CHIN. PHYS. LETT. Vol. 28, No. 4 (2011) 047804

Femtosecond Time-Resolved Resonance-Enhanced CARS of Gaseous Iodine at Room Temperature *

HE Ping(贺平)[1,2], FAN Rong-Wei(樊荣伟)[1], XIA Yuan-Qin(夏元钦)[1], YU Xin(于欣)[1], YAO Yong(姚勇)[3], CHEN De-Ying(陈德应)[1,3]**

[1] *National Key Laboratory of Science and Technology on Tunable Laser, Institute of Opto-electronics, Harbin Insitute of Technology, Harbin 150080*

[2] *College of Basic Sciences, Harbin University of Commerce, Harbin 150028*

[3] *Department of Electronic and Information Engineering, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen 518055*

(Received 7 December 2010)

Time-resolved resonance-enhanced coherent anti-Stokes Raman scattering (CARS) is applied to investigate molecular dynamics in gaseous iodine. 40 fs laser pulses are applied to create and monitor the high vibrational states of iodine at room temperature (corresponding to a vapor pressure as low as about 35 Pa) by femtosecond time-resolved CARS. Depending on the time delay between the probe pulse and the pump/Stokes pulse pairs, the high vibrational states both on the electronically ground states and the excited states can be detected as oscillations in the CARS transient signal. It is proved that the femtosecond time-resolved CARS technique is a promising candidate for investigating the molecular dynamics of a low concentration system and can be applied to environmental and atmospheric monitoring measurements.

PACS: 78.47.Jd, 06.60.Jn, 42.65.Dr, 33.20.Tp DOI: 10.1088/0256-307X/28/4/047804

Femtosecond laser pulses, with their short duration and broad spectral width, allow a multitude of processes for the preparation, manipulation and investigation of liquid or solid molecular coherences.[1] In addition to observing the dynamics of a system,[2–6] they also open up interesting possibilities for controlling time evolution and even manipulating a chemical reaction.[7,8] Femtosecond time-resolved coherent anti-Stokes Raman scattering (CARS) has been successfully used to observe the dynamics of liquid and solid systems with high concentrations, which can produce strong CARS signals.[9–14] However, its application in low pressure gaseous systems, such as atmospheric monitoring measurements, seem more challenging for this spectroscopy technique. As is known, iodine has long served as a model system in the development of new femtosecond spectroscopic techniques. To obtain strong CARS signals, earlier studies on femtosecond CARS in iodine molecular systems have been processed with iodine heated to about 360 K with a higher vapor pressure.[15,16] Although high vapor pressures can favor CARS signal enhancement, higher temperatures limit the application of the femtosecond time-resolved CARS technique in real-time atmospheric monitoring measurements at room temperature. In addition, a major common drawback of these studies is the growing complexity of the spectra at high temperature and the ensuing difficulty of modeling them due to non-resonant background and the non-availability of the pertinent broadening coefficients.[17]

In this Letter, we realize the detection of the high vibrational states of gaseous iodine at room temperature (corresponding to a vapor pressure as low as about 35 Pa) with the femtosecond time-resolved CARS technique. The high vibrational states of iodine molecules both in electronically ground states and excited states have been successfully investigated.

The schematic of the experimental system is illustrated in Fig. 1. There were 40 fs, 800 nm laser pulses with a pulse energy of 2.5 mJ and repetition rates of 1 kHz, generated by a Ti:sapphire regenerative amplifier (Coherent Inc.), and were used to pump two optical parametric amplifiers (OPAs, TOPAS, Light Conversion). Two independent wavelengths in the range 570–760 nm can be generated by the two OPAs. The output of OPA1 was split into two parts by a 50% beam splitter to obtain the pump and probe pulses, while the output of OPA2 serves as the Stokes pulse.

The CARS process requires a spatial overlap and, for the start of the experiment, also a temporal overlap of the pulses in the sample. The pulses were delayed with respect to each other during the experiment, using computer controlled (with a minimal step-size of 1.66 fs) linear translation stages in Michelson interferometer arrangements. The temporal overlap of the laser beams is determined using the optical Kerr effect[18] for ultraviolet beams. The points of the delay stages at which the three pulses coincided in time

*Supported by the National Natural Science Foundation of China under Grant No 60878018, and the Harbin Science and Technology Innovation Fund (RC2007QN017030).

**To whom correspondence should be addressed. Email: dychen@hit.edu.cn

© 2011 Chinese Physical Society and IOP Publishing Ltd

was labeled as time zero ($t = 0$). After the time zero was set, the pump and Stokes pulses were set to always coincide with each other, while the probe pulse was delayed with respect to the pump-Stokes pulses. For the CARS we have applied three-dimensional forward geometry (Folded BoxCARS),[19] which fulfills the phase matching condition and spatially separates the CARS signal to enable background-free detection. In this geometry, the three pulses will pass the three corners of the front side of a box. After interaction with the sample, the CARS signal will emerge from the fourth corner of the opposite side of the box.

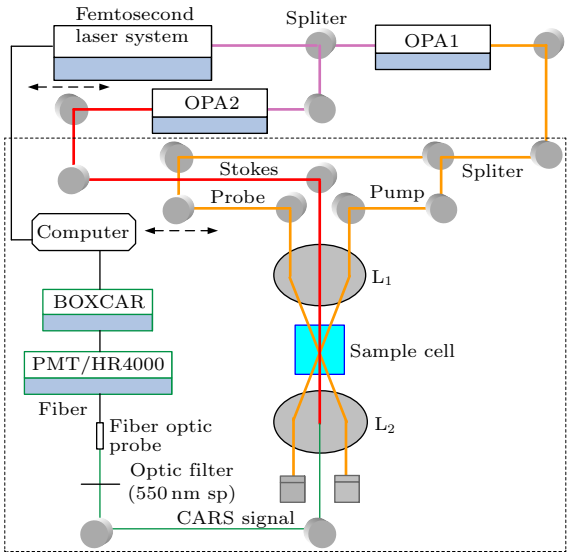


Fig. 1. Experimental setup: femtosecond laser system, beam path of the BOXCARS arrangement and the detecting system.

The three pulses were passed through the top of a lens L_1 with a 300 mm focal length and then focused onto the cell containing the iodine samples. The CARS signal was collimated by a second achromatic lens L_2 of focal length 300 mm. The signal could be easily separated from the incident leaser pulses by a spatial magic filter (because the direction of the signal is different from that of the incoming laser beams). Extreme care was taken to minimize background due to scattering from the walls of the sample cell and the stray light from the incoming pump. Stokes and probe beams were filtered out using a high quality optical filter with a high transmission ($T > 90\%$) at 300–550 nm and high reflectance ($R > 99\%$) in 550–900 nm. By testing the background noise intensity, the background can be neglected when compared to the CARS signal intensity. The spectra of the CARS signal, pump, probe and Stokes pulses were recorded with a HR4000 spectrometer (Ocean Optics). The CARS signal was collected by a silica fiber and detected with a fast photomultiplier tube (PMT). The CARS signal-to-noise ratio was further enhanced using a boxcar integrator (SR250).

Solid iodine was placed in the vacuum quartz sample cell and the sample cell was bathed in the room, for iodine, at about 293 K, corresponding to a low saturation vapor pressure of about 35 Pa.[20] To our knowledge, this is the lowest pressure investigation in molecular dynamics for gas phase molecules.

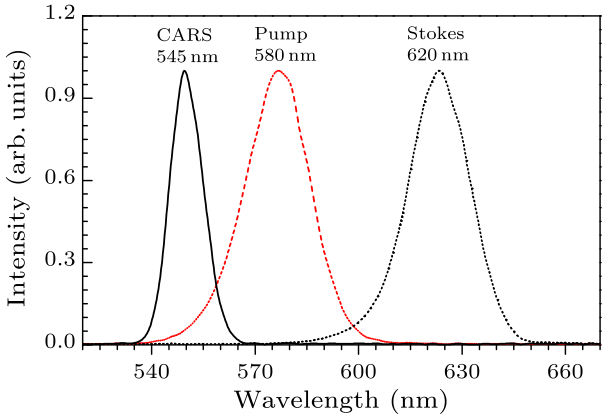


Fig. 2. Spectra of CARS signal, the pump and Stokes excitation pulses in iodine vapor.

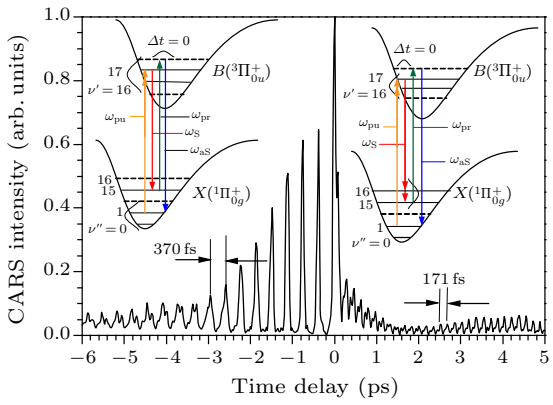


Fig. 3. Femtosecond time-resolved resonance-enhanced CARS transient for pump wavelength $\lambda_{pu} = \lambda_{pr} = 580$ nm and Stokes wavelength $\lambda_S = 620$ nm. Excited state dynamics are observed for negative time delays, whereas ground-state dynamics are observed for positive delays. The insert shows the energy diagrams of the CARS progress for $\Delta t < 0$ and $\Delta t > 0$, indicating the relative timing of the laser pulses.

Figure 2 shows the measured spectra of the pump, Stokes and CARS pulses. The CARS signal at 545 nm is generated by a Stokes wavelength at 620 nm and the pump and probe wavelength at 580 nm. From this figure it can be obtained that the pump, Stokes and CARS linewidths are 623 cm^{-1}, 567 cm^{-1} and 397 cm^{-1}, respectively.

Figure 3 shows a typical CARS transient for iodine obtained with pump and probe wavelengths $\lambda_{pu} = \lambda_{pr} = 580$ nm and a Stokes wavelength $\lambda_S = 620$ nm, detecting the CARS signal at $\lambda_{aS} = 545$ nm. For the input wavelengths used in this experiment, we

would expect to find the CARS signal centered at $\omega_{aS} = (\omega_{pu} + \omega_{pr}) - \omega_S = 18345\,\mathrm{cm}^{-1}$ (545 nm). The data show clear evidence of two regions, at negative and positive time delays, exhibiting different behaviors.

For the negative time delays ($\Delta t < 0$), the extended period of oscillations show a period of about 370 fs, corresponding to a vibrational wave number spacing of about $90\,\mathrm{cm}^{-1}$. In this procedure, the molecules are excited by the 580 nm=17241 cm^{-1} pulse, then they set out from the X ground state and reach the B excited state. Because of the pump pulse line width ($651\,\mathrm{cm}^{-1}$), the molecules can be provided by $\nu'' = 0$ and 1 of the ground state. The vibrational state around $\nu' = 16$ [21] (including $\nu' = 17$) of the B state has been prepared. The insert in Fig. 3 ($\Delta t < 0$) emphasizes the vibrational beat patterns of the excited state, the molecules are from the $\nu'' = 1$ vibrational state of the ground state and pumped to the excited states of $\nu' = 16$ and 17. The vibrational beat frequency between these two states ($\nu' = 16$ and 17 energy state) is $90\,\mathrm{cm}^{-1}$.

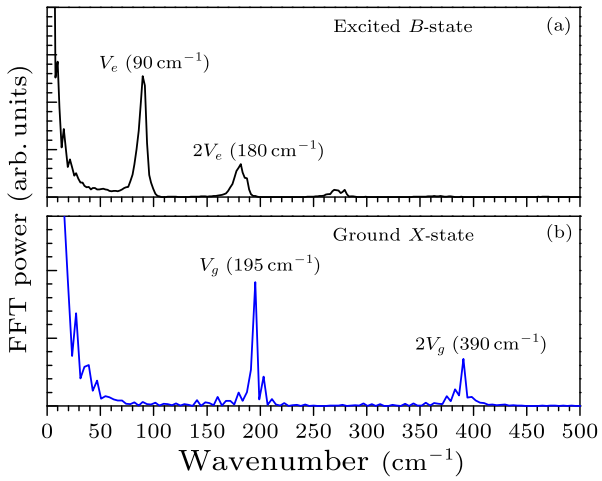


Fig. 4. Fourier transform power spectra of the iodine transient at $\lambda_{aS} = 545$ nm, from Fig. 3, for negative (a) and positive (b) time delays. The line spacing in the power spectra correspond, as expected, to the spacing of levels in the excited B state and the ground X state, respectively.

For the positive time delays ($\Delta t > 0$), as the energy difference between the pump and the Stokes results in a Raman resonance with the vibrational eigenstate around $\nu'' = 16$ in the ground X state, wavenumber spacings of about $193\,\mathrm{cm}^{-1}$ can be expected.[22] The dynamics can be tracked by scanning the delay of the last pump pulse completing the CARS process [see the insert in Fig. 3 ($\Delta t > 0$)]. In effect, the oscillations found for positive time delays ($\Delta t > 0$) have a period of 171 fs, corresponding to the wavepacket motion prepared by coherent two-photo pumping [pump/Stokes (dump)] around the sixteenth vibrational level in the ground X state of iodine. This is consistent with vibrational energy spacing in the ground X state of iodine as observed from continuum resonance Raman experiments.[22] It should be mentioned that this result agrees very well with earlier results[16] except that those researchers did not observe ground state wave-packet dynamics due to the narrower bandwidths of their laser pulses.

The fast Fourier transform (FFT) power spectra of the data from Fig. 3 are exhibited in Fig. 4. Again, the power spectra in in Fig. 4(a) confirms that the oscillations in the transient signal result from a coherent superposition of vibrational eigenstates with an energy spacing centered around $90\,\mathrm{cm}^{-1}$ [370 fs ($90\,\mathrm{cm}^{-1}$)]. This corresponds to the spacing between two neighboring vibration eigenstates in the region of the B state in iodine at $\nu' = 16$, the levels are accessed by the pump pulse at 580 nm. Figure 4(b) shows that the $\Delta t > 0$ region of Fig. 3 corresponds to the observation of vibrational wave-packet dynamics in the ground X state, with energy spacing centered around $195\,\mathrm{cm}^{-1}$. This corresponds to the energy spacing between $\nu'' = 15$ and 16 energy levels. As is expected, selecting different parts of the time-resolved resonance-enhanced CARS signal corresponds to monitoring different state dynamics (the ground X-state or the excited B-state) of the gaseous iodine molecules.

In summary, we have demonstrated the femtosecond time-resolved resonance enhanced anti-Stokes Raman scattering (CARS) technique and spontaneous resonance-enhanced Raman measurements for investigating the high vibrational states of low pressure gaseous molecules. Gaseous system molecular iodine is used as the sample. It should be mentioned that the iodine vapor is investigated at room temperature, corresponding to vapor pressure as low as 35 Pa. By simply changing the time delay of the laser pulses, the high vibrational dynamics of iodine molecules on either the electronically ground-state or excited-state potential energy surface can be tracked and detected. The presented results prove the availability of fs CARS technique in simultaneous electronically excited and ground high-vibrational state measurement at low concentrations, and show that the fs CARS technique has great potential in the measurement of low-concentration wave-packet dynamics. The results achieved at room temperature also show that the spectroscopic technique can be applied to those environmental and atmospheric monitoring applications that require versatile and real-time measurements.

References

[1] Wang Z H, Zhang X Z, Xu J J, Wu Q, Qiao H J, Tang B Q, Rupp R, Kong S H, Chen S L, Huang Z H, Li B, Liu S G and Zhang L 2005 *Chin. Phys. Lett.* **22** 2831

[2] Mukamel S 1995 *Principles of Nonlinear Optical Spectroscopy* (New York: Oxford University)
[3] Zewail A H 1996 J Phy 1994 *Femtochemistry: Ultrafast Dynamics of the Chemical Bond* (Singapore: World Scientific) vols 1 and 2
[4] Zewail A H 1994 *Femtochemistry: Ultrafast Dynamics of the Chemical Bond* (Singapore: World Scientific) vols 1 and 2
[5] Domcke W and Stock G 1997 *Adv. Chem. Phys.* **100** 1
[6] Tannor D J 2007 *Introduction to Quantum Mechanics: A Time-Dependent Perspective* (Sausalito, CA: University Science Press) p 400
[7] Zewail A H 2000 *J. Phys. Chem.* A **104** 5660
[8] Dantus M and Lozovoy V 2004 *Chem. Rev.* **104** 1813
[9] Winkler K, Lindner J, Bürsing H and Vöhringer P 2000 *J. Chem. Phys.* **113** 4674
[10] Krynicki K 1966 *Physica* **32** 167
[11] Smith D W G and Powles J G 1966 *Mol. Phys.* **10** 451
[12] Gordalla B C and Zeidler M D 1986 *Mol. Phys.* **59** 817
[13] Jonas J, DeFries T and Wilbur D J 1976 *J. Chem. Phys.* **65** 582
[14] Ropp J, Lawrence C, Farrar T C and Skinner J L 2001 *J. Am. Chem. Soc.* **123** 8047
[15] Lausten R, Sminova O, Sussman B J, Grafe S, Mouritzen A S and Stolow A 2008 *J. Chem. Phys.* **128** 244310
[16] Schmitt M, Knopp G, Materny A and Kiefer W 1997 *Chem. Phys. Lett.* **270** 9
[17] Lang T, Kompa K L and Motzkus M 1999 *Chem. Phys. Lett.* **310** 65
[18] Ho P P and Alfano R R 1979 *Phys. Rev.* A **20** 2170
[19] Eckbreth A C 1978 *Appl. Phys. Lett.* **32** 421
[20] Dennis R, Keefe O and John H 1982 *J. Chem. Eng.* **27** 77
[21] Joel Tellinghuisen 1973 *J. Chem. Phys.* **58** 2822
[22] Kiefer W and Bernstein H J 1972 *J. Mol. Spectrosc.* **43** 366