destroys the isomer and regenerates the parent.

**II. EXPERIMENTAL AND THEORETICAL APPROACH**

There are three components to our study of the isomerization of the parent, CH₂ClI, to the isomer, iso-CH₂Cl—I: frequency-domain spectroscopy, time-domain spectroscopy, and quantum chemistry calculations on the two isomers and on the structures that connect them.

**A. Frequency-domain spectroscopy**

We reproduce the vibrational and electronic spectra of the parent and iso-compound in Ar originally observed by Maier *et al.* and also obtain new spectra in CH₄ and N₂ matrices. Because the details of sample preparation and spectroscopy are the same as before, we only describe them briefly here. Pulsed deposition of premixtures of solvent and solute having ratios greater than 500:1 at 23 K generates 50 to 100 \( \mu \text{m} \)-thick samples, and we perform the photolysis and subsequent spectroscopy at 5 K. Photons at 220 nm from a frequency-doubled, Nd:YAG-pumped nanosecond dye laser excite the lowest energy electronic transition of the CH₂ClI parent. In the matrix, excitation followed by cage recombination during the laser pulse generates a steady-state population of the isomer. Difference spectra taken before and after photolysis match those previously reported in Ar and N₂ matrices, verifying formation of the isomer with the appearance of features at 435 nm and 750 nm and concomitant loss of the feature at 265 nm in the parent. As initially reported, the isomer is photolabile, and irradiating it with 440-nm light from a dye laser destroys the isomer and regenerates the parent.

**B. Time-domain spectroscopy**

The matrix-isolation equipment and sample preparation for the time-domain experiments are different from those used in the frequency-domain experiments. We use solvent-solute ratios of approximately 220:1 to increase the column density of the isomer while keeping the samples thin enough to minimize scattering losses. Sample deposition from a continuous flow for 1 h onto a 2.5 cm diameter CaF₂ window held at approximately 30 K yields 50 to 70 \( \mu \text{m} \)-thick samples that transmit more than 50% of the probe light. The exterior windows in the spectrometer are CaF₂ as well. Infrared spectra of selected samples taken before and after irradiation with ultrafast pulses of 267-nm light show the same loss of parent absorption and growth of isomer absorption as produced by nanosecond pulses.

The immobility of the sample and the persistence of the isomer after photolysis require that we use two procedures that are uncommon to transient absorption spectroscopy. As shown in the schematic drawing of the apparatus in the top panel of Fig. 2, the third harmonic of a Ti:Sapphire regenerative amplifier provides 267-nm light, \( \lambda_{\text{photolysis}} \), for photolysis of CH₂ClI. We direct an approximately 2–5 \( \mu \text{J} \) pulse of this light into the cryostat in a 2-mm spot and also send a 1-mm diameter probe beam through at a small angle to the photolysis
beam. These visible, tunable probe pulses, $\lambda_{\text{probe}}$, come from nonlinear conversion of tunable infrared light from a double-pass, $\beta$-barium borate optical parametric amplifier (OPA). We quadruple that light to make 435-nm pulses or mix it with 800-nm light to make pulses in the range of 485 to 510 nm. Because we cannot refresh the sample between laser pulses, we use a third photon to convert the population of the isomer back to the parent. This 150-$\mu$J, 800-nm “recovery” pulse, $\lambda_{\text{recovery}}$, is in a 5-mm diameter beam that counter-propagates through the sample and interacts with it more than 10 ns after the photolysis-probe pair passes through. A computer-controlled delay stage controls the arrival time of the photolysis pulse relative to the probe pulse, but the timing of the recovery pulse is always the same.

The small signals that we measure with photodiodes responding from near-ultraviolet to near-infrared wavelengths require that we detect only the intended probe wavelength. We use calcite polarizers to reject residual 800-nm and near-infrared light from the OPA and from mixing processes, and we use glass filters and dielectric mirrors to reject visible light from parasitic processes in the nonlinear light conversion. Transmission through these optics limits our instrument response to 1 ps at full-width, half-maximum (FWHM). A small fiber-optic coupled spectrometer with 3-nm FWHM resolution measures the central frequency and bandwidth, typically 4 to 6 nm, of the probe light. The probe pulses are not transform-limited, and we take no steps to correct for temporal dispersion.

The bottom panel of Figure 2 is a timing diagram for one series of transient absorption measurements. A mechanical chopper blocks every other photolysis pulse ($\lambda_{\text{photolysis}}$), and we measure the change in transmission of the probe pulse ($\lambda_{\text{probe}}$) due to photolysis as a function of the time between the two. The stable isomer remains in the sample volume and produces an overall decrease of the probe transmission. For every laser pulse, we also subject the sample to an 800-nm pulse ($\lambda_{\text{recovery}}$) that isomerizes the iso-compound back to the parent, increasing the transmission of the probe and producing the step pattern shown in red in Fig. 2. We make only 250 consecutive transient absorption measurements before blocking the photolysis beam with a fast shutter. The recovery pulse then continues returning population from the isomer to the parent, which we follow by monitoring the increase in the probe transmission. We measure the transmission of the sample before any irradiation with ultraviolet light, indicated by the horizontal dotted line in Fig. 2, and require that the transmission of the probe light returns to within 2% to 3% of this value before allowing the photolysis beam to enter the sample again. We repeat this sequence several times before changing the delay between photolysis and probe beams in order to obtain data for a different time interval between the two.

The data are averages of 10 or more scans encompassing about 80 different time delays. Each scan requires three to six repetitions of the scheme in the bottom panel of Fig. 2 at each delay to provide an acceptable signal-to-noise ratio. We make measurements changing the time delay between the photolysis and probe pulses with positive-going time steps and then with negative-going time steps and require similar signal amplitudes and kinetic behavior between these two consecutive scans. Thus, we know that there is no sample degradation during the measurement. We translate the cryostat to interrogate a new portion of the sample after every second scan to prevent sample degradation, which we can identify as a loss of signal intensity and the inability of the recovery pulse to increase the transmission of the probe to the predefined limit. Each data point is an average of about 7500 transient absorption measurements, and typical changes in optical density (OD) range from 25 to 300 $\mu$OD, depending on the detection wavelength.

C. Calculations

We calculate vibrational frequencies, electronic transition frequencies and strengths, and reaction paths using various quantum chemistry methods with the Sadlej-pVTZ basis set. $38$ Second-order Møller-Plesset perturbation theory (MP2)
and hybrid density functional theory (DFT: B3LYP, M06) provide vibrational frequencies and intensities for five stationary points on the CH2ClI surface. We calculate the band positions and oscillator strengths for the electronic transitions $S_n \rightarrow S_0$ ($n = 1 \ldots 5$) using a suite of time-dependent density functional theory methods (TDDFT: TD-B3LYP, TD-CAM-B3LYP, TD-M06, TD-M06-2x). Several of these restricted calculations show instabilities in the wavefunctions, but similar calculations with unrestricted wavefunctions produce quantitatively similar results without instabilities. The intrinsic reaction coordinate calculations use a MP2 treatment. Natural bond orbital (NBO) analysis provides chemically intuitive descriptions of the bonding character of the isomer and transition state between parent and isomer. The calculations use the Gaussian suite of programs with the NBO package.

III. RESULTS
A. Vibrational frequencies, electronic transitions, and isomerization coordinate

The ground electronic state of the isomer is a closed-shell singlet with a stable triplet state about 1750 cm$^{-1}$ higher in energy. Calculations show that this triplet state is a doublet CH2Cl radical and loosely associated I atom and that the NBO bond order between the two is zero. Because preliminary TDDFT calculations on the triplet state find no transitions in our probe region, we do not consider it in analyzing the spectra. The calculated vibrational frequencies for the isomer, CH2Cl–I, agree with previously published spectra as well as with the difference spectra taken after both fs and ns photolysis. The TDDFT calculations of the electronic energies for the isomer have discrepancies with the observed energies that are similar to those for other halomethane isomers. The low-energy feature at 750 nm in Fig. 1(b) is an overlap of the $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$ transitions, and the predominant feature at 435 nm is the $S_1 \rightarrow S_0$ transition. In order to estimate the extinction coefficients, we use our calculated and measured integrated infrared intensities to determine the column density of the isomer in the frequency-resolved experiment and then integrate the two visible absorption bands for the same sample. Thus, we estimate the extinction coefficients at 435 nm and 750 nm to be $\varepsilon_{435} = 18 \pm 1000$ L/mol cm and $\varepsilon_{750} = 1640 \pm 140$ L/mol cm, in accord with previous estimates.

Figure 3(a) shows a cut through the potential energy surface along two direct isomerization coordinates of CH2CII. Intrinsic reaction coordinate calculations for gas-phase structures show that isomerization back to the parent from iso-CH2CI–I has a 71 kJ/mol (5990 cm$^{-1}$) barrier and that isomerization from iso-CH2I–Cl has an 82 kJ/mol (6930 cm$^{-1}$) barrier along this direct pathway. These direct pathways are the ones that avoid large separations between CH2Cl and I, as we expect for motion constrained by the solid cage. Even though the CH2I–Cl isomer is energetically accessible, we do not observe significant amounts of it in either the time-domain or frequency-domain measurements, as described below. The NBO analysis summarized in Fig. 3(b) finds that only three resonance structures contribute more than 5% along these isomerization pathways: a covalently bonded structure, an ion-pair in which the carbon-bonded halogen is positive, and an ylide in which the carbon carries a formal negative charge and the carbon-bonded halogen a positive charge. The covalently bound motif dominates the structure of the parent, but ion-pair character makes the largest contribution for both of the isomers, CH2Cl–I and CH2I–Cl. The transition states between the parent and each of the isomers occur where the dominant contribution changes from the covalently bound structure to the ion-pair structure. Although the covalently bound structure largely describes the ground state of the parent, the excited state appears to have a large amount of ion-pair character. The change in the principal contribution between two bonding motifs at the transition state suggests that the barrier arises from the interaction of the ion-pair state and the covalently bound state.

B. Transient absorption measurements

The blue and red lines in Fig. 1(b) are the electronic absorption spectra of the parent CH2CI and the isomer CH2I–I, respectively, and these are the only species we interrogate. The electronic spectra and vibrational absorption
spectra of the isomer that we measure in Ar are consistent with those of Maier et al.\textsuperscript{14,15} and the similarity of the spectra following irradiation with ultrafast and nanosecond lasers shows that both irradiations initiate the same process. The electronic absorption spectrum of the isomer, shown in Fig. 4, changes only slightly with the identity of the matrix, having a maximum at 434 nm in Ar, 441 nm in N\textsubscript{2}, and 447 nm in CH\textsubscript{4}. For the transient spectroscopy measurements, we vary the probe wavelength across the isomer absorption feature in this region, from the maximum near 435 nm to the low-energy edge near 510 nm, and perform one experiment on the smaller band at 800 nm. The magnitude of the changes in the transient absorption spectra are consistent with these static spectra, decreasing from about 230 μOD at λ\textsubscript{probe} = 485 nm to 30 μOD at λ\textsubscript{probe} = 510 nm. The static spectra show at most minor amounts of the isomer CH\textsubscript{2}I–Cl,\textsuperscript{16,44} and we do not probe its band center, which we calculate to be near 306 nm.\textsuperscript{40}

FIG. 4. Electronic absorption spectra of the CH\textsubscript{2}Cl–I isomer in Ar, N\textsubscript{2}, and CH\textsubscript{4} matrices. The maximum moves to successively longer wavelengths for the series of matrices. The vertical arrows mark the probe wavelengths.

Figures 5–7 show the static absorption spectra of the isomer in the three different matrices along with transient absorption signals at different probe wavelengths. We are insensitive to the possible presence of an additional dissociation pathway producing spin-orbit excited I, I\textsuperscript{*}, which has a 50% gas-phase quantum yield for photolysis from CH\textsubscript{2}ClI at 266 nm.\textsuperscript{45} One possible quenching pathway for I\textsuperscript{*} is electronic-to-vibrational energy transfer to the CH\textsubscript{2}Cl fragment. However, this new influx of vibrational energy is simply another formation pathway of the excited isomer, and if quenching of I\textsuperscript{*} occurs in about 1 ps,\textsuperscript{46} our probe cannot differentiate between isomer formation from I and from I\textsuperscript{*}.

The transient absorption signal has a time-independent negative component that we attribute to fluorescence or phosphorescence in the matrix following irradiation at 267 nm. Its amplitude depends linearly on both the photolysis pulse energy and column density of CH\textsubscript{2}ClI. We correct for this background by subtracting an average of the data points in a scan at negative delay between the photolysis and the probe pulses (Δt ≤ −4 ps) from the signal. Because the non-uniform thickness of the matrix gives a different column density and transient absorption signal for each sample area we interrogate, we internally normalize each scan to a region of five or more consecutive data points either in an asymptotic region or in the flattest region of the time evolution. We average these baseline-adjusted and normalized time evolutions for the analysis described below. In general, neither slight variations in the regions we select for determining the offset nor wholesale changes in the normalization range significantly alter the parameters extracted from the fits.

The solid lines, S(t), in Figures 5, 6, and 7 are least-squares fits of a sum of exponentials,

\[ S(t) = \sum_{i=1}^{n} A_i \exp\left(-\frac{(t-t_0)}{\tau_i}\right) + S_\infty, \]

to the data where A\textsubscript{i} and τ\textsubscript{i} are the amplitude and time-constant for each exponential, S\textsubscript{\infty} is the long-time offset, t\textsubscript{0} is the time at which the photolysis and probe pulses overlap, and n is the number of exponentials, which is two or three. The definition of temporal overlap between photolysis and probe pulses is arbitrary and small changes to the start of the fitting range alter τ\textsubscript{i} outside the statistical uncertainty of any one fit. The uncertainties we report reflect this variation in τ\textsubscript{i} with
fitting ranges that give reasonable fits as determined by eye. All fits retain $A_i$, $\tau_1$, $\tau_2$, and $S_{\infty}$, as free parameters, while holding $t_0$ and $\tau_3$, if present, at the value given by an initial fit. Fixing $t_0$ does not change $\tau_1$ or $\tau_2$ outside the uncertainties of the free fits but serves to further refine $A_i$. Measurements from different days and different matrix samples give fit parameters within the reported uncertainties.

The time evolution obtained probing near the 435-nm maximum of the isomer absorption has two disparate time constants, as shown in Fig. 5 for CH$_4$, Fig. 6 for N$_2$, and Fig. 7 for Ar and listed in Table I. The shorter time constant $\tau_1$ is nearly the same in both of the molecular matrices. However, the longer time constant $\tau_2$ differs between the molecular matrices and has a relatively complicated dependence on $\lambda_{\text{probe}}$. Interpreting $\tau_2$ for long probe wavelengths is comparatively simple because it primarily reflects the relaxation of vibrationally excited molecules, which are the most important absorbers on the low-energy side of the transition. However, interpretation is more complicated at shorter wavelengths where the probe interrogates both vibrationally excited and vibrationally relaxed molecules. The time evolution depends on the balance between population leaving excited vibrational levels and entering lower levels, which can produce large and variable values of $\tau_2$. Thus, we only compare the values of $\tau_2$ among the matrices for long probe wavelengths.

Figure 8 shows the rise in the signal in the CH$_4$ matrix and the corresponding fits on an expanded time scale. The signal for $\lambda_{\text{probe}} = 510$ nm, the lowest energy with which we probe this feature, rises three times faster than that for $\lambda_{\text{probe}} = 435$ nm, with a larger amplitude. Measurements from different days and different matrix samples give fit parameters within the reported uncertainties.

Table I. Time constants and amplitudes of multiexponential fits in CH$_4$, N$_2$, and Ar matrices.

<table>
<thead>
<tr>
<th>$\lambda_{\text{probe}}$ (nm)</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_3$ (ps)</th>
<th>$A_2/A_1$</th>
<th>$A_3/A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>435</td>
<td>3.1 ± 0.3</td>
<td>37 ± 5</td>
<td>...</td>
<td>0.65 ± 0.04</td>
<td>...</td>
</tr>
<tr>
<td>485</td>
<td>2.3 ± 0.3</td>
<td>49 ± 13</td>
<td>...</td>
<td>0.14 ± 0.03</td>
<td>...</td>
</tr>
<tr>
<td>500</td>
<td>1.4 ± 0.1</td>
<td>276 ± 122</td>
<td>...</td>
<td>−0.23 ± 0.03</td>
<td>...</td>
</tr>
<tr>
<td>510</td>
<td>1.1 ± 0.2</td>
<td>42 ± 7</td>
<td>...</td>
<td>−0.54 ± 0.06</td>
<td>...</td>
</tr>
<tr>
<td>N$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>435</td>
<td>3.9 ± 0.7</td>
<td>183 ± 33</td>
<td>...</td>
<td>1.0 ± 0.2</td>
<td>...</td>
</tr>
<tr>
<td>485</td>
<td>2.1 ± 0.2</td>
<td>460 ± 130</td>
<td>...</td>
<td>−0.38 ± 0.04</td>
<td>...</td>
</tr>
<tr>
<td>500</td>
<td>1.3 ± 0.4</td>
<td>58 ± 7</td>
<td>...</td>
<td>−1.1 ± 0.4</td>
<td>...</td>
</tr>
<tr>
<td>510</td>
<td>1.4 ± 0.3</td>
<td>24 ± 3</td>
<td>700</td>
<td>−0.76 ± 0.07</td>
<td>−0.33 ± 0.05</td>
</tr>
<tr>
<td>Ar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>435</td>
<td>5.6 ± 0.9</td>
<td>100 ± 48</td>
<td>...</td>
<td>0.29 ± 0.06</td>
<td>...</td>
</tr>
<tr>
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<td>220 000</td>
<td>−0.33 ± 0.01</td>
<td>−62 ± 9</td>
</tr>
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</table>
= 435 nm, and the size of the second exponential, \( A_2 \), grows relative to \( A_1 \) at longer probe wavelengths, indicating a more extensive decay of the transient signal at long time. Because the measurements with \( \lambda_{probe} \geq 500 \) nm interrogate predominantly vibrationally excited species, they provide a view of the formation of the vibrationally excited isomer and allow us to follow the flow of vibrational energy. The changes of the transient absorption with probe wavelength are consistent with isomerization followed by intramolecular vibrational relaxation and energy flow into the surroundings.

We also probe the weaker \( S_1/S_2 \leftarrow S_0 \) transition at \( \lambda_{probe} = 800 \) nm using the fundamental frequency of the laser, and Fig. 5 shows the transient absorption of CH2Cl–I at that wavelength in a CH4 matrix. The 25 \( \mu \)OD maximum absorption at 800 nm, compared to 300 \( \mu \)OD at 435 nm, is consistent with the ratio of measured extinction coefficients of the two bands. The time evolution at 800 nm is the same as we observe by probing the \( S_3 \leftarrow S_0 \) transition, but the exceptionally small signal prevents extraction of reliable fit parameters. The dotted line through the \( \lambda_{probe} = 800 \) nm data is a fit using the same values of \( \tau_1 \) as obtained for \( \lambda_{probe} = 485 \) nm with the other parameters being free. We choose \( \lambda_{probe} = 485 \) nm for comparison as both wavelengths are on the low-energy side of their respective bands. The results for the Ar matrix are similar to those for the molecular matrices, as Fig. 7 shows for two probe wavelengths. The initial rise (\( \tau_1 = 6 \) ps) for \( \lambda_{probe} = 435 \) nm is twice as long in the Ar matrix as in the CH4 and N2 matrices, but the qualitative behavior of the transients is similar.

### IV. DISCUSSION

The two distinct time constants that are apparent in the time evolution of the isomer shown in Figs. 5–7 point to a sequential process in which the absorption at the probe wavelength \( \lambda_{probe} \) changes with time and in which the details of the transient absorption depend strongly on the probe wavelength. One of the most striking features, illustrated in Fig. 5, for example, is the change from two successive increases in absorption at \( \lambda_{probe} = 435 \) nm to an initial increase followed by a decrease at \( \lambda_{probe} = 510 \) nm. The time evolution of the signal reflects changes in absorption during the formation and stabilization of the isomer CH2Cl–I following initial deposition of 450 kJ/mol (37600 cm\(^{-1}\)) in the parent CH2CII by the 267-nm excitation photon. The probe-wavelength dependence of the transient absorption likely arises from sampling different portions of the ensemble of newly born isomers because probing on the low-energy side of the isomer absorption preferentially interrogates vibrationally excited molecules.

### A. Isomer formation

Excitation of an isolated CH2CI molecule with a 267-nm (37600 cm\(^{-1}\)) photon populates a C–I \( \sigma^* \) orbital and promptly breaks the C–I bond homolytically, providing approximately 19300 cm\(^{-1}\) of energy to the CH2Cl and I fragments. About 40% (7700 cm\(^{-1}\)) of that available energy appears as kinetic energy of the fragments, leaving 11600 cm\(^{-1}\) available for internal excitation of CH2CI and electronic excitation of I.47 The situation is potentially very different in a matrix, where the recoiling fragments collide inelastically with the dense surroundings. Resonance Raman studies of A-band photolysis of CH2CI both in cyclohexane solution and in the gas phase show that the early-time dynamics of the impulsively driven modes of the polyatomic fragment are similar in both cases even though there are subtle differences for other modes.48,49 Thus, we expect that the initial partitioning of available energy is likely to be similar in all three environments, and our primary concern is the fate of the kinetic energy of the fragments during collisions with the matrix.

Figure 9 shows the calculated potential energy surface in the region of the isomer along with sketches of the isomer formation process, where the dashed line illustrates the new repulsive part of the potential that the matrix introduces. Collisions with the wall redistribute the initial translational and internal energy and allow the excited molecule to sample a variety of geometries, including those of the isomer. Ultimately, rearrangement to the stable isomer requires both reaching the appropriate geometry and removing energy to trap the isomer in its minimum. It is likely that with more than 7000 cm\(^{-1}\) of kinetic energy the system will readily cross the barrier between isomer and parent as it loses energy, and we cannot distinguish single and multiple crossings. Thus, detection of the transient absorption on the isomer transition shown in Fig. 1(b) requires that the energized fragments associate and lose enough internal energy to remain in the vicinity of the isomer geometry. The growth of the transient absorption that we observe reflects this rearrangement and initial, but incomplete, relaxation.
Measurements\textsuperscript{26–31,33} and simulations\textsuperscript{50–53} of the photodissociation of I\textsubscript{2} in cryogenic matrices provide a point of comparison to help understand the early-time behavior of the recoiling fragments in our experiments. These studies examine the effects of high-energy collisions with the matrix and show that with an initial kinetic energy of 5000 cm\textsuperscript{-1} the diatomic system loses at least 2500 cm\textsuperscript{-1} of kinetic energy in the first collision with the matrix cage only 200 fs after photoinitiation.\textsuperscript{30} Simulations show that the more kinetic energy a system carries into a collision with the wall, the more energy it loses in a single collision.\textsuperscript{30} As Fig. 9 illustrates, even if the system loses 2000 cm\textsuperscript{-1} of energy in the first collision with the cage, the recombination products contain more than 15 000 cm\textsuperscript{-1} of energy above the minimum energy of the isomer, and an energized isomer must lose an additional 9000 cm\textsuperscript{-1} to have a total internal energy less than the calculated barrier between the isomer and the parent. The energized recombination products explore the large configuration space available to them as they relax into either the parent or isomer minimum. A statistical view of this process suggests that the available influx from highly excited species and loss to relaxed species, determine the pathways. The simplest interpretation is that the primary distinction we make between the formation and initial relaxation of the isomer (\(\tau_1\)) and further loss of energy to the surroundings (\(\tau_2\)) is the fast relaxation rate due to the removal of a large amount of energy in the first collisions with the surroundings, in analogy with the situation in I\textsubscript{2} photolysis in matrices, and the subsequent slower loss of the remaining vibrational energy. Even after the initial removal of several thousand cm\textsuperscript{-1} of energy, the isomer retains substantial excitation. The studies of I\textsubscript{2} in Kr observe an immediate loss rate of 2000 cm\textsuperscript{-1}/ps during the collisions when the system retains more than the gas-phase dissociation energy,\textsuperscript{30} suggesting that after a few ps the energized CH\textsubscript{2}Cl–I isomer still contains about 10 000 cm\textsuperscript{-1} of vibrational energy. The slower removal of this energy accounts for the second time scale in the transient absorption. Near the center of the band, the second component of the time evolution appears as a rise, suggesting population of lower energy states of the isomer that dominate near band center. However, as Figs. 5–7 and Table I show, this second component becomes a decay for longer probe wavelengths, indicating relaxation of the vibrationally excited molecules that preferentially absorb there. The intermediate probe wavelengths near \(\lambda_{\text{probe}} = 485\) nm reflect both influx from highly excited species and loss to relaxed species, and, as described above, the values of \(\tau_2\) for these are larger and have substantial uncertainties.

We know that some of the excited isomers eventually lose enough energy to the surroundings to become stable reaction products. However, our measurements do not definitively determine the pathways. The simplest interpretation is that we are observing transfer of energy from this highly excited molecule to the surrounding matrix, in analogy to relaxation of vibrationally excited molecules in liquids. For example, similar measurements probing the low-energy side of the electronic transition show that CH\textsubscript{2}I\textsubscript{2} molecules with 6000 cm\textsuperscript{-1} and 9000 cm\textsuperscript{-1} of vibrational excitation transfer energy to CCl\textsubscript{4} solvent molecules in about 70 and 40 ps, respectively,\textsuperscript{54} times that are on the order of the values we obtain for \(\tau_2\). Photodissociation of CH\textsubscript{2}ClI in solution\textsuperscript{16,17} generates the same CH\textsubscript{2}Cl–I isomer as formed in the matrix, and time-resolved measurements observe an appearance and decay that are similar to the ones we observe in matrices.\textsuperscript{17} The time constant is \(\tau_1 = 1.5\) ps for the shortest, wavelength-dependent growth of the absorption,\textsuperscript{17} and it disappears over 50 to 100 ps.\textsuperscript{16,17} We have measured similar time scales at \(\lambda_{\text{probe}} = 435\) nm following the photolysis of dilute CH\textsubscript{2}ClI in room-temperature cyclohexane, where the signal rises with \(\tau_1 = 4.4\) ± 0.4 ps and decays with \(\tau_2 = 68\) ± 4 ps. The isomer CH\textsubscript{2}I–I formed by photolysis of CH\textsubscript{2}I\textsubscript{2} in super-critical CO\textsubscript{2} loses vibrational

![FIG. 9. A schematic drawing of the evolution of the CH\textsubscript{2}Cl–I isomer.](image-url)
energy to the solvent in 20–40 ps, again pointing to vibrational relaxation time scales that are relatively insensitive to the details of the condensed-phase surroundings.

There are relatively few time-resolved measurements of vibrational relaxation in matrices, but the time scales are roughly consistent with those we infer. For example, relaxation of the C=O stretch of acetic acid in an Ar matrix at 15 K takes about 80 ps, and, similarly, population relaxation in W(CO)6 requires 100 to 200 ps in CH4, Ar, and N2 matrices at 20 K. The most extensive time-resolved experiments on relaxation in a matrix are the detailed investigation of HONO by Botan, et al. They observe state-specific relaxation times ranging from 20 ps to 400 ps depending on the vibrational mode and find that relaxation into the matrix can occur before complete equilibration of the vibrations in the excited molecule. The matrix is clearly not a weak perturber in the system they study.

Molecular dynamics simulations of I2 dissociation in rare-gas crystals show that each successive collision of the iodine atoms with the cage sends shockwaves of energy through the lattice, leaving elevated temperatures near the chromophore. In addition, flow of energy from the vibrationally relaxing isomer can heat the solvent cage. It is possible that energy lost during the relaxation partially mobilizes the solvent shell, creating a region of elevated temperature that facilitates energy removal from the solute. The similar values of $\tau_2$ in liquid acetonitrile and cyclohexane solvents and in solid methane, nitrogen, and argon matrices suggest that similar mechanisms govern the vibrational relaxation in the matrix and in the liquid. Because these time constants do not vary dramatically with the identity of the matrix, it is likely that the vibrational relaxation pathways are similar in all three matrices, even though polyatomic matrices, with their additional degrees of freedom, potentially offer more pathways for energy flow.

V. SUMMARY

Time-resolved electronic absorption measurements of the isomer CH2Cl–I allow us to follow its formation and relaxation in three cryogenic matrices, CH4, N2, and Ar. We probe the isomer at wavelengths between 435 and 510 nm that are in its strong electronic absorption band. Probing the low-energy side of this transition monitors the relaxation of the vibrational energy of iso-CH2Cl–I. The isomer forms with high levels of vibrational excitation in about 1 ps after photodissociation of CH2ClI. The fast formation process resembles the behavior observed for photodissociation of I2 in rare-gas matrices, in which the recoiling fragments lose large amounts of energy to the matrix on the first collision. The intermolecular vibrational relaxation rate of the highly excited isomer does not depend strongly on the identity of the matrix and occurs on time scales that are similar to those observed for halomethane isomers in liquids and in supercritical CO2.

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41See supplementary material at http://dx.doi.org/10.1063/1.3633697 for the calculated vibrational frequencies (Table S1), for the difference spectra (Figure S1), and for the electronic energies of the isomer (Table S2).