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Ultrafast vibrational dynamics of nascent diiodide fragments studied by femtosecond transient resonance impulsive stimulated Raman scattering

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Impulsive stimulated resonance Raman scattering performed with femtosecond pulses comprises an all time domain Raman technique providing vibrational spectra of the ground state chromophore. We report the first application of this technique to record Raman free induction decays of nascent diiodide ions, undergoing rapid vibrational relaxation following triiodide photodissociation in ethanol solution.

I. INTRODUCTION

Ultrafast transient absorption spectroscopy is an invaluable tool for unraveling chemical dynamics in solution.¹ However, the inherent lack of fine structure in liquid phase electronic absorption spectra, makes it advantageous to supplement this tool with transient vibrational spectroscopy^{2,3} for verifying the identity of the absorbing species. Impulsive stimulated Raman scattering (ISRS) is a purely time domain pump-probe spectroscopy which induces coherent vibrational motion and follows its decay in Raman active modes.⁴ Its implementation requires pump and probe pulses that are shorter than a single period of the observed vibration, allowing simultaneous excitation of numerous ground state vibrational levels into a coherent superposition.

When the impulsive photoexcitation is performed on resonance (RISRS), the amplitude of the generated vibrational coherence is greatly enhanced, allowing its detection through periodical spectral shifts of the absorption band.⁵⁻⁷ When the excited surface is directly dissociative, the problem of prolonged spectral modulations in absorption due to excited state vibronic coherences is alleviated,⁸ allowing selective probing of vibrational motions induced in the ground state.

Simulations of the RISRS process are most easily visualized in coordinate space.^{5,9} The impulsive pump or "push" pulse preferentially depletes probability density from populated geometries in the ground state for which the vertical potential gap to the excited state matches the resonance condition. This "coherent depletion" process involves all vibrational levels populated in the ground state which carry oscillator strength within the push pulse spectrum, and results in coherent redistribution of population into a number of ground state levels above and below each such vibronic state.

Following a pushing interaction, the coherent superposition will oscillate and dephase, giving rise to decaying spectral modulations in the transient absorption. The dependence of the phase and intensity of these oscillations on the potential topologies, the parameters of both pump and probe pulses, and the initial incoherent distribution of population over the ground state vibrational levels, results in

an extremely rich spectroscopy. Pending a quantitative simulation involving all of these, we focus attention primarily on the last. In view of the fact that coherent transfer of population is only to a few neighboring levels, the vibrational coherence mirrors the initial incoherent distribution of population in the ground state vibronic manifold. Grossly speaking, one approximately records a Raman free induction decay (FID) of the vibrational distribution at the instant of the push excitation.⁷ The FID duration defines the minimum time that a dynamic variable must be followed in order to reconstruct its power spectrum. Impulsive Raman is accordingly one of the most rapid methods for obtaining vibrational spectral information.

In a recent publication we reported a detailed study of triiodide ion photodissociation in ethanol solution.¹⁰ Following photolysis the nascent diiodide fragments are created in a partly coherent vibrational superposition, giving rise to periodic spectral shifts of the fragment absorption band. Within a few hundred femtoseconds these oscillations subside, and give way to an overall narrowing of the product absorption band, taking place within a few picoseconds. This was assigned as the spectral signature of vibrational relaxation in the product ions.

In order to obtain corroboration of this assignment, an additional method is necessary for directly probing the vibrational relaxation. Transient RISRS, or TRISRS, with its characteristic high time resolution, was chosen in order to extract the temporal evolution of the vibrational distribution. This involves a sequence of three pulses. A primary UV photolyzing pulse initiates triiodide dissociation. At a certain delay with respect to the photolysis a secondary intense push pulse sets in motion ground state coherent vibration. This coherent motion is followed via periodic transmission modulations of a continuously delayed weak probing pulse. In essence, a RISRS experiment has been conducted on a transient species. The I_2^- fragment ions exhibit a substantial optical density at the fundamental frequency of our amplified laser source throughout the process of relaxation, and all vibrational levels above $v \approx 2$ are susceptible to the RISRS excitation process at this frequency. Therefore, the fundamental laser output is an ideal source of push pulses for probing the nascent I_2^- photo-

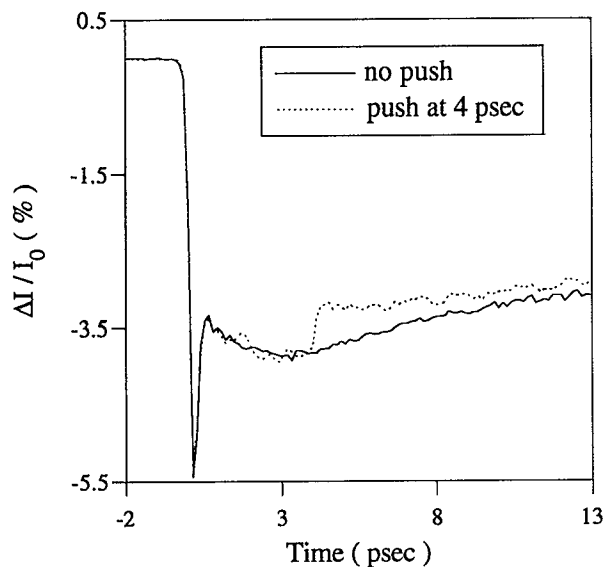


FIG. 1. Transient transmission data at 840 nm with and without the secondary TRISRS push interaction at a delay of 4 ps.

products. In this report the experimental feasibility of TRISRS probing is demonstrated, and in this case the method provides evidence that rapid band narrowing observed in our transient absorption experiments is due to vibrational relaxation of the newly formed diiodide fragment ions.

II. EXPERIMENT

The laser system has been described in detail elsewhere.¹⁰ Its ultimate output consists of 55–65 fs pulses, centered at 616 nm, containing 20–30 μJ of energy. One portion is frequency doubled to produce a UV excitation pulse, initiating triiodide photolysis in solution. A second delayed portion comprises the push pulse at 616 nm. The third portion is continuously delayed to produce the experimental scans, and generates a white continuum from which a single frequency band probe is isolated by interference filtering. The UV excitation beam is chopped and the transient transmission of the probe pulse is detected using a lock-in amplifier, comprising the TRISRS signal (SR 530). A 200 micron flow cell equipped with ultrathin quartz windows was employed, with sample concentration of a few millimolar in ethanol.

III. RESULTS AND DISCUSSION

TRISRS data were collected at three push delays, 2, 2.7, and 4 ps after the excitation pulse. To clarify the sequence of events, Fig. 1 depicts an overlay of two transient transmission scans probed at 840 nm, with and without the introduction of a push pulse. The push induces a substantial bleach which recovers partially within the 13 ps scan. The TRISRS bleaches at the three delays are shown in Fig. 2. The data for a 2 ps push delay involves probing at 680 nm, while results at later delays were obtained with an 840 nm probe pulse. The zero of time in Fig. 2 relates to the center of the pushing pulse in all three scans. At all these

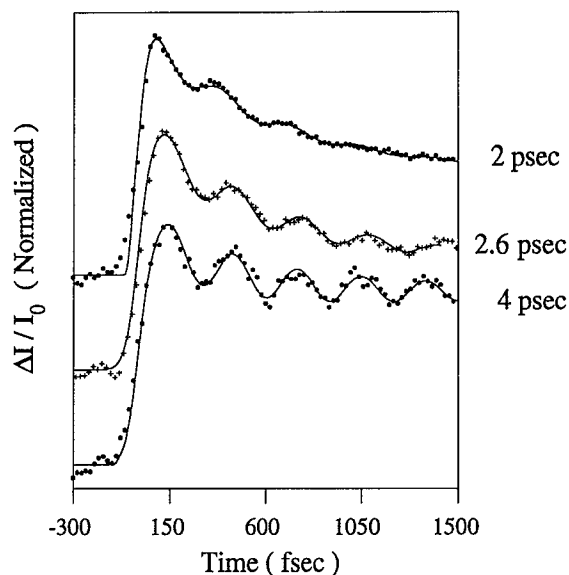


FIG. 2. TRISRS data recorded at three different push delays. Oscillations in transmission are fit to a convolved analytical response. See text for details.

delays periodical oscillations of the transient transmission are observed. Fits generated by a nonlinear least-squares method are depicted, after convolution with our instrument response, along with the data. The experimental points were fit to the functional form of Eq. (1)

$$S(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{t'} I_{\text{push}}(t'') G(t' - t'') I_{\text{probe}}(t' - t) dt' dt'', \quad (1)$$

where both push and probe pulses are squared hyperbolic secant functions of 65 fs full width at half-maximum (FWHM), and the Green's function is given in Eq. (2)

$$G(t) = A + B \exp(-\Gamma t) + C \sin(\omega t + \phi) \exp(-t/\tau). \quad (2)$$

This functional form affords a reasonable fit to the data at all delays. The parameters of the decaying sine function are shown in Table I. As the push delay increases from 2 to 4 ps, the central frequency of the oscillations varies from 103 to 112 cm^{-1} and the characteristic decay time increases monotonically by more than a factor of 2.

The observed oscillations can be unequivocally attributed to ground state TRISRS excited vibrational coherences in the I_2^- fragments. Their phase, and its change with the variation of probe frequency, agree qualitatively with this assignment. Explaining the depth of spectral modulation at different probing frequencies as a function of the delay will require the completion of numerical simulations. Qualitatively, at the shortest push delay both push and

TABLE I. Fitting parameters.

Push delay (ps)	ω (cm^{-1})	τ (ps)	ϕ (radians)
2.0	102 ± 4	0.5 ± 0.2	0.2 ± 0.4
2.67	105 ± 3	0.9×0.2	-1.2 ± 0.4
4.0	112 ± 2	1.2 ± 0.3	-2.0 ± 0.4

probe pulses are to the blue of the central I_2^- absorption band, and the oscillatory contribution to the transmission should resemble a cosine, whereas in the later two delays, a negative cosine contribution would be expected. While a full change of 1π in phase is not observed upon the variation of probe frequency, and the initial phase is not exact, the trend of change is correct. The zero of time delay between the pushing and probing pulses has been determined by the rise of the push bleach signal. Considering the uncertainty in our determination of time zero, and the possibility of small contributions of self phase modulation coherent artifacts at the very early time delays, this may be within our margin of error.

Within this conceptual framework, the mean vibrational energy content of the fragment ions will be retrieved from the frequency of spectral oscillations, and dephasing parameters from the dynamics of their dissipation. The first push delay immediately supersedes the decay of spectral oscillations induced by bond fission, and the fragment ion population must contain substantial excess vibrational energy. It may, however, have undergone some cooling since its inception about 200 fs after the UV excitation at which time it is determined to be centered at $\nu \approx 20$.^{10,11} Using the documented vibrational constants of I_2^- , the coherence frequency of 102–103 cm^{-1} indicates that the earliest TRISRS induced superposition is made up of levels centered around $\nu \approx 13$. The ultrafast rate of coherence dephasing (~ 500 fs) must involve mechanisms beyond anharmonicity, such as pure dephasing and population relaxation. Inhomogeneity of the solvent following the violent act of bond fission may also contribute to rapid vibrational dephasing.

As the push delay is increased, the I_2^- ions have relaxed further, leading to a reduction of both the first and second moments of the vibrational distribution. Accordingly, the frequency and the time scale of TRISRS coherence dephasing should increase. The frequency will increase due to the larger level spacings closer to the bottom of the potential well. The dephasing is prolonged because of a reduction in the rate of pure dephasing at low ν levels,¹² and a reduced contribution of anharmonicity which is proportional to $\omega_e \chi_e$ times the second moment of the distribution. These trends are in fact observed. Within 4 ps of push delay, the modulations have already reached the asymptotic vibrational frequency within our experimental error. These results, along with the previous transient transmission data, show that the diiodide ions lose most of their excess vibrational energy within a few picoseconds. This finding agrees with a growing body of work on vibrational relaxation of molecular ions in polar solvents,^{2,3} and particularly in the case of recombinant diiodide in condensed media.^{14–16}

We briefly discuss the major attributes of the TRISRS method and its potential for general application. The ultimate aim of transient vibrational spectra is to regain the time evolution of vibrational power spectra with utmost simultaneous temporal and frequency resolution. This capability is most crucial in cases where the dynamics of the material system are rapid, and bring about modest changes

in the vibrational spectrum. Being a purely time domain method, TRISRS is limited only by time-energy uncertainty. In contrast hybrid time-frequency techniques such as incoherent transient Raman are problematic whenever this limit is approached. In our results distinct Raman responses are obtained at push delays that differ nearly by the mean dephasing time of the spectral modulations. An incoherent Raman probing pulse no longer in duration would therefore need to be chosen in order to fully time resolve the relaxation. However, such a short probe would already continuously excite the ensemble in transition throughout the delays spanned by these pushing times, and broaden the transient spectral response severely.

The TRISRS scheme is experimentally straightforward, and polyatomic molecules with a short enough pulse will simultaneously afford vibrational coherence decays of a number of active modes.⁷ It is the only method capable of probing the evolution of the molecular sample with a time resolution which is a fraction of a period, and therefore is well suited to cases where vibrational relaxation takes place within a few coherent recurrences. The fact that the phase of spectral modulations is available increases the information content of the measurements concerning the vibrational distribution and the potential topology.

The limitations of this method are the necessity of intense push pulses which could, in certain cases, substantially perturb the evolving system, and the fact that extremely short pulses are required in order to apply this technique to high frequency modes. Accordingly, TRISRS is predicted to become an effective transient vibrational spectroscopy for intermediate to low frequency Raman active modes. We have only explored a limited range of the experimentally available parameters, which include the frequencies and durations of the push and probe pulses. An implementation of TRISRS employing all variable parameters should afford an even fuller characterization of the molecular ensemble studied.

Finally, we advocated this method as a spectroscopy for resolving fine spectral structure through an ultrashort measurement, yet the decay dynamics have been fit to a single exponential, or in frequency domain to a single Lorentzian line. It is important to stress that despite the simple fitting models applied, the method has the potential to detect more complex features in coherence decay such as a Gaussian relaxation due to inhomogeneity of local environments etc.¹⁷

In summary, the experimental feasibility of the TRISRS method has been demonstrated. In the presented case study it provides mean vibrational frequencies and dephasing times for diiodide ions undergoing rapid dissipation of excess vibrational energy to the solvent. Results indicate that vibrational energy of the fragment ions is released within a few picoseconds, and when highly excited, the ions undergo vibrational dephasing very rapidly. Coupled to quantitative theoretical analysis this spectroscopy will provide a useful and generally applicable tool for probing vibrational processes in rapidly evolving species.

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