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Effects of the air pressure on the wave-packet dynamics of gaseous iodine molecules at room temperature

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ABSTRACT

Based on ultrafast laser pulses, time-resolved resonance enhancement coherent anti-Stokes Raman scattering (RE-CARS) is applied to investigate wave-packet dynamics in gaseous iodine. The effects of air pressure on the wave-packet dynamics of iodine molecules are studied at pressures ranging from 1.5 Torr to 750 Torr. The RE-CARS signals are recorded in a gas cell filled with a mixture of about 0.3 Torr iodine in air buffer gas at room temperature. The revivals and fractional revival structures in the wave-packet signal are found to gradually disappear with rising air pressure up to 750 Torr, and the decay behaviors of the excited *B*-state and ground *X*-state become faster with increasing air pressure, which is due to the collision effects of the molecules and the growing complexity of the spectra at high pressures.

1. Introduction

Ultrafast spectroscopy techniques have been successfully applied to chemistry and biology, providing important dynamics information and insight into molecules and their environment. One of the most important applications of this technology is to problems in condensed phase molecular dynamics where ultrafast electronic dephasing times often obscure the spectroscopic and dynamical information being sought.

Coherent anti-Stokes Raman scattering (CARS) has been proved to be an efficient tool for studying molecular dynamics and determining molecular vibration–rotation wave-numbers, relaxation channels and rates under various conditions. When combined with ultrafast laser pulses, CARS can reveal detailed dynamics within excited molecules in both gas [1,2] and condensed phases [3–5]. CARS has been applied to high-resolution spectroscopy of NO by Doerk and Ehlbeck [6] and Pott and Doerk [7] and time-resolved CARS techniques have been widely employed in condensed-phase studies of vibrational dephasing and molecular orientational motion [8–12]. However, traditional vibrational or rotational CARS techniques have limited sensitivity and thus are not suitable for detection of minor species in wave-packet dynamics and plasmas. This difficulty can be overcome by tuning one or more of the pump, Stokes and probe beams into resonance with an electronic transition of the molecule. One can achieve great enhancement in the signal, relative to accompanying nonresonant background. The resonance enhancement coherent anti-Stokes Raman scattering (RE-CARS) signal has previously been applied to iodine [13], N_2 [14] and organic molecules [15]. In our previous work, we have demonstrated RE-CARS of gaseous iodine at room temperature [16]. Further details of our RE-CARS experiments can be found in two recent publications [17,18]. In fact, ultrashort pulse RE-CARS spectroscopy of complex samples requires more careful consideration of the various interactions in order to properly describe the observed signals.

In this paper, we report the first measurement of the effects of the environment pressure on the wave-packet dynamics of gaseous iodine molecules. In the experiments, the RE-CARS spectra of iodine were recorded using a gas cell at air pressures ranging from 1.5 Torr to 70 Torr. Time-resolved RE-CARS technique can be used to perform quantitative measurements of iodine vibrational level information in air-pressure environments for which traditional laser-induced fluorescence techniques become less accurate and more complicated, primarily owing to electronic quenching and background interferences. The effects of molecular collisions on RE-CARS signal were recorded through changing the air pressures in the sample cell at room temperature.

2. Experimental

The experimental setup used for the RE-CARS scheme is as follows (Fig. 1(a)). A commercial femtosecond laser system Ti: sapphire regenerative amplifier (Coherent Inc.) at 800 nm (2.5 mJ,

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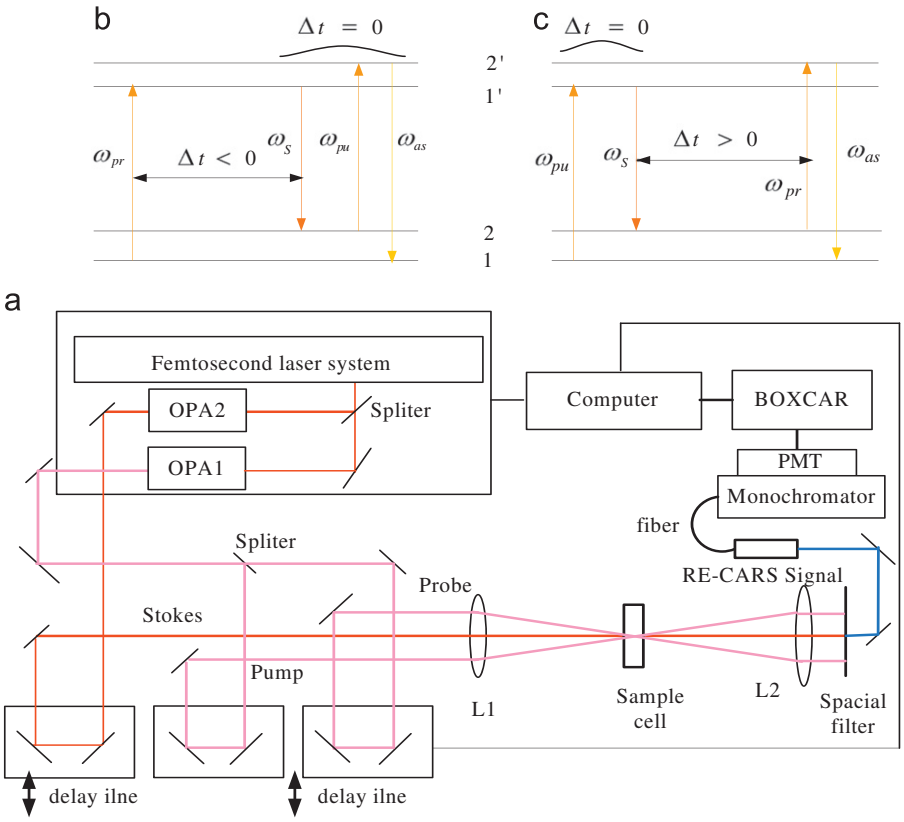

Fig. 1. (a) Experimental setup: femtosecond laser and detecting system, (b) and (c) Energy level diagrams, illustrating the resonant vibration interactions contributing to the fs time-resolved CARS signal for negative $\Delta t < 0$ and positive $\Delta t > 0$ delays between the pump/Stokes laser pair at $\Delta t = 0$ and the delayed probe pulse, respectively.

1 kHz, and 40 fs) was used to pump two non-collinear optical parametric amplifiers (NOPAS, Light Conversion). Two independent wavelengths in the range 570–760 nm can be generated by the two NOPAS. The output of NOPA1 with central wavelength of 571 nm was split into two parts by a splitter to obtain the pump (3.5 μJ/pulse) and probe (5.7 μJ/pulse) pulses, while the output 611 nm of NOPA2 serves as the Stokes pulse (8.5 μJ/pulse).

The RE-CARS process requires a spatial overlap of the beams in the sample. At the start of the experiment, a temporal overlap of the pulses is required, and the pulses were delayed with respect to each other by means of Michelson interferometer arrangements (with a minimal step-size of 1.66 fs). The temporal overlap of the beams was obtained using a cross correlation setup with second harmonic generation, as well as sum frequency mixing in a thin, phase-matched BBO crystal. The position of the delay stages at which the beams coincide in time was labeled as time zero. For the CARS, a folded BOXCARS configuration was employed to separate the signal from the incoming pump and probe beams [19] The phase-matching condition is fulfilled in this geometry and the three beams will pass through the three corners of the front side of a box. After interaction with the sample, the CARS signal emerges out from the fourth corner of the opposite box side.

The three beams were focused into the quartz gas cell containing iodine using a 300 mm focal lens. The gas cell was bathed in the room temperature to maintain a low saturation iodine vapor pressure of about 0.3 Torr [20]. The RE-CARS signal beam is filtered by a spatial filter. The signal is then collimated by a 300 mm achromatic lens. It is finally collected by a silica fiber into a monochromator, and after dispersion detected by a fast photomultiplier tube (PMT). The RE-CARS signal-to-noise ratio (SNR) was further enhanced using a boxcar integrator (SR250).

Here, the basic idea of the fs time-resolved RE-CARS experiment is presented. The energy diagrams of RE-CARS are shown in Fig. 1(b) and (c). In the experiment, we have employed three different frequency lasers to generate the CARS signal (the pump and probe fields derive from the same laser beam). Defining the overlap of pump/Stokes (dump) pulses to be $t=0$, while the probe one arrives at a different time. If the wavelengths of the pump/Stokes pulses are tuned to be in accordance with the $B(^3\Pi^+_{0u}) \leftarrow X(^1\Sigma^+_{0g})$ electronic resonance, the RE-CARS signal will successfully probe either the dynamics of the excited ($\Delta t < 0$)or ground state ($\Delta t > 0$)of wavepacket dynamics depending on the forward or backward data collection between the probe pulse and the pump/Stokes pulse pair.

3. Results and discussion

The fs time-resolved RE-CARS signal was recorded using a gas cell filled with iodine vapor in air buffer gas for a range of pressures varying from 1.5 Torr to 750 Torr. Effects of the air pressure on the iodine RE-CARS signal were investigated at room temperature, corresponding to a low saturation vapor pressure of about 0.3 Torr for iodine.

Fig. 2(a) and (b) show a typical RE-CARS transient for the excited *B*-state and ground *X*-state of iodine obtained with pump and probe wavelength $\lambda_{pu}=\lambda_{pr}=571$ nm and a Stokes wavelength $\lambda_S=611$ nm, detecting the RE-CARS signal at $\lambda_{aS}=536$ nm. The pulse energies were 3.5 μJ, 8.5 μJ, and 6.7 μJ for the pump, Stokes and probe beams, respectively.

For negative delay times of probe ($\Delta t < 0$), the transient is characterized by beats with a period of about 340 fs, corresponding to an energy difference of 98 cm^{-1}. This agrees well with the