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Femtosecond time-resolved coherent anti-Stokes Raman scattering for the simultaneous study of ultrafast ground and excited state dynamics: iodine vapour

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Abstract

Femtosecond time-resolved coherent anti-Stokes Raman scattering (CARS) is applied in order to investigate molecular dynamics in the gas phase. As model system iodine vapour is chosen. By changing the timing of the laser pulses of this non-degenerate four-wave mixing technique, the wavepacket motion on both the electronically excited and the ground states can be detected as oscillations in the coherent anti-Stokes signal. Different decay times are found for the amplitudes of the excited and ground-state beats. The results are compared with transients obtained from a conventional pump–probe technique, where laser-induced fluorescence is used for detection. © 1997 Elsevier Science B.V.

1. Introduction

Recent advances in time-domain spectroscopy have enabled spectroscopists to capture chemical processes directly on the time scale of the fastest elementary steps [1,2]. In the gas phase nearly all experiments were performed on the femtosecond timescale in order to investigate the dynamics on potential energy surfaces of reactive and nonreactive systems [1,3–6].

For bound systems, Baumert et al. reported on the observation of ground-state wavepacket dynamics for Na_2 [7] and Na_3 clusters [8]. In femtosecond pump–probe multiphoton ionization experiments they induced ground-state wavepackets by stimulated emission pumping. For strong pump laser fields the Fourier spectrum of the transient Na_2^+ signal showed besides the frequencies belonging to the excited states also a feature corresponding to a ground-state vibration. Similar experiments were performed for K_2 clusters [9,10].

The high intensity achieved by femtosecond laser pulses favours the application of nonlinear methods like four-wave mixing (FWM) spectroscopies for the study of ultrafast intramolecular dynamical processes. Compared with time-resolved resonance Raman scattering, time-resolved femtosecond coherent anti-Stokes or Stokes Raman scattering (CARS or CSRS, respectively) open new possibilities for the study of processes of ultrafast molecular dynamics [11–18].

However, these methods have not been exploited on the subpicosecond time scale for gas-phase studies until recently. Hayden and Chandler [18] reported the application of femtosecond time-resolved coherent Raman techniques to excite and monitor the evolution of vibrational coherence in gas-phase samples of benzene as well as of 1,3,5-hexatriene. The transient sig-

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nal which they observed showed a weak modulation which is due to a beating involving isotopically pure benzene and benzene molecules having one carbon-13 ($\Delta\tilde{\nu} \approx 8$ cm^{-1}). Using "incoherent" light from a broadband dye laser in order to achieve femtosecond time resolution in time-delayed degenerate and nondegenerate FWM Yang et al. [17] investigated I_2 in the vapour phase. Their signals revealed oscillations corresponding to excited state wavepacket dynamics, but no ground-state contribution could be detected. Recently, nonlinear FWM techniques were incorporated as probe method in pump–probe experiments to obtain the femtosecond dynamics of atomic and molecular systems in the gas phase by Motzkus et al. [19]. They also suggested temporal pulse schemes which would probe the ground-state dynamics.

In the present work, we report the application of femtosecond time-resolved CARS on the investigation of the dynamics of coherently excited states for the electronically excited and ground states of iodine molecules in the gas phase. First, we introduce the methodology employed in our experiments. In Section 3, a brief description of the experiment is provided. Results of the transient CARS measurements are presented in Section 4, including a discussion of their relation to pump–probe studies. Finally, concluding remarks are given in Section 5.

2. Methodology

In the following, we describe the basic idea of the femtosecond time-resolved four-wave mixing experiment. In Fig. 1 we outline the spatial beam configuration as well as the temporal pulse sequence applied for the investigation of the wavepacket dynamics in the electronically excited and ground states of iodine. The potential energy surfaces involved in the coherent anti-Stokes scattering (CARS) process are shown together with a scheme of the transitions.

Three laser fields interact with the ensemble of I_2 molecules. Two laser pulses have the same frequencies, $\nu_{pu} = \nu_{pu_\tau}$, and furtheron will be referred to as pump laser pulses. The third laser (Stokes) is tuned to a lower frequency, ν_S, in such a manner that the difference between pump and Stokes laser frequencies is resonant with a vibrational transition in the ground state (we will show experimental results for a frequency difference tuned to the second overtone of iodine, $\Delta v = 3$, see below). While one of the pump pulses (ν_{pu}) and the Stokes pulse are coincident in time ($t = 0$), the second pump pulse (ν_{pu_τ}) arrives at a different time.

Depending on the relative timing of the pulses, different dynamics are probed. (i) In the first scenario, the pump pulse pu_τ interacts with the molecules before the other two pulses arrive ($\Delta t < 0$). The ultrashort pulse pu_τ generates a wavepacket by coherently exciting several rovibronic eigenstates of the bound B state of the iodine molecules. Since the femtosecond pulse duration is shorter than the vibrational period, the pump prepares a coherent superposition of a few vibrational states (determined by the bandwidth of the pulse), resulting in a wavepacket oscillating on the excited potential energy surface. This coherently prepared wavepacket is probed by the two coincident pulses pu and S and can be seen from the amplitude of the coherent anti-Stokes Raman scattering (aS). (ii) If, however, the pump pulse pu_τ follows an interaction of the two laser fields at $t = 0$ ($\Delta t > 0$), it acts as a probe of the response of the coherently vibrational excited molecules. In this case, the evolution of the vibrational coherence of the electronically ground-state wavefunctions of I_2 can be monitored, that were prepared by the coincident pump and Stokes laser pulse. Again, the wavepacket motion is reflected in the transient, anti-Stokes signal.

3. Experimental

Fig. 2 shows a schematic of the experimental setup, which will be described shortly in the following. The output of a 76 MHz mode-locked Ti:sapphire laser (Coherent MIRA) was passed into a Nd:YAG-pumped regenerative Ti:sapphire amplifier (Clark-MXR) operating at 1 kHz. The pulses were stretched to a duration of $\leqslant 200$ ps before amplification. The output pulses were recompressed yielding less than 100 fs with an energy of ≈ 1.5 mJ at 800 nm. In order to have two different colors available, the 800 nm pulse train was split into two parts by means of a 1 : 1 beam splitter. Using two four-pass OPGs (optical parametric generators) from Light Conversion, two independent wavelengths could be chosen. The laser pulses were produced using sum frequency generation

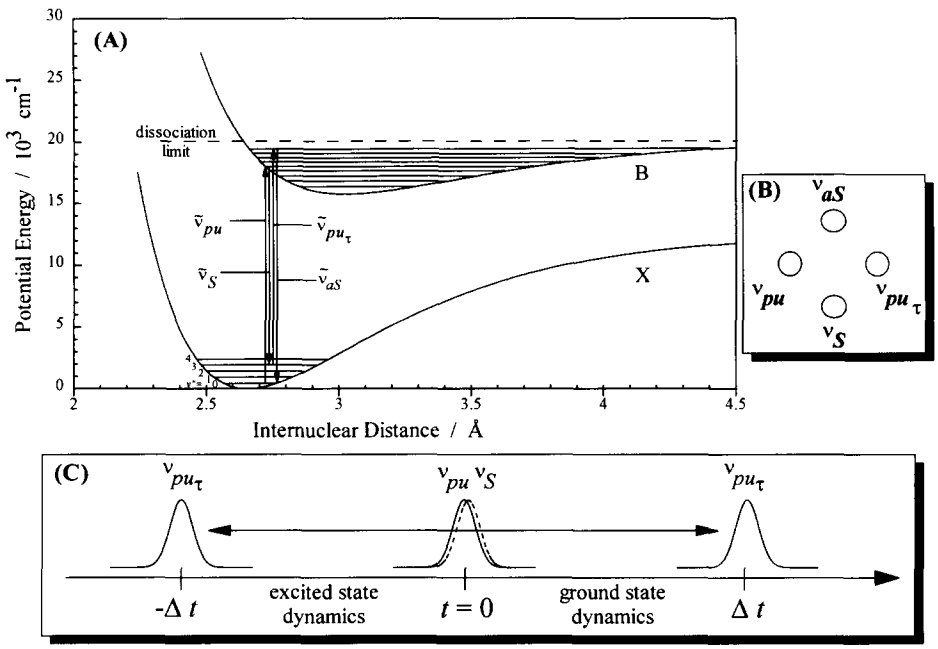

Fig. 1. Methodology of the time-resolved CARS experiment. (A) Schematic of the bound potential energy surfaces relevant to the femtosecond CARS study of iodine. The energy diagram of the CARS process is inserted. (B) Spatial beam configuration. (C) Temporal pulse sequence. For details see text.

between signal and idler output of the OPG as well as second harmonic generation of either the signal or the idler light. The pulses were finally compressed in double-pass two-prism arrangements resulting in temporal pulse widths of about 70 fs.

One of the OPG outputs was branched by a 1 : 1 beam splitter to produce the two pump pulses pu and pu_τ. The two pump beams were then aligned parallel to one another and spatially overlapped at the common focus in the sample cell by the achromatic lens L1. The Stokes beam S (output of the second OPG) was aligned parallel to and spatially separated from the two pump pulses and passed through the top of lens L1, focusing in the same region as the two pump beams. This folded BOXCARS configuration (see also panel B of Fig. 1) was employed in order to separate the signal from the incoming pump and probe beams [20]. In this geometry the phase-matching condition is fulfilled.

The pump pulses and the probe pulses could be delayed in time relative to each other by means of Michelson interferometer arrangements. In the experiments presented in this Letter, the pump pulse pu and the Stokes pulse S were kept temporally overlapped and fixed. The CARS transients were recorded as a function of delay time $\pm\Delta t$ between the pump pulse pu_τ and the two fixed and time coincident pulses pu and S (see panel C of Fig. 1). The relative timing between the different pulses was varied with a computer-controlled actuator that allowed for optical delay up to 3 ns with a minimal stepsize of 6 fs. The determination of the position of temporal overlap (time zero) between the different beam pairs was made using a cross correlation apparatus with second harmonic generation as well as sum frequency mixing in a thin, phase-matched BBO crystal.

The fs CARS signal pulse aS generated in the sample cell travels in a direction determined by the phase-matching condition. This direction is different from that of the incident laser beams (see panel B of Fig. 1), and the signal could thus be easily separated by a spatial filter. The CARS signal beam was collimated by a second achromatic lens L2. After filtering the straylight by means of a monochromator (Acton SpectraPro-500), the anti-Stokes signal was detected by a fast photomultiplier tube (RCA C31024 A). The

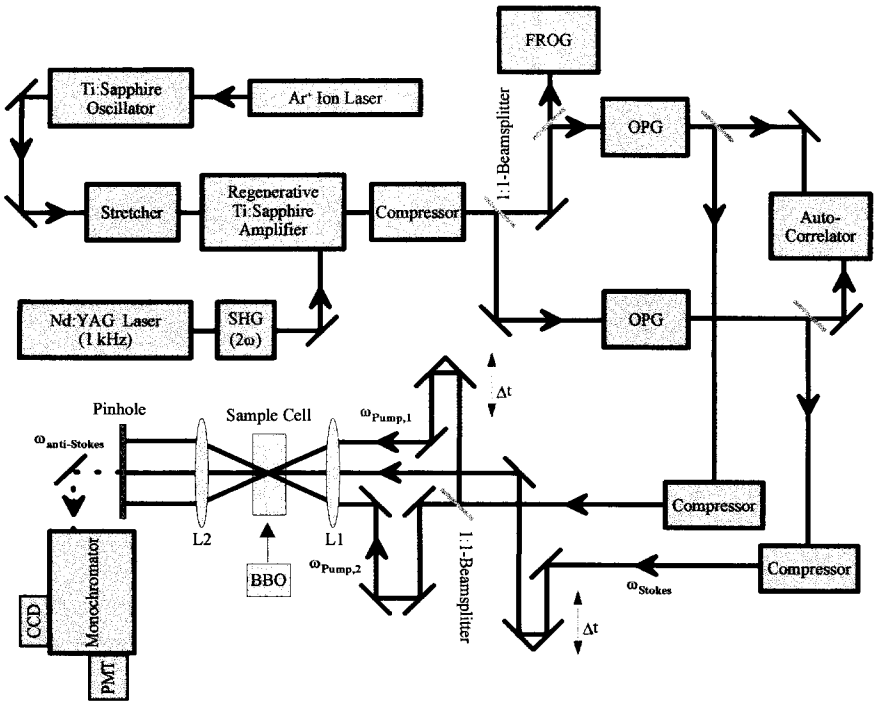

Fig. 2. Experimental setup showing the femtosecond laser system and the beam path of the BOXCARS arrangement. Computer controlled actuators were used to vary the relative arrival time of the femtosecond pulses. Only one actuator was moved in the experiment to obtain a transient.

signal-to-noise ratio was enhanced by use of a boxcar integrator (EG&G model 4121B) in gated-integrator mode, as well as by numerical averaging of several pulses.

In order to increase the vapour pressure, the iodine was kept in a heated cell at about 353 K.

4. Results and discussion

Fig. 3 shows a typical CARS transient obtained for a pump wavelength $\lambda_{pu} = \lambda_{pu_r} = 559$ nm and a Stokes wavelength $\lambda_S = 579$ nm detecting the coherent anti-Stokes signal at $\lambda_{aS} = 539$ nm. The transient shows the expected vibrational beat patterns at the excited state vibrational frequency for negative delay times ($\Delta t < 0$), as well as less intense oscillations having about twice this frequency at positive delay times ($\Delta t > 0$), which are assigned to the ground-state vibrational dynamics.

The insert in Fig. 3 emphasizes the vibrational beat patterns of the ground state ($\Delta t > 0$). The peak at zero time delay was omitted for this presentation. The fitted curve is an fast exponential decay (time constant 0.37 ps) overlayed by a simple sine function. The short time oscillations show a period of 160 fs, corresponding to the wavepacket motion prepared by coherent two-photon pumping (pu and S) around the third vibrational level in the ground X state of iodine (compare inserts in Fig. 3). The average period of the oscillations corresponds to a vibrational wavenumber spacing of about 208 cm^{-1}. This agrees with the vibrational energy spacing in the ground X state of iodine as observed from continuum resonance Raman experiments [21]. If we subtract the fitted exponential decay from the experimental data, the amplitudes of the oscillations seem to stay at about the same level at least during the observed range of delay times.

The excited state signal ($\Delta t < 0$) exhibits well defined beats with a separation of about 380 fs, corresponding to a vibrational wavenumber spacing of about 88 cm^{-1}. This value agrees with the experimen-

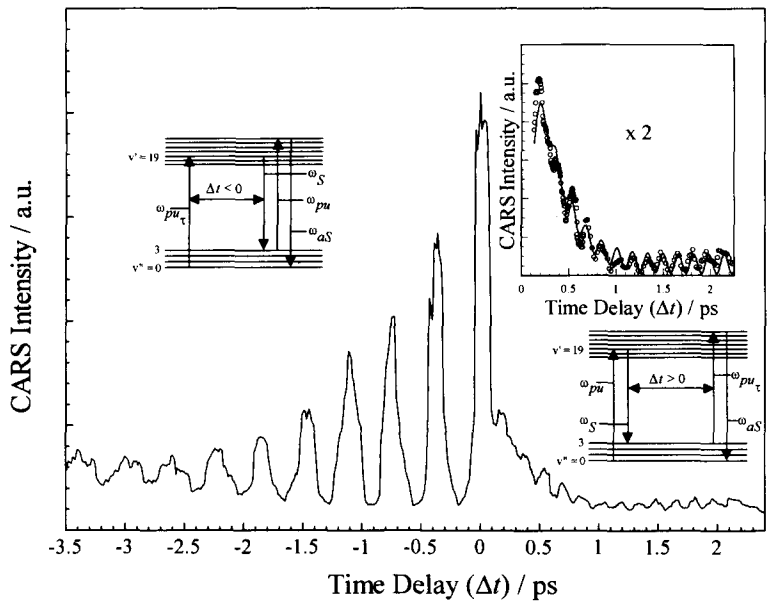

Fig. 3. Femtosecond CARS transient obtained for a pump wavelength $\lambda_{pu} = \lambda_{pu_\tau} = 559$ nm and a Stokes wavelength $\lambda_S = 579$ nm detecting the CARS signal at $\lambda_{aS} = 539$ nm. The wavepacket dynamics in the B sate (negative delay times, $\Delta t < 0$) as well as in the ground state (positive delay times, $\Delta t > 0$) of iodine can be resolved. The insert shows the ground-state contribution together with a curve resulting from a fitting procedure. The peak at zero time delay was subtracted before. Energy diagrams of the CARS process are shown for both $\Delta t < 0$ and $\Delta t > 0$, indicating the relative timing of the laser pulses.

tal vibrational energy spacings (vapour phase) in the B state around $v' = 19$ [22,23], which is reached by the $\lambda_{pu} = 559$ nm ($= 17889$ cm^{-1}) laser pulse from the ground state. Therefore, at this wavenumber the vibrational states around $v' = 19$ of the B-state are prepared. In contrast to the ground-state oscillations, the amplitude of the beat patterns found for $\Delta t < 0$ decay rapidly for increasing $|\Delta t|$.

In order to confirm our results we have recorded CARS transients with different pump and Stokes wavelengths, keeping the energy difference resonant with the second overtone of the I_2 ground-state vibration. While the period of the oscillations seen for $\Delta t < 0$ changes with the wavelength of the exciting pump laser (λ_{pu_τ}), no change could be seen for the less intense beat pattern for $\Delta t > 0$. The latter observation confirms our assumption that the pump laser pu_τ probes the temporal evolution of the wavepacket which is prepared on the ground-state potential energy surface at $t = 0$ by the interaction of the pu and S fields. Because the energy difference is constant in all experiments, always the same vibrational levels in the ground state are excited. Furthermore, even for slight changes of the energy difference between the pump and Stokes lasers, we would not expect remarkable changes as the ground-state potential is virtually harmonic in the accessed range.

In contrast to this, for $\Delta t < 0$ by varying the pump wavelength within the bound portion of the B state (620 to 536 nm) (i.e. starting the wavepacket propagation at different points in the vibrational manifold [24]), we observe different periods in the coherent evolution of wavepackets in the B state. Curve A of Fig. 4 shows the fs pump–probe signal obtained by laser-induced fluorescence, ($\lambda_{LIF} = 340$ nm) for $\lambda_{pu} = 620$, and $\lambda_{pr} = 310$ nm (compare e.g. to results obtained in Ref. [24]). With curves B to D in Fig. 4 we show a selection of the CARS transients for three different wavelength combinations: B ($\lambda_{pu} = \lambda_{pu_\tau} = 620$ nm, $\lambda_S = 645$ nm, $\lambda_{aS} = 596$ nm), C ($\lambda_{pu} = \lambda_{pu_\tau} = 559$ nm, $\lambda_S = 579$ nm, $\lambda_{aS} = 539$ nm), and D ($\lambda_{pu} = \lambda_{pu_\tau} = 536$ nm, $\lambda_S = 554$ nm, $\lambda_{aS} = 518$ nm). We found that the period of the oscillation increases as the pump energy is increased. The CARS transients show oscillations with an average period of 300, 380, and 480 fs for the B, C, and D transient, respectively. Cal-

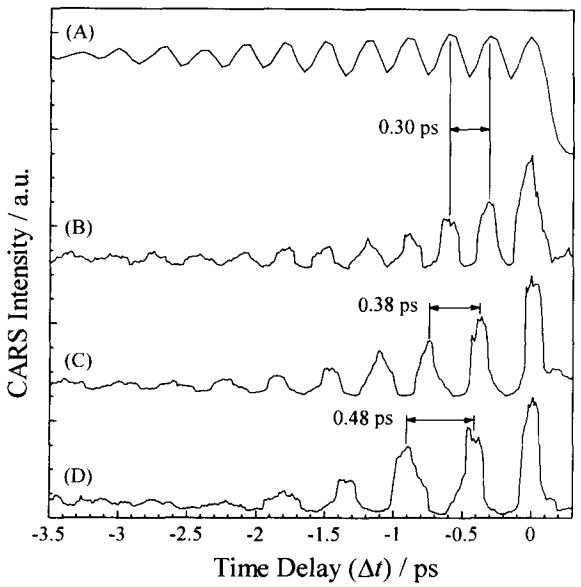

Fig. 4. Femtosecond pump-probe (A) and CARS transients for different pump laser wavelengths (B–D). (A) pump (λ_{pu} = 620 nm)–probe (λ_{pr} = 310 nm) with laser-induced fluorescence (λ_{LIF} = 340 nm) detection. CARS transients for (B) λ_{pu} = λ_{pu_r} = 620 nm, λ_S = 645 nm, λ_{aS} = 596 nm; (C) λ_{pu} = λ_{pu_r} = 559 nm, λ_S = 579 nm, λ_{aS} = 539 nm; (D) λ_{pu} = λ_{pu_r} = 536 nm, λ_S = 554 nm, λ_{aS} = 518 nm.

culations of these oscillation periods have also been made using the available spectroscopic data of the B state, and good agreement was found between the calculated and observed periods. In Fig. 4 curves (A) and (B) we compare the result of this nonlinear fs CARS gas-phase technique (curve B) with that obtained by the pump–probe technique using laser-induced fluorescence (LIF, curve A) [3,24]. Excellent agreement is found for the period of the oscillations as well as for the decay of the amplitudes between the two transients, the latter being taken with the same pump wavelength (λ_{pu} = λ_{pu_r} = 620 nm). This observation points to the same decay mechanism (vibrational dephasing, rotational relaxation) for the CARS process compared to the pump–probe experiment if $\Delta t < 0$ [25]. In contrast to the pump–probe experiments, in the CARS experiment no contributions from other electronically excited states [24] could be detected. This is due to the high selectivity of the FWM process.

The peak at zero time delay is slightly higher than it would be expected from the decay behaviour of the excited state oscillations. This is due to a coherent artifact [26]. The basic mechanism of this coherence effect is an interchange of the role of the pump and probe pulses which is possible during the temporal overlap of the pulses.

The decay behavior for $\Delta t > 0$ is more complicated. Up to now we do not have a conclusive explanation for the fast decay at short time delays. The much slower decay of the amplitudes of the oscillations belonging to the ground state may be explained by the smaller anharmonicity of the ground-state potential, resulting in a slower vibrational dephasing.

5. Conclusion

In this paper we have demonstrated the feasibility of time-resolved coherent anti-Stokes Raman scattering (CARS) for the investigation of the wavepacket dynamics in gas-phase molecules. As an example we have applied this technique to iodine vapour. By simply changing the timing of the lasers, interacting with the molecular ensemble, the dynamics on both the electronically excited and ground-state potential energy surface can be probed.

There are several advantages of this nonlinear four-wave mixing (FWM) technique: (i) CARS is a coherent process yielding a coherent signal, which can easily be separated from the exciting lasers. Therefore, this method results in background-free signals. (ii) CARS can be applied even when fluorescing states can not be accessed and ion detection is not feasible. (iii) Due to the many free parameters of the FWM process (wavelength, timing, polarizations), not only certain molecular states can be selected but also different decay mechanisms can be separated.

Further investigations making use of the flexibility of the time-resolved CARS technique are in progress and will be published. A paper presenting quantum mechanical simulations of our results is in preparation [27].

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