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Photolysis of Triiodide Studied by Femtosecond Pump−Probe Spectroscopy with Emission Detection

Peter Gilch,* Ingmar Hartl,† Qingrui An, and Wolfgang Zinth
Sektion Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany

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The photodissociation of triiodide into diiodide and iodine in ethanol solution was studied by a novel femtosecond pump−probe technique. The dispersed emission of the triiodide sample was recorded as a function of the delay between a 407 nm pump pulse and a 815 nm probe pulse. The most prominent feature of the resulting time dependent spectra is a strong anti-Stokes (with respect to the probe wavelength) contribution. This contribution rises with a delay of ~500 fs and decays on the 2 ps time scale. The decay of the anti-Stokes spectrum is discussed in terms of the cooling dynamics of nascent diiodide for which the technique presented here gives a more direct access than transient absorption spectroscopy.

Introduction

Small iodine molecules and ions are popular guinea pigs for the study of ultrafast processes in gas and condensed phase (see, e.g., refs 1−5). They are well suited for such experiments, because their electronically excited states are often repulsive and their vibrational frequencies are very low.[6] The first property allows for an easy triggering of the ultrafast reactions by a (femtosecond) laser pulse, and the second property facilitates the observation of vibrational coherences with moderately short laser pulses. One iodine system that has been studied in detail by femtosecond transient absorption and resonance Raman spectroscopy is triiodide I_3^- in polar solution.[2,4,7,8] The results of these experiments are summarized as follows. When either of two absorption bands of triiodide are excited, the following reactions occur:[2,9]

$$I_3^- \xrightarrow{h\nu} I_3^-* \rightarrow I_2^- + I* \tag{1}$$

$$I_3^- \xrightarrow{h\nu} I_3^-* \rightarrow X \tag{2}$$

Excited triiodide I_3^-* dissociates within a few hundred femtoseconds to form diiodide I_2^- in its electronic ground state $^2\Sigma_u$ and an iodine I* atom in one of its spin−orbit states ($^2P_{3/2}$ or $^2P_{1/2}$)[2,4] (see eq 1). Recently, in addition to this established mechanism, a process competing with the dissociation has been proposed by Ruhman et al.[9,10] In this process, an intermediate denoted X by the authors is formed, the nature of which is still to be elucidated. It has been suggested that this intermediate might be a bound excited state of triiodide. Ruhman et al. observed the X intermediate when exciting triiodide in ethanol solution with 307 nm light. At this wavelength, mainly the high-frequency UV transition of triiodide is excited (see the spectrum in Figure 1). The group of Vöhringer performed experiments with 400 nm light exciting exclusively the low-energy band.[4] They analyzed their 400 nm data solely in terms of the dissociation reaction given in eq 1. When comparing 400 nm excitation (low energy transition) with 266 nm excitation (high energy transition), they found differences in the yield of the diiodide formation.[11] For 400 nm, they observed a yield of 100%, whereas it was determined to be 80% for 266 nm. Therefore, the additional decay path way observed by the Ruhman group might only be accessible when the higher frequency band is excited.

The dissociation (eq 1) of triiodide after excitation of the low energy band occurs within a few hundred femotoseconds.[4] Because of this short reaction time, the photoproduct diiodide

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* To whom correspondence should be addressed. Fax: +49-89/2180-9202. E-mail: Peter.Gilch@physik.uni-muenchen.de.

† Present Address: 30 Systems, 26081 Avenue Hall, CA 91355.

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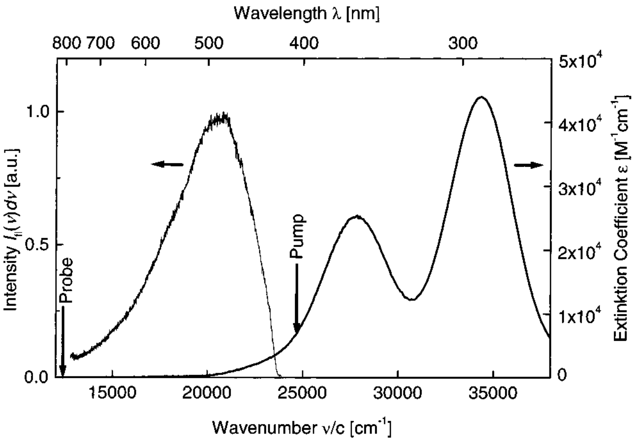

Figure 1. Absorption and emission spectra of triiodide in ethanol. For the emission spectrum, the excitation was tuned to 407 nm. The Raman lines of the ethanol solvent have been subtracted, the spectral sensitivity of the spectrometer has been corrected for, and the spectrum has been multiplied by the $\tilde{\nu}^{-2}$ factor to account for the constant wavelength (and not wavenumber) resolution of the spectrograph.

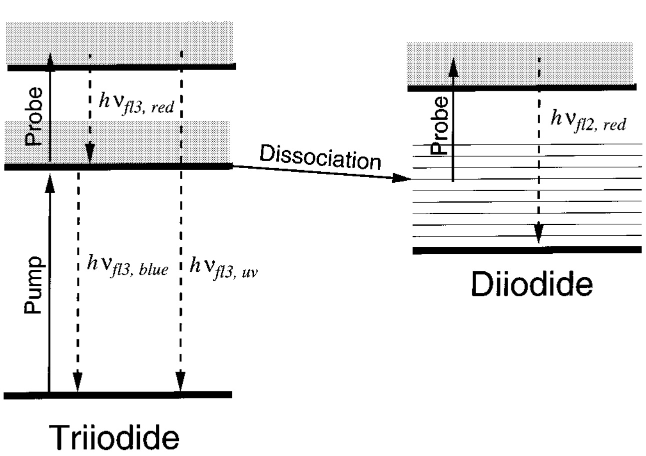

Figure 2. Jabloniski diagram of the photophysics of triiodide. Thick horizontal lines symbolize electronic states, thin lines symbolize vibrational states of diiodide. Dissociation continua are represented by shaded areas. Solid arrows stand for absorption processes, dashed arrows stand for fluorescence emission.

I_2^- is vibrationally hot and coherently excited, storing initially a part of the excess energy of the reaction.

The value of this energy depends on the spin−orbit state in which the iodine ($^2P_{3/2}$ or $^2P_{1/2}$) atom is formed. The energies of these states differ by 7600 cm^{-1}.[12] If the low energy absorption band of triiodide is excited, presumably the upper spin−orbit state ($^2P_{1/2}$) of iodine is formed.[4,7,11] Assuming that the upper state is formed, the excess energy of the photoproducts amounts to 4000 cm^{-1}, otherwise it amounts to 11600 cm^{-1}. This energy is partially stored in the vibrational mode of the I_2^- ion. The decay of this vibrational excitation has been examined by several groups. Ruhman et al. used transient absorption spectroscopy[13] and impulsive stimulated Raman scattering[14] to monitor the cooling dynamics after 307 nm excitation of triiodide. Barbara et al. photoexcited diiodide and recorded the recovery of the ground-state bleach of diiodide.[3,15,16] All of these studies indicate that the relaxation is biphasic. Most of the vibrational energy seems to be dissipated in some 100 fs, whereas relaxation at the bottom of diiodide potential well occurs in 3−4 ps. These results have been confirmed in principle by Vöhringer et al. They worked with 400 nm pump light to excite triiodide which makes their results most comparable with the experiments described here. They recorded the absorption spectrum as a function of pump−probe delay[4] and used the shape of these spectra as an indicator for the vibrational excitation of nascent diiodide. They found that 1.5 ps after excitation only a small amount of energy of ~200 cm^{-1} corresponding to roughly two vibrational quanta of I_2^- is still stored in its vibrational mode. The decay time of this vibrational energy was determined to be 3.5 ps.

The study of the short time dynamics (<1.5 ps) of the vibrational excitation by absorption methods is difficult for the following two reasons. At early times, wave packet dynamics are superimposed on the signal and obscure the reconstruction of the time-dependent spectra. To monitor *high* vibrational excitations of diiodide via transient absorption, a spectrally very broad detection window is necessary[3,14] which might cover transitions to other electronic states. The simulated spectra in ref 3 indicate that around the maximum of cold diiodide the spectra of vibrationally excited diiodide molecules are essentially flat. Therefore, for a precise determination of the excitation, one has to observe the two maxima in the spectra which arise from the two dominant antinodes of the vibrational wave function for high quantum numbers. Simulations of Banin et al.[13] demonstrate that these two maxima occur at ~1100 and ~560 nm, respectively, for a broad vibrational excitation centered at $v = 17$; that is, as stated above, a very broad detection window is necessary to monitor high vibrational excitations. If a smaller detection window is used, it will be difficult to monitor the high vibrational excitation expected during the first several 100 fs by time-dependent absorption spectroscopy.

The vibrational wave packet motion mentioned above can give access to the vibrational cooling during that period. Because of the anharmonicity of the diiodide ground-state potential, the oscillation period of this motion should decrease during cooling. This has indeed been observed.[4,17] Analysis of this frequency shift yielded a relaxation time of ~400 fs with an amplitude of 1400 cm^{-1}; that is, at early times, the vibrational relaxation seems to be much faster than at later times. This frequency shift has later been examined in more detail by the same group using impulsive stimulated Raman scattering.[17] An LPSVD analysis of their data revealed three oscillatory components. Two components have frequencies close to the fundamental (113 cm^{-1}) and the first harmonic of diiodide. These frequencies are observed nearly immediately after the photolysis of triiodide and change weakly and smoothly with time. The third component has initially a frequency of ~70 cm^{-1} and rises quite abruptly to the value of the fundamental within some 100 fs. The behavior of the first two components can be attributed to the cooling of diiodide, and the third component calls for another mechanism. It has been attributed to a strengthening of the diiodide force constant which occurs while the photofragments separate which is in conflict with the cooling mechanism mentioned above. Therefore, other techniques allowing the study of the cooling dynamics during the first few 100 fs are desirable.

We here present an alternative and more direct method to study the dynamics of the formation and the vibrational relaxation of diiodide. In the present experiment, the fluorescence of the sample is observed after illumination of a I_3^- solution with two laser pulses: A 407 nm pump pulse excites I_3^- and initiates its photodissociation. A delayed 815 nm probe pulse excites the generated I_2^- molecules, and their fluorescence emission is used to monitor the vibrational excitation of I_2^-. The fluorescence emission is generated by the different intermediates of the reaction sequence (see Figure 2): (i) The excitation of I_3^- by the pump pulse populates the state I_3^{-*}

which may fluoresce with photons $h\nu_{\mathrm{Fl3,blue}}$. (ii) The probe pulse may interact via excited-state absorption with I_3^{-*} leading to emission from higher excited states of I_3^- ($h\nu_{\mathrm{Fl3,red}}$, $h\nu_{\mathrm{Fl3,uv}}$). The promotion of I_3^{-*} to a higher excited state of course depopulates this state and, therefore, reduces emission from I_3^{-*}. (iii) When I_2^- is formed, the probe pulse, being strongly absorbed by I_2^-, brings this molecule to one of its excited electronic states I_2^{-*}. Contribution i does not depend on the pump−probe delay, and contributions ii and iii are sensitive to this delay and, therefore, allow us to monitor the decay of I_3^{-*}, the formation of I_2^-, and (as we will explain later on) the vibrational cooling of nascent I_2^-.

Experimental Section

The basic parts of the experimental system have been described in refs 18 and 19. The frequency-doubled output (407 nm, 5 μJ) of a 1 kHz titanium sapphire laser/amplifier system was used to excite the triiodide sample. A part (10 μJ) of the 815 nm fundamental of the laser system constitutes the probe beam which crosses the pump beam in the sample under a small angle of ∼5°. The emission of the sample was collected by reflective optics, dispersed by an imaging spectrograph, and recorded by a back-illuminated liquid-nitrogen-cooled CCD camera (for details on the detection setup, see ref 18). Scattered laser light at the fundamental and the second harmonic was suppressed by suitable notch filters. The spectral sensitivity of the spectrometer−detector setup has been corrected for with a blackbody radiator as a reference. It should be stressed that in this experiment detection of the emission was not gated. The experimental response function (cross correlation function) was determined by a two photon absorption method. The sample was replaced by a 0.1 mm thick cuvette containing neat 1-methylnaphthalein. This liquid is transparent at 815 and 407 nm. Multiphoton absorption processes of the pump and the probe pulse induce a fluorescence emission that is enhanced by ∼60% when both pulses coincide. Recording of this fluorescence (spectrally integrated) as a function of the delay time yields a measure for the cross correlation function. For the experiments described here, the cross correlation time was determined to be 300 fs (fwhm). The present setup can also be used to determine emission lifetimes via an inverse Raman effect. A detailed description will be given in a forthcoming publication.[20] The time-resolved absorption measurements were performed in the group of M. E. Michel-Beyerle at the TU München (for details of the setup, see ref 21). The sample was prepared by dissolving 100 mg of I_2 and 100 mg of KI in 50 mL ethanol. This corresponds to a concentration of 8 mM I_3^- and an absorbance at 407 nm (excitation wavelength) of 5.6 OD in the 1 mm cuvette used. The sample solution was flown rapidly through the cuvette to prevent local heating of the solution. Measurements were performed at room temperature and with magic angle polarization between pump and probe beams.

Results

Fluorescence Spectrum and Quantum Yield of I_3^-. Although I_3^- has been thoroughly characterized by the usual spectroscopic methods, to our knowledge, no fluorescence spectrum of this ion has been published. This spectrum and the fluorescence quantum yield allow to obtain a rough estimate of the excited-state lifetime of I_3^-. The spectrum was recorded with the same setup as used for the time-resolved measurements except for the blocked probe beam and a reduced sample concentration of 2.7 mM. Inner filter effects on the emission spectrum could be excluded by comparing spectra of samples with an optical path length of 1 mm and 0.1 mm. The 407 nm excitation wavelength corresponds to the red edge of the lowest absorption band of I_3^-. The emission spectrum corrected for Raman contribution of the solvent and the spectral sensitivity of the setup is depicted in Figure 1. The emission spectrum is broad and structureless and peaks at 21 000 cm^{-1}. For the determination of the fluorescence quantum yield ϕ_f, the fluorescence intensity was referenced to the fluorescence of phenazine in methanol which was chosen because of its absorption band lying close to that of triiodide and its low emission quantum yield. The yield of phenazine in turn was determined to be 0.06% by comparing its integrated emission with that of coumarin 47 in ethanol ($\phi_f = 73\%$[22]). The validity of this yield was checked by an estimate based on the Strickler−Berg relation and the published lifetime of phenazine[23] which yields the same magnitude. The fluorescence quantum yield of I_3^- obtained this way is 5.8×10^{-5}. An estimate for the excited-state lifetime τ_s of triiodide can be calculated by the relation

$$\phi_f = \frac{\tau_s}{\tau_0} \tag{3}$$

where τ_0 is the radiative lifetime. This lifetime was determined via the Strickler−Berg relation[24] using the absorption and emission data to be 6.9 ns which in turn yields (eq 3) an excited state lifetime of 400 fs. Of course, this value only gives the order of magnitude of the excited state lifetime, particularly because of some conceptional difficulties when applying the Strickler−Berg relation to transitions involving repulsive states. A more precise result from a time-resolved experiment will be given below.

Time-Dependent Emission Spectra. The emission spectrum of the I_3^- sample depends on the relative temporal delay between 407 nm pump and 815 nm probe pulse. If the probe pulse precedes the pump pulse (large negative delay times), the emission spectrum $I_{\mathrm{Fl}}(-\infty)$ is a superposition of the pump induced fluorescence of I_3^- and the Raman signal of the ethanol solvent induced by the probe pulse (see insert in Figure 3a). For positive delay times, the emission of the sample is enhanced (see Figure 3a). The maximum enhancement amounts to ∼10% of the total emission and has a distinctly different spectral signature than the emission observed at negative delay times. Details of the enhancement can be seen if the emission recorded at large negative delay times $I_{\mathrm{Fl}}(-\infty)$ is subtracted leading to the enhanced emission signal $\Delta I_{\mathrm{Fl}}(t_D) = I_{\mathrm{Fl}}(t_D) - I_{\mathrm{Fl}}(-\infty)$.

The Stokes Part of the Emission. The enhanced emission on the Stokes side is broad and nearly structureless (Figure 3). The increase of the emission when approaching the probe wavelength suggests that a maximum falls into this spectral region. The inevitable blocking of the scattered probe laser light prevents a determination of this maximum. Except for a weak shoulder at 850 nm (Figure 3b), which decays in some 100 fs, the Stokes spectrum virtually does not change its shape with time. This applies to the 1 ps time scale on which the vibrational cooling dynamics is expected to occur (Figure 3a) and to the 10−100 ps time scale on which the recovery of ground-state triiodide takes place (Figure 3 parts b and c).

The Stokes signal rises instantaneously, i.e., within the temporal resolution of our setup (see integrated Stokes signal in Figure 4). The signal then falls off slightly to a minimum around 700 fs and, after reaching a second maximum around 2 ps, decays on the 10 ps time scale. The time dependence of the Stokes signal strongly resembles that of the transient absorption recorded in the same spectral region (Figure 4, open circles).

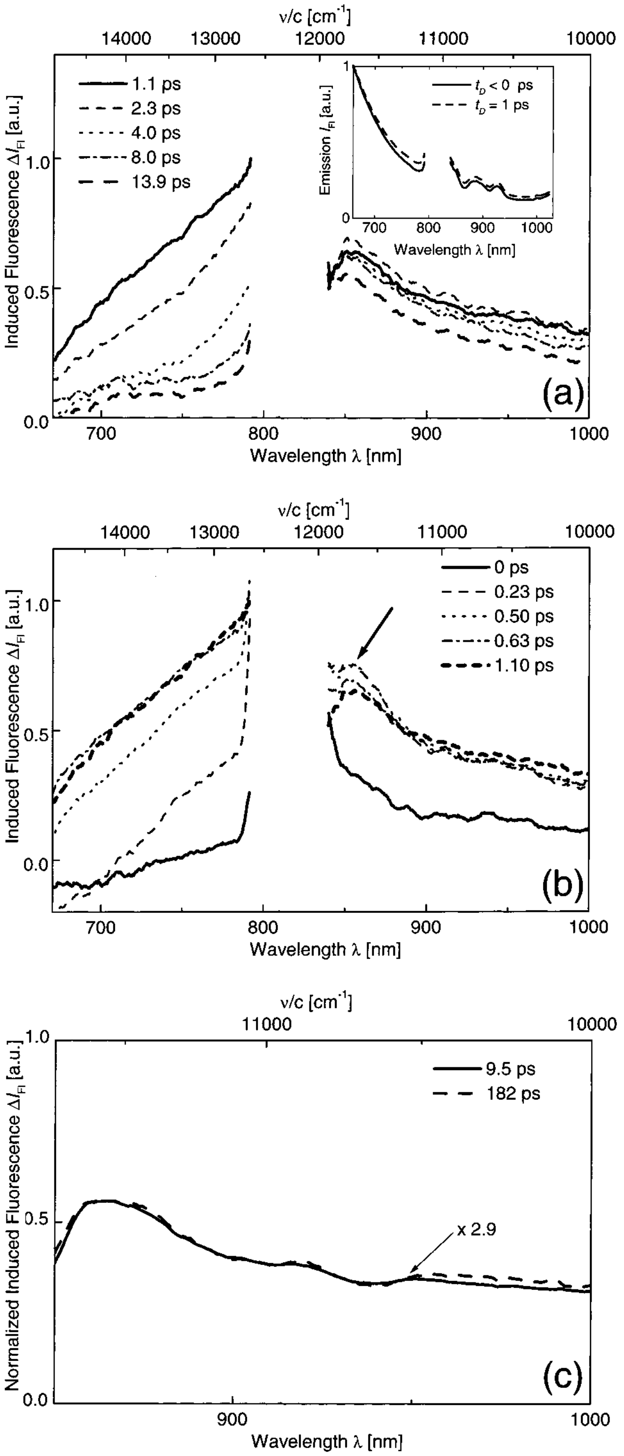

Figure 3. Induced emission spectra of triiodide as a function of delay time. The pump wavelength was set to 407 nm, whereas the probe wavelength was tuned to 815 nm. The induced emission spectra were obtained by subtracting the emission spectrum at large negative delay times from the spectrum at the given delay time (for the absolute emission spectra, see inset in a). (a) Decay of the induced emission spectra (1.1−13.9 ps). (b) Rise of the induced emission spectra (0−1.1 ps). (c) Long-term evolution of the Stokes part of the induced emission spectrum. For the sake of comparison, both spectra have been scaled to the same height.

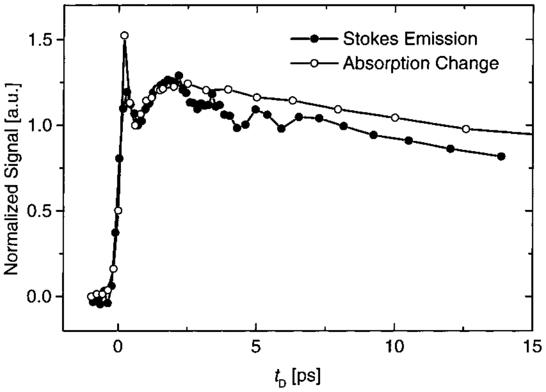

Figure 4. Time dependence of the integrated Stokes part (850−990 nm) of the induced emission depicted in and of the transient absorption recorded at 825 nm.

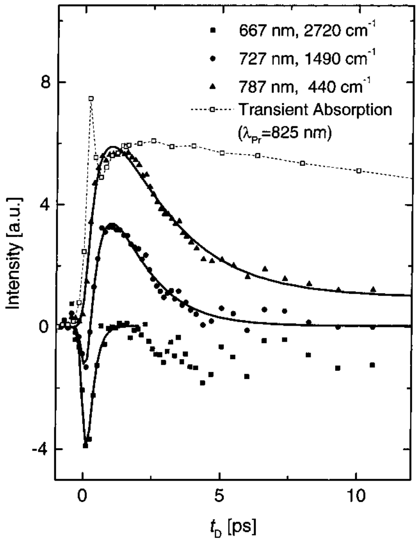

Figure 5. Time dependence of the anti-Stokes part of the induced emission spectra. The time traces were obtained by integrating over 14 nm broad ranges of the spectra given in Figure 3. The center wavelengths of these portions are given in the legend. The solid lines describe the results of a fit as described in the text.

This absorption change has been assigned to the excited-state absorption of I$_3^-$ at early delay times and to the ground-state absorption of I$_2^-$.[4] On the basis of the absorption data alone, it is difficult to pinpoint the decay of I$_3^-$* and the rise of I$_2^-$. Our results show that the decay of the first spike of the transient absorption data is accompanied by a change in the Stokes emission spectrum (the decay of the 850 nm shoulder) suggesting that during that decay a change of the electronic character of the emitter occurs. Concerning the ensuing slight rise of the absorption from 700 fs until 2 ps and the subsequent decay the Stokes emission give no further information, contrary to the anti-Stokes emission to which we will turn now.

The Anti-Stokes Part of the Emission. The rise of the anti-Stokes part of the induced emission spectrum is delayed with respect to the instantaneous rise of the Stokes part or equivalently the transient absorption (Figure 3b). The time dependence of the anti-Stokes emission for some wavelengths is compared with the absorption data in Figure 5. The delay of several 100 fs for the rise of the anti-Stokes emission is clearly visible. In addition, a negative signal at time zero is observed. This negative signal consists of a broad and weak contribution extending throughout the anti-Stokes part and a stronger, sharp feature at 660 nm. A broad negative signal indicates a reduction of the I$_3^-$ fluorescence emission induced by the probe pulse. A possible mechanism for such a reduction works as follows: during the lifetime of I$_3^-$*, the probe pulse can promote excited triiodide to higher lying states S$_n$ (see Figure 1). This process depletes the S$_1$ state and concomitantly reduces the S$_1$ → S$_0$ emission which in turn should cause a negative signal following the emission spectrum of I_3^-.

The sharp spectral feature around 660 nm with a width of 15 nm (not shown) which is not present in the emission spectrum of triiodide must have a different origin. This wavelength of 660 nm corresponds to a shift relative to the probe pulse of $\sim$2900 cm^{-1}. The shift coincides with the most intense Raman line of the ethanol solvent.[25] We, therefore, attribute this reduction to an inverse Raman scattering.[26] In a stimulated Raman process, fluorescence photons of I_3^- with a wavelength of $\sim$660 nm are annihilated, whereas simultaneously, photons with the wavelength of the probe pulse (815 nm) are created. Concomitant with this wavelength shift, the 2900 cm^{-1} vibration of ethanol is excited. This inverse Raman process can only occur when the fluorescence light and the probe pulse overlap in time; in other words, the negative signal follows the fluorescence lifetime of I_3^- convoluted with the experimental response function. This allows us to determine the fluorescence lifetime by fitting the spectrally integrated inverse Raman signal with an exponential convoluted with a Gaussian (fwhm 300 fs, see the Experimental Section) representing the experimental response function. We thereby determine the fluorescence lifetime to be 240 fs. It is worth noting that the temporal width of the inverse Raman signal coincides with the spike seen in the absorption measurement. The fluorescence lifetime of 240 fs is shorter than the rise time of the anti-Stokes emission (Figure 5). A numerical analysis shows that this rise time increases from 500 to 700 fs when moving from the blue edge (680 nm) to the red edge (780 nm) of the anti-Stokes spectrum. At a first glance, Figure 5 seems to indicate the contrary. This apparent contradiction is due to the fact that the amplitudes of negative contribution are large at shorter wavelengths.

The decay of the anti-Stokes emission occurs on the time scale of $\sim$2 ps. The decay time depends on wavelength and increases when moving to the red. For instance, at the blue edge of the anti-Stokes spectrum, the decay time is 1.4 ps, whereas it is 2.3 ps at the red edge. This observation is equivalent to a red-shift of the anti-Stokes spectrum with time, which is clearly seen in Figure 3a.

Discussion

As pointed out in the Introduction, there is an uncertainty about the photoproducts of the 400 nm photolysis of triiodide. Because two products, diiodide and the X intermediate, discussed in the literature, absorb at our probe wavelength of 815 nm,[9] it is crucial for the interpretation of our data to clarify whether the X intermediate is also formed under our experimental conditions. Ruhman et al.[9] determined the lifetime of the X intermediate to be 45 ps at room temperature. The Stokes emission spectrum recorded at such long delay times ($t_D = 180$ ps) has virtually the identical shape as the spectrum recorded $\sim$10 ps after excitation, i.e., before the decay of the X intermediate (Figure 3c). So either the X intermediate is not formed in the 400 nm photolysis of triiodide or this intermediate is not detectable with our method. In either case, if X is not formed here or our method is insensitive to X, our results can be interpreted assuming that diiodide and iodine are the only photoproducts (eq 1).

We will now turn to the question under which circumstances our pump−probe emission experiment can yield additional information on the vibrational excitation. Assume that a pump pulse prepares a vibrationally hot product state P_{hot} via electronic excitation of a reactant and subsequent ultrafast chemical reaction. When the probe pulse interacts with P_{hot} before the vibrational cooling is terminated, P_{hot} will be promoted to an electronically excited state, which will again be vibrationally excited even if the probe pulse is tuned to the 0−0 transition of the product state (see Figure 6). It is the emission of this state which is detected in our difference emission measurements. The information content of the spectrally resolved $P^* \rightarrow P$ emission depends crucially on the shape of the electronic potential surfaces involved in the transition. We consider the following three classes: (i) The surfaces of P and P^* are bound (Figure 6a). The hot molecule P_{hot} is transferred to the P^* state where vibrational relaxation occurs. Fluorescence emission predominately originates from the vibrational ground state of P^* because vibrational relaxation in polar solvents typically occurs on the picosecond time scale,[27] whereas radiative lifetimes are much longer.[24] For the time integrated fluorescence detection of our setup, the signal would be dominated by the fluorescence from the vibrational ground state of P^*. The only information on the vibrational cooling of P_{hot} would be due to changes of the absorption of P_{hot} in the course of the cooling process. The shape of the emission spectrum would not be influenced, and the experiment should yield information similar to transient absorption spectroscopy. (ii) The P surface is bound, and the P^* surface is repulsive. A hot P_{hot} molecule promoted to the P^* surface by the probe beam starts to dissociate immediately. This reaction is accompanied by a drastic decrease of Franck−Condon overlap with the ground state.[6] Therefore, fluorescence emission occurs prior to significant motion on the P^* surface and has a very small quantum yield. In other words, the initial (vibrational) state of the emission is identical to the final state reached in the absorption process of the probe pulse. A molecule P_{hot} with an excess energy of E_{exc}, excited by a probe pulse of the energy $h\nu_{\mathrm{probe}}$ can, therefore, emit fluorescence light up to a frequency of $(E_{\mathrm{exc}}/h) + \nu_{\mathrm{probe}}$; the emission spectrum will contain a Stokes and an anti-Stokes part (see Figure 6b). The anti-Stokes fluorescence is a direct indicator of the amount of vibrational excitation; as P_{hot} cools the blue

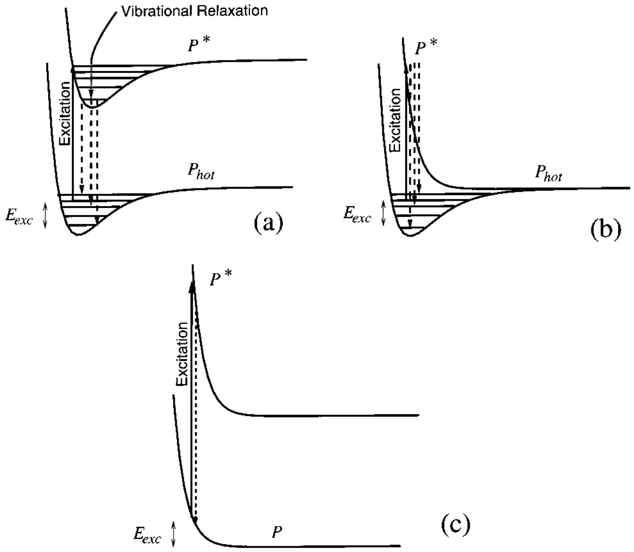

Figure 6. Schematics of possible potential energy surfaces relevant to the interpretation of the induced emission spectra. (a) Lower and upper surfaces are bound. In the excited-state, vibrational relaxation occurs prior to fluorescence emission. The emission quantum yield is large, and the emission spectrum is not influenced by the vibrational excitation. (b) The lower surface is bound, and the upper surface is repulsive. Fluorescence light is predominately emitted prior to vibrational relaxation and contains information on the vibrational excitation E_{Exc}. The emission quantum yield is small. (c) Both surfaces are repulsive.

edge of the anti-Stokes spectrum moves to the red. Of course, in a quantitative analysis of this excitation, the Franck−Condon factors have to be taken into account. In short, the vibrational excitation can be probed by an emission technique without gating because the repulsive nature of the upper electronic state provides an “internal” gating. (iii) Both states are repulsive (Figure 6c). Here the appearance of an anti-Stokes emission depends on the relative slope of the two surfaces. An anti-Stokes signal can only be expected if the slope of the upper state surface is more shallow than that of the lower.

The three molecular species I_3^-, I_3^{-*}, and I_2^- present in our pump−probe experiment on I_3^- are now classified accordingly. Triiodide in its ground-state belongs to class ii because its excited states are repulsive as the numerous transient absorption studies discussed in the Introduction demonstrate. The first excited state S_1 of triiodide can be promoted to a higher lying excited state S_N by the 815 nm probe pulse. Energetically, this S_N state could be identical with the excited state directly accessible by 270 nm excitation (see the absorption spectrum in Figure 1) which is known to be repulsive (see above). In this case, the probe pulse would induce a transition between two repulsive surfaces; that is, I_3^{-*} belongs to class iii. Diiodide as a stable molecular ion has a bound ground state. Its excited states are known to be repulsive or weakly bound.[28,3] There are experimental indications that when I_2^- is photoexcited to its repulsive excited states the bound state $^2\Pi_{3/2,g}$ is populated via recombination of the photofragments[29,16] (the population of a bound state is, however, questioned in ref 30). The question arises how this bound state influences the emission pattern observed here. Population of this state is only expected to occur via excitation of diiodide by the probe pulse; there are no indications that excited diiodide is formed during the 400 nm photolysis of triiodide.[11] The 815 nm probe pulse places the diiodide vibrational wave packet well above the dissociation threshold of the $^2\Pi_{3/2,g}$ state (see the potential curves in ref 28) even if I_2^- is vibrationally cold. Diiodide promoted to this state by the probe pulse will first dissociate and then because of caging partially recombine.[16] Emission from recombined excited diiodide will be strongly red-shifted with respect to the probe pulse (the energy difference between the minima of the $^2\Pi_{3/2,g}$ and the ground state corresponds to a wavelength of 1250 nm). Therefore, the bound excited state should not contribute to the anti-Stokes emission, and diiodide can be assigned to class ii.

Directly after photoexcitation the only transient species is I_3^{-*}. Experimentally, we observe only a weak anti-Stokes emission during the first 100 fs. This is expected because I_3^{-*} as a class iii species should not give rise to a large anti-Stokes signal even if I_3^{-*} contained a large amount of excess energy. In addition, the excitation at 407 nm takes place in the red-wing of the lowest absorption band of I_3^- depositing only a small amount of excess energy. It is only after the decay of I_3^{-*} that a large amount of excess energy is stored in the vibrational degrees of freedom of the molecular system which could either be the mode of nascent diiodide or the modes of geminately (hot) recombined triiodide. Concerning the contribution of the hot triiodide to the anti-Stokes signal, an estimate based on the empirical potential energy surfaces of triiodide as first parametrized by Benjamin et al.[31] indicates that it requires a vibrational excitation of ≥ 6000 cm^{-1} to shift its ground-state absorption from 370 nm to the 815 nm probe wavelength. In principle, such an amount of excess energy is available upon recombination of diiodide and iodine (see above). However, there are several arguments which render a contribution of hot triiodide to the anti-Stokes signal rather unlikely. First, larger values for the vibrational excitation than the one discussed above are required if the vibrational energy is not localized in symmetric stretch vibration. An involvement of the antisymmetric stretch, the two degenerate bending vibrations, and the modes of the surrounding solvent molecules increase this value considerably. Second, the transient absorption spectrum recorded by Kühne et al.[4] 1.5 ps after excitation strongly resembles the spectrum of diiodide and shows no contributions of a hot triiodide ground state absorption. Third, by spectrally integrating this absorption band, they came to the conclusion that geminate recombination occurs on a time scale of some picoseconds or longer,[4] whereas the rise time of the anti-Stokes signal is well below 1 ps. We, therefore, at the present stage of analysis, do not consider contributions of hot triiodide to the anti-Stokes signal and assign this signal to hot diiodide.

The decay time of I_3^{-*} was determined here to be 240 fs employing the inverse Raman effect. This is consistent with the estimate based on the fluorescence quantum yield. The I_3^{-*} decay time is shorter than the rise time of the anti-Stokes signal which spans the range of 0.5−0.7 ps. We associate this rise time with the formation of diiodide which as a class ii entity can show an anti-Stokes emission if it is vibrationally hot. The observation that the decay time of I_3^{-*} emission is shorter than the formation time of I_2^- is in apparent contradiction to the simple reaction scheme given in eq 1. However, decay and rise times of a one step reaction are only equal for rate-type (exponential) processes. The experimental observation of vibrational wave packets even in the diiodide products[2,4] gives clear evidence that the dissociation of I_3^{-*} should not be viewed as an exponential process but rather as a motion of a vibrational wave packet on a repulsive surface. Because the Franck−Condon factors vary strongly during such a motion, the time constant of 240 fs may be related to motion out of Franck−Condon region of the I_3^{-*} surface. The appearance of the anti-Stokes emission then reflects the formation of hot I_2^-. The dip in the transient absorption data depicted in Figure 4 supports this interpretation. The rise times range from 0.5 to 0.7 ps depending on the wavelength. This time scale compares well with the appearance of the diiodide vibrational wave packet observed in transient absorption spectroscopy[13,11] which is one indicator for the formation time of diiodide. A similar time is obtained by quantum dynamics and molecular dynamics calculations using empirical LEPS surfaces.[11,31,32] There are, however, other experimental results which indicate that nascent diiodide still changes its electronic character after that formation time of ∼400 fs. The transient absorption signal slightly increases until approximately 2 ps after the photolysis pulse.[4,11] In addition, the initial anisotropy of diiodide as measured in a photolysis-pump−probe experiment decays from 0.7 to 0.4 within the same time.[17] As the common origin of these signals, the authors propose a change in the electronic structure of diiodide during the separation of the diiodide and the iodine atom. In other words, it takes about 2 ps until “free” diiodide is formed. The rise of anti-Stokes does not reflect this change of electronic structure. The formation time of diiodide determined here is very close to the appearance time of vibrational wave packet motion seen in transient absorption experiments (see above).

There is, however, no doubt that nascent diiodide is vibrationally hot. The degree of vibrational excitation of nascent diiodide is imprinted in the anti-Stokes part of the emission spectra presented here. A larger anti-Stokes shift monitors a higher vibrational state. The rise and decay times determined by fitting portions of the anti-Stokes emission, therefore, give an estimation of the population dynamics of segments of the vibrational ladder of diiodide. In the instant of formation, diiodide should have its highest vibrational excitation. Indeed, the rise time at the blue edge (0.5 ps) of the anti-Stokes signal is shorter than at the red edge (0.7 ps). Not only does the red rise time reflect the formation dynamics of diiodide but also the population transfer from higher vibrationally excited states to lower ones. The maximum of the anti-Stokes emission is reached ∼1 ps after photoexcitation. At that time, the anti-Stokes spectrum ranges roughly from -2800 cm^{-1} (relative to central frequency of the probe laser) to 0 cm^{-1}. As the vibrational frequency of diiodide is 114 cm^{-1},[33] the 2800 cm^{-1} shift corresponds to a vibrational excitation of ∼24 quanta. The center of the anti-Stokes spectrum at 1 ps is ∼1400 cm^{-1} giving a rough estimation of the vibrational excitation at that time. The anti-Stokes spectrum then decays and shifts to the red on a time scale of 2 ps. In light of the results on the change of electronic structure of nascent diiodide on the same time scale[17] discussed above, a possible contribution of these changes on the anti-Stokes emission has to be taken into consideration. Such changes might go along with variation of the energy gap and thereby the excess energy available for the anti-Stokes emission. We consider such a contribution as not very likely for the following two reasons. First, the rise of anti-Stokes emission is faster than the decay of initial anisotropy which was taken as the indicator of electronic changes (see above). If the rise is insensitive to this change, it is unlikely that the decay is. Second, the transient absorption signal at the probe wavelength changes only very weakly during the decay of the anti-Stokes signal (see Figure 5). If there were a large change in the energy gap, a more pronounced change of this signal should occur. As a consequence, the analysis of the anti-Stokes decay is based on the assumption of a constant energy gap. The decay time of the anti-Stokes signal increases with decreasing anti-Stokes shift as expected for a vibrational cooling process. For instance, the time constant is 1.4 ps for a shift of 2400 cm^{-1}, whereas it is 2.3 ps for 400 cm^{-1}. A characteristic time for the cooling is on the order of ∼2 ps which is close to the somewhat longer time constant of 3.5 ps determined by transient absorption spectroscopy.[4] However, the time constant of ref 4 is supposed to have a small amplitude of only 250 cm^{-1} of vibrational excitation, whereas our results strongly suggest that the picosecond cooling time constant has a much larger amplitude. In the transient absorption measurement, the dominant amplitude was reported to be 1400 cm^{-1} with a decay time of 400 fs. Such a contribution is clearly missing in our data.

Conclusions

A new technique is used for the study of the photoreaction of triiodide. Monitoring the induced emission in a pump−probe experiment gives additional information on product dynamics as compared to conventional pump−probe absorption spectroscopy. The transition of excited triiodide into diiodide which is accompanied by only minor changes in the transient absorption spectrum is clearly visible in the induced emission spectrum. Formation of nascent diiodide was found to occur within 0.5 ps. The emission of excited triiodide decays in 0.24 ps. The difference between these two values is related to the nonexponential wave packet type character of the dissociation. The amount of the vibrational excitation of nascent diiodide could be estimated from the anti-Stokes part of the fluorescence spectrum. The peak energy stored in the vibrational mode is ∼1400 cm^{-1} at 1 ps. The vibrational excitation decays on the 2 ps time scale.

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