Selective excitation of molecular mode in a mixture by femtosecond resonance-enhanced coherent anti-Stokes Raman scattering spectroscopy*

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Femtosecond time-resolved coherent anti-Stokes Raman scattering (CARS) spectroscopy is used to investigate gaseous molecular dynamics. Due to the spectrally broad laser pulses, usually poorly resolved spectra result from this broad spectroscopy. However, it can be demonstrated that by the electronic resonance enhancement optimization control a selective excitation of specific vibrational mode is possible. Using an electronically resonance-enhanced effect, iodine molecule specific CARS spectroscopy can be obtained from a mixture of iodine–air at room temperature and a pressure of 1 atm (corresponding to a saturation iodine vapour as low as about 35 Pa). The dynamics on either the electronically excited state or the ground state of iodine molecules obtained is consistent with previous studies (vacuum, heated and pure iodine) in the femtosecond time resolved CARS spectroscopy, showing that an effective method of suppressing the non-resonant CARS background and other interferences is demonstrated.

Keywords: ultrafast spectroscopy, coherent anti-Stokes Raman scattering, vibrational analysis, resonance enhancement

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1. Introduction

Femtosecond (fs) time-resolved spectroscopy enables investigators to have a direct view of ultra-fast wave-packet dynamics, which evolves on molecular potential-energy surfaces after coherent excitation.[1−4] Many research groups use the ultrashort pulses to learn more about molecular and reaction dynamics even in complex biological systems. These experiments have led to interesting prospects for observing and controlling chromosome evolution, where spectral resolution is demanded. Unfortunately, the use of fs laser pulses is restricted by the spectral resolution considerably due to the inherently broad spectral bandwidth.[5−7] Several modes falling within the broad spectrum of fs pulses can be coherently excited.[8−10] This is especially severe in the case of biological relevant species, which are always typically characterized by a large number of electronic and vibrational degrees of freedom. The separation of such individual vibrational frequencies and interpretation of these results are challenging. Moreover, these measurements depend on polarization discriminating spurious background signals,[11] and thus require highly controlled conditions, such as the use of non-scattering and optically transparent samples.

In this paper, some of the foregoing limitations are addressed in the gas phase molecular iodine and air mixtures with the coherent enhancement effect using the femtosecond coherent anti-Stokes Raman scattering (CARS) spectroscopy. Iodine has long served as a model system in the development of new femtosecond techniques, such as time-resolved photoelectron spectroscopy[12] and femtosecond time-resolved coherent nonlinear spectroscopy.[13−15] Our approach is to make full use of the electronic resonance enhancement effect[16−21] by tuning the frequencies of the pump/Stokes pulses responsible for the CARS process

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into the B ← X electronic resonance. The resulting strong resonance enhancement allows us to optimally control the electronically non-resonant fs CARS spectroscopy. On the other hand, excitation with high-intensity femtosecond pulses can result in high optical gain and associated high brightness of the CARS spectroscopy, which makes the realization of a selective excitation of specific vibrational mode possible and which is also the key to our observation of higher order revivals in the wave-packet signal. The CARS spectroscopy can successfully probe the dynamics of iodine molecules on either the excited state or ground state, depending on the delay between the probe pulse and the pump/Stokes (dump) pulse pair.

2. Methodology

In our experiments, we prepared iodine–air mixture samples at room temperature and a pressure of 1 atm (1 atm = 1.01325×10^5 Pa, the corresponding saturation pressure of iodine is about 35 Pa). We have employed two different frequency lasers to generate the CARS signal. The signal at $\nu_{\rm aS}$ arises from the interaction between the Stokes laser beam at ν_2, pump and probe beams at a higher frequency ν_1 with the molecular system.

Due to the energy conservation, $\nu_{\rm aS} = 2\nu_1 - \nu_2$ must hold, which is shown in Fig. 1(a). Figure 1(b) describes the phase matching geometry for the initial laser beams and the signal, in which all polarizations are parallel. We have chosen the BOXCARS arrangement[22,23] so that we can separate the CARS signal from other background beams using the spatial separation [see Fig. 1(c)]. In experiment, the Stokes pulse (10 μJ/pulse, 1 kHz and 40 fs) and the pump pulse (5.5 μJ/pulse, 1 kHz and 40 fs) reach the sample molecules at the same time, while the probe one (6.5 μJ/pulse, 1 kHz and 40 fs) arrives at different times. Dynamics in different energy levels can be probed as a result of the relative arrival times of the three pulses. The point of the delay stage at which the three pulses are coincident in time is labeled as time zero ($t = 0$). As shown in Fig. 2, when the probe pulse interacts with the molecules before the pump-Stokes pulse pair, we denote this condition as $\Delta t < 0$. It prepares a coherent superposition of a few vibrational states on the excited states, with the femtosecond pulse duration much shorter than the vibration period. This coherent wave packet is probed by the two coincident Stokes and pump pulses, generating the CARS signals. On the contrary, if the probe pulse follows an interaction after the pump-Stokes pulse pair, as the $\Delta t > 0$ condition, the vibration of the electronic ground state can be detected. The CARS signal was collected by a silica fiber and detected with a fast photomultiplier. The CARS signal-to-noise ratio (SNR) was further enhanced using a boxcar integrator (SR250).

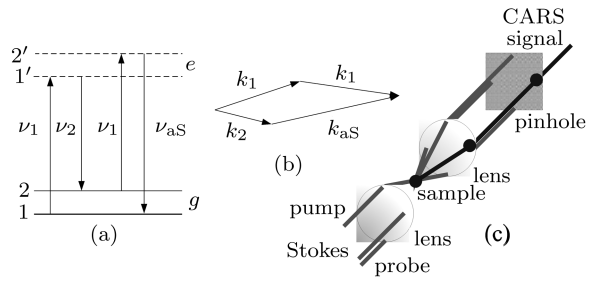


Fig. 1. (a) Energy diagram of the experiment, (b) phase matching diagram, and (c) BOXCARS setup used in our experiment.

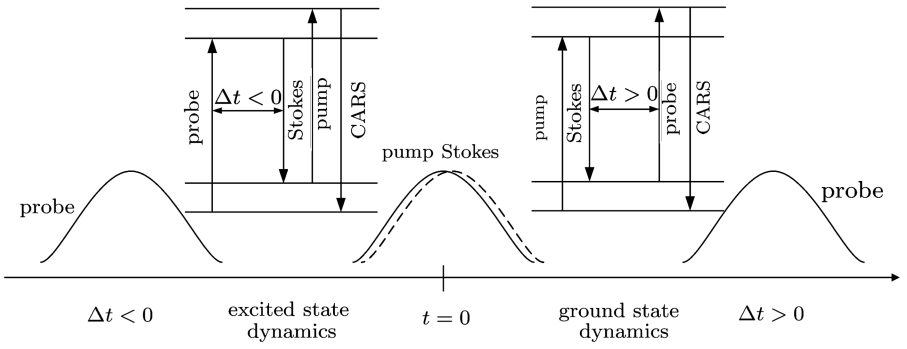


Fig. 2. Energy diagrams of the CARS process for both $\Delta t < 0$ and $\Delta t > 0$, indicating the relative timing of the laser pulses.

3. Results and discussion

The following fs CARS experimental results discussed were obtained using a mixture of iodine and air. Figure 3 shows the time-resolved CARS signal at various probe delay times. The curve of panel (a) in Fig. 3 shows a typical CARS transient signal obtained for a pump wavelength $\lambda_{\rm pu} = \lambda_{\rm pr} = 620$ nm and a Stokes wavelength $\lambda_{\rm S} = 645$ nm, detecting the CARS signal at $\lambda_{\rm aS} = 597$ nm. The transient signal $\Delta t > 0$ shows the expected vibrational beat patterns at the ground state vibrational frequency, which are contrary to more intense oscillations having about half this frequency at negative delay times ($\Delta t < 0$), and assigned to the excited-state vibrational dynamics. For the positive time delays ($\Delta t > 0$), the extended period of oscillations shows a period of 162 fs, corresponding to the wave-packet motion induced by coherent two-photo pumping (pump/Stokes) around $\nu = 6$ vibrational level in the ground X state of iodine. The approximate period of oscillations corresponds to a vibrational wave-number spacing of about 206 cm^{-1}. This is consistent with vibrational energy spacing in the ground X state of iodine as observed from continuum resonance Raman experiments.[24] The excited B-state signal ($\Delta t < 0$) exhibits beats with a separation of about 300 fs, corresponding to a vibrational wave-number spacing of about 111 cm^{-1}. This is consistent with the experimental vibrational energy spacing (vapor phase) in the B state around $\nu' = 7$.[25,26] It should be mentioned that the results presented here accord very well with earlier results[16] except that in those studies the ground X-state wave-packet dynamics due to the longer temporal pulse widths of their laser pulses (about 100 fs) was not observed.

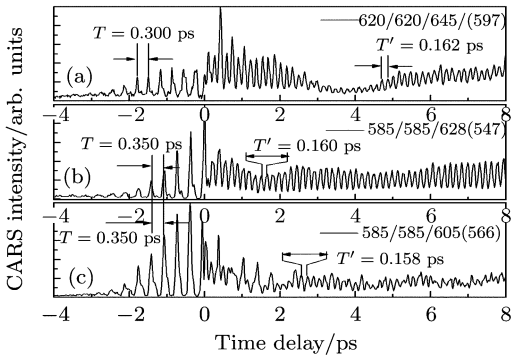


Fig. 3. Femtosecond time-resolved resonance-enhanced CARS transient signals. Here, the excited state dynamics is observed for negative time delays, whereas ground-state dynamics is observed for positive delays. Observations are based on the central wavelengths of the pump and Stokes pulses, which correspond to where the CARS signal is expected to be strongest.

To further confirm the results and demonstrate the resonance-enhancement suppressing electronically non-resonant fs CARS spectroscopy method, a large number of CARS transient signals with different pump and Stokes wavelengths were recorded, which are in resonance with the ground X-state and B-state transitions. Figures 3(b) and 3(c) show two selective excitations of typical resonance enhanced CARS transient signals obtained from two different wavelength combinations: (b) $\lambda_{\rm pu} = \lambda_{\rm pr} = 585$ nm, $\lambda_{\rm S} = 628$ nm, and $\lambda_{\rm aS} = 547$ nm and (c) $\lambda_{\rm pu} = \lambda_{\rm pr} = 585$ nm, $\lambda_{\rm S} = 605$ nm, and $\lambda_{\rm aS} = 566$ nm. They represent a beat frequency with the same average period of 350 fs for the negative time delays ($\Delta t < 0$) and 160 fs and 158 fs for the positive time delays ($\Delta t > 0$) respectively. Oscillation periods were also calculated using available spectroscopic data on vibrational wave-packet dynamics in either excited B state or ground X state. By selecting different pump and Stokes wavelengths of the time-resolved resonance-enhancement CARS spectroscopy, the monitoring of different dynamic behaviours of the gaseous iodine molecules can be realized.

An important aspect is how many vibrational levels of the prepared wave packets span and how well the experimental technique probes these levels. Only using a time-resolved CARS technique, the observation is limited to the coherences between the levels of a specific subset prepared. Thus, the probe step used was limited to Frank–Condon factors, which rely on the wavelength chosen. In this experiment, however, the electronic resonance enhancement effect is fully utilized, creating favourable conditions for investigators to observe and discriminate the subtle vibrational levels. From the known relative concentration of the gaseous iodine and air mixture molecules at room temperature (adjusted by pressure), the iodine-vapour pressure in the mixture studied in this paper was estimated to be as low as about 35 Pa,[27] which is 2 order lower than the pressure reported in the previous studies. Because it is a quadratic relationship between the CARS intensity and the induced nonlinear polarization, the CARS efficiency is estimated to increase at least 10^4 by resonance enhancement.[28] Also, the excitation with high intensity fs pulses can bring about high brightness of the CARS spectroscopy signal, which is the key to the investigating of higher-order revivals in wave-packet signals, i.e., high selectivity and high sensitivity of detection. These, combined with the femtosecond time-resolved CARS spec-

tra presented, can be used to track and detect wave-packet dynamics over a significant fraction of its periodic trajectory. The fractional revivals[29,30] from the rephrasing and the partial rephrasing of the wave-packets can also be obtained. As an illustrative example, we presente another selection of typical resonance-enhanced CARS transient at $\lambda_{aS} = 565$ nm obtained from $\lambda_{pu} = \lambda_{pr} = 600$ nm and $\lambda_S = 640$ nm. As illustrated in Fig. 4, excited B-state wave-packet dynamics is shown at negative time delays. The value of the resonance-enhanced CARS reveals the time ordering of the various fractional revivals of the wave packets. The 1/2, 1/6, and even 1/18 fractional revivals are detected. This is the highest order fractional revival reported for a molecular wave-packet.

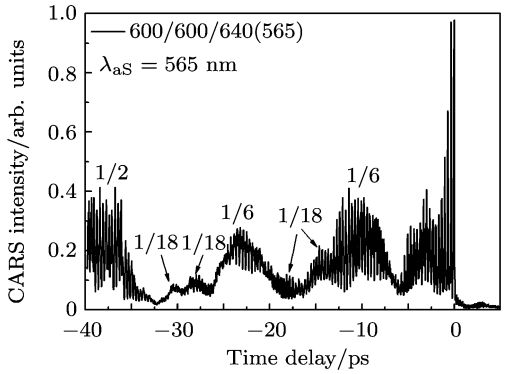


Fig. 4. Femtosecond time-resolved resonance-enhanced CARS transient signals showing packet dynamic behaviuors in the excited B state and ground X state of iodine. ($\lambda_{pu} = \lambda_{pr} = 600$ nm, $\lambda_S = 640$ nm, $\lambda_{aS} = 565$ nm).

4. Conclusions

In this paper, we obtained fs time-resolved CARS spectroscopy from the mixture of iodine and air. Selective excitation of molecular mode in the mixture is realized using electronic resonance enhancement effect in combination with the high-intensity femtosecond pulses that can bring high brightness of the CARS spectroscopy. The sensitivity and the resolution of the CARS spectroscopy are improved greatly and non-resonant background CARS signals are suppressed successfully. The subtle wave-packet fractional revivals are obtained with the enhancement SNR of the fs-CARS technique. By simply changing the timing of the laser pulses, the subtle dynamics of iodine molecules on either the ground-state or excited-state potential energy surfaces can be tracked and detected. Using different combinations of pump, probe and Stokes laser pulses, the dynamic behaviours of different molecular vibrational states can be detected. The results presented in this paper prove the availability of the fs time-resolved resonance-enhanced CARS spectroscopy in mode-selective investigations of the iodine molecular dynamics in iodine–air mixture. It is also shown that the fs resonance-enhanced CARS technique has a great potential in tracking and detecting nuclear dynamics over a significant fraction of its periodic trajectory, since a major advantage common to this technique is the reduced complexity of the spectra at low pressures and easy to model them due to the suppression of non-resonant background. The results obtained at room temperature prove that the resonance-enhanced CARS spectroscopy can be used for quantitatively detecting and identifying the molecular species in ambient environments.

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