Heterodynedetected timedomain measurement of I2 predissociation and vibrational dynamics in solution

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An understanding of the molecular mechanisms that produce broad and structureless electronic absorption spectra is central to studies of chemical dynamics in liquids and solutions. Such broadening often reflects the perturbation of the electronic and nuclear degrees of freedom of the solute by the solvent medium. The spectral consequence of these interactions, however, is to mask the structural and dynamic information necessary to formulate molecular-level descriptions of chemical processes. The preparation and detection of the evolution of coherent vibrational motion (i.e., nuclear wave packets) of chromophores in solution by direct time-domain methods is an experimental approach that facilitates the extraction of the molecular vibrational spectrum. For photochemically reactive species in liquid media, such studies may reveal nuclear motion along the reaction coordinate and also probe the role of the absorber–bath interactions.

With this goal in mind we have chosen to study a simple molecular solvent and iodine as the (reactive) chromophore. The reaction is the predissociation of the B state of I₂, which is believed to occur via solvent-induced coupling of the B(0Σ⁺ 3II) and dissociative (1Σ⁺ 3II) states. It has been theoretically shown that vibrational coherences in both ground and excited electronic states, as well as populations, are prepared when an ultrafast pulse interacts with an electronically resonant molecular sample. Several experimental techniques have been demonstrated to detect these vibrational coherences under conditions of electronic resonance. However, the ground or excited state assignment of these vibrational responses has not always been clearly made, particularly for chromophores (i.e., dye molecules) in solution. The results reported here allow clear assignment of all nuclear dynamic contributions to the signal.

The timescales of iodine recombination and relaxation following predissociation have been reported. Condensed phase transient absorption and resonance Raman studies have monitored the geminate recombination and vibrational relaxation on the picosecond time scale. Harris and co-workers established that B-state predissociation in chlorinated methane solvents occurs in less than two picoseconds. The spontaneous B → X resonance Raman scattering of I₂ in a variety of solvents has been analyzed by Senion and Strauss. As a result of a Raman excitation profile study, they conclude that the optical dephasing time of I₂ in n-hexane is about 300 fs and that the major line broadening mechanism for the B → X transition in solution is ascribed to inhomogeneity. However, early estimates of a long excited state lifetime resulted in uncertainty as to the origin of the homogeneous broadening.

In this communication we report time-domain measurements of the ultrashort-pulse optically induced dichroism of I₂ in solution. The excitation and probe pulses at 580 nm are resonant with the broad B → X (630–450 nm) absorption band. Our approach is a form of polarization spectroscopy, where the decay of the pump–probe induced anisotropy is probed via optical heterodyne detection.

The time dependence of the heterodyne-detected optically induced transient dichroism signal for pump–probe pulses separated in time by t₃ is described by

\[ S(t₃) \sim R(t₃)W(t₃), \]

where \( R(t₃) \) describes the overall rotational reorientation relaxation of the anisotropy induced by the first pulse and \( W(t₃) \) is the time-dependent change in the energy of the signal field. In what follows we concentrate on \( W(t₃) \), the work done on the detected optical field by the pump–probe induced material polarization.

We have derived expressions for \( W(t₃) \) using a density matrix treatment for a four-level system consisting of two vibrational levels of two dipole-coupled electronic states excited by pulses of finite duration but shorter than all the relevant material dephasing times of the system. A full account will be given elsewhere. It is found that in dichroism measurements of such a four level system the energy of the probe beam will be transiently affected, in general, by three material responses of differing molecular origin: (i) excited state population, (ii) excited state vibrational coherence, and (iii) ground state vibrational coherence. Since the amplitude of the three contributions to the signal are determined by products of the same Franck–Condon factors it is anticipated that their initial contributions to the dichroic response will be similar in magnitude. The optical dephasing time \( T₂ \) does not affect such pump–probe signals.

The sample is excited and probed by tunable 30 fs FWHM Gaussian pulses at 100 kHz repetition rate. The dichroic part of the molecular nonlinear response function is selected by means of an in-phase local oscillator that is derived from the probe pulse and is adjusted to be 20 times the homodyne intensity. In practice, the dichroism is obtained by taking the difference of two scans each with the same magnitude local oscillator but of opposite sign. The π shift of the local oscillator phase is obtained by rotating the polarization analyzer that

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**Heterodyne-detected time-domain measurement of I₂ predissociation and vibrational dynamics in solution**

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follows the sample by equal amounts in opposite directions. This differencing approach removes the homodyne and any small residual birefringence signal from the dichroism measurement.\(^{28,29}\) mM I\(_2\) (Aldrich) in n-hexane (Baker spectrophotometric grade) was flowed in a 1 mm cell to avoid thermal heating and lensing effects and has an optical density of 0.15 at 580 nm. All measurements are performed at 295 K. The energies of the pump and probe beams at the sample are 3–4 nJ and 100–200 pJ, respectively. A mechanical chopper is used to amplitude modulate the pump beam. The induced modulation of the probe beam transmitted through the analyzer is detected by a photomultiplier tube and is processed in a lock-in amplifier (SRS 530) referenced to the amplitude modulation. The lock-in signal is recorded for each step of the optical delay line (1 s accumulation) and approximately 4 scans are averaged together.

The optically induced dichroism of I\(_2\) in n-hexane excited and probed by 30 fs pulses centered at 580 nm is shown in Fig. 1(a). Also shown in this figure is the intensity autocorrelation of these pulses. Following the time of pump–probe overlap (\(\approx 50\) fs) and coherent artifact effects,\(^{30}\) the most obvious feature of this dichroic response is the oscillation with an \(\approx 150\) fs period that persists for several picoseconds. This oscillation corresponds to a level spacing of \(211 \text{ cm}^{-1}\) in the vibrational superposition.

Linear prediction singular value decomposition\(^{30}\) analysis was used to determine the number of parameters for the exponentially damped cosinusoidal terms that describe the data set. This method of analysis has been used to determine the frequency, phase, and time constant of vibrational wave packets in dye molecules.\(^{11}\) Standard non-linear least-squares approaches to data fitting are not very reliable due to the number of parameters involved.

Figure 1(b) shows a singular value analysis performed with the assumption (see below) that the experimental data results from a sum of exponentially damped cosinusoidal functions

\[
S(t_d) = \sum_i A_i \cos(\omega_i + \phi_i) e^{-\omega_i t_d},
\]

where \(\omega_j\) is a vibrational frequency difference in either electronic state. The fit to the data for pump–probe time delays \(t_d\) is excellent and the corresponding parameters are summarized in the figure caption. This analysis finds three damped oscillatory components and two purely exponentially damped components. The oscillatory components are identified with the ground state fundamental (\(\Delta \nu = 1\)), 211 cm\(^{-1}\), the first overtone (\(\Delta \nu = 2\)), 424 cm\(^{-1}\), and with the excited state vibrational spacing of 107 cm\(^{-1}\). The ground state frequencies of iodine in solution are known from resonance Raman spectra while the observed excited state frequency is almost the same as the \(B\)-state gas phase value.\(^{31}\) The vibrational coherence contributions to the dichroic response are characterized by cosinusoidal modulations whose phases are zero for the ground state wave packet and nearly \(\pi\) for the excited state wave packet, respectively. Intuitively, a sign or \(\pi\) phase shift in the signal reflects the gain/loss, i.e., absorptive vs emissive character of the system response to the probe pulse.

The time constants \((\tau_j)\) of the ground and excited state components are significantly different. In the case that rotational reorientation is slow compared to vibrational dephasing the damping constant is the vibrational dephasing time \(T_{2v}\). When both times are similar the rotational contribution must be removed from the damping constant to obtain the vibrational dephasing time. As the fit in Fig. 1(b) demonstrates (see caption) these two conditions apply to the excited and ground state vibrational coherences respectively.

A single exponential relaxation component \((\omega = 0)\) of comparable magnitude, decay time and sign to the excited state vibrational coherence is also clearly evident in the data. This response is identified with the excited state population and decays with its characteristic \(T_1\) relaxation time. The other longer lived exponential term with the same sign as the ground state oscillatory term is assigned to rotational relaxation.

Figure 2 shows the real part of the Fourier transformed iodine dichroism response of Fig. 1. The real spectrum of the dichroism signal shows positive peaks at zero, 211 and 424 cm\(^{-1}\) and negative peaks at \(\approx 12\) and 107 cm\(^{-1}\.\(^{32}\) Overtone bands appear in the dichroism signal for the same reason they appear in the spontaneous resonance Raman spectrum. In this case the overtone response is stimulated since it falls within the spectral bandwidth of the pump pulse. The sign of the peaks, in the case of \(t_{\text{pulse}} < T_2\), indicates the electronic origin of the frequency components.

The excited state parameters provide direct information about the subpicosecond predissociation dynamics of the \(I_2\ B\) state in solution. The excited state vibrational response decays via both population loss and pure dephasing. Therefore, in general, the oscillatory and exponential contributions to the excited state signal will decay with different time constants. In the present case, however, we find \(T_{2v} \approx T_1 \approx 200\) fs. This result implies that vibrational dephasing results predominantly from population decay of both excited state vibronic levels involved in the vibrational coherence.

The finding that pure dephasing is not the dominant mechanism for the decay of the excited state vibrational coherence is in accord with the resonant light scattering studies of Sension and Strauss.\(^{21}\) No resonance fluorescence is discernible in their published spectra, indicating\(^3\) that pure dephasing is slow compared to the population decay. This observation alone suggests that the lifetime of the iodine \(B\) state \((T_1)\) should be \(\frac{1}{2}T_2\) or \(\approx 150\) fs, a value not inconsistent with our directly observed value of 200 ± 50 fs. Experimental uncertainties aside, the two measurements refer to somewhat different quantities. The resonance Raman estimate represents an average over the entire absorption band, whereas the induced dichroism signal samples only the portion of the excited state surface accessible within the laser bandwidth.

Previous studies have found that the optical dephasing rate of molecules in solution, such as CS\(_2\), azulene, and...
Optically-Induced Dichroism of Iodine in n-Hexane

5mM Iodine in n-Hexane

Dichroism
Autocorrelation

(a)

Time (ps)

(b)

Time (ps)

Linear Prediction-Singular Value Decomposition of Iodine Dichroism

FIG. 1. (a) Solid line, transient dichroic response of I₂ in n-hexane. Dashed line, pump-probe pulse intensity autocorrelation. (b) Data analysis of transient dichroism signal. Experimental data, +. Solid line, fitted curve. Fitting parameters frequency, amplitude, phase, time constant: ω₁ = 211 cm⁻¹, A₁ = 0.21, ϕ₁ = 4 ± 10 deg.; ω₂ = 424 cm⁻¹, A₂ = 0.04, ϕ₂ = −19 ± 20 deg.; ω₃ = 900 ± 100 fs; A₃ = 0.16, ϕ₃ = −155 ± 10 deg.; ω₄ = 0 cm⁻¹, A₄ = 0.43, ϕ₄ = 180 deg.; ω₅ = 180 ± 50 fs; A₅ = 0 cm⁻¹, A₅ = 0.32, ϕ₅ = 0 deg.; τ₅ = 1350 ± 100 fs. Components 1, 3, and 4 have been plotted individually in the lower portion of the figure offset by −0.6 units.

dyes,₁²,₁³ occurs on the time scale of 10–50 fs and results primarily from pure dephasing. The present results for iodine stand in strong contrast with these observations for electronically highly excited (or conjugated) polyatomic molecules with large transition dipole moments. A similar conclusion was recently obtained for SO₂ in solution by a resonance Raman approach.₁⁵

In general, 1/T₂ = 1/(1/T₁e + 1/T₁g) + 1/T₂*, where e

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and g refer to excited and ground states and $T_1^g$ is the pure dephasing contribution to the optical dephasing. In the present case $T_1^g > T_1^e$ and the lack of fluorescence emission implies $T_1^g > T_1^e$. Therefore, the optical dephasing of iodine appears to be entirely due to population decay, that is $T_1$ processes, on the time scale of 200 fs. This population decay could be vibrational relaxation or dissociation of the B state. Solution phase vibrational relaxation within the $X$ and $A$ states of iodine occurs on the picosecond timescale.\(^\text{19,20}\) We therefore conclude that curve crossing (i.e., reaction) takes place within three vibrational periods ($T_1 = 200$ fs) with near unit quantum efficiency. The solvent dependence of the dissociation rate will be presented in a future manuscript.\(^\text{23}\) The slow pure dephasing of the optical transition can be understood from the low-frequency spectral density of the solvent and the absence of a change in charge character or dipole moment on optical transition can be understood from the low-frequency spectral density of the solvent and the absence of a change in charge character or dipole moment on optical transition.

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\(^{26}\)The apparent peak at 12 cm$^{-1}$ results from the difference in spectral width of the two exponential contributions to the dichroic response, components 4 and 5 in Fig. 1(b).


