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Vibrationally selective radiative and non-radiative transitions in gaseous hydrogen molecules

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ABSTRACT

An efficient vibrationally selective technique to build-up the $v''=1$ vibrational levels in gaseous hydrogen is demonstrated using *stimulated Raman pumping* (SRP). Both photo-acoustic Raman spectroscopy (PARS) and coherent anti-Stokes Raman spectroscopy (CARS) are used to study non-radiative and radiative ($v''=0$ and $v''=1$) transitions in gaseous H_2 molecules. The population fraction in the $v''=1$ vibrational level has been estimated using combined photo-acoustic and coherent anti-Stokes Raman spectroscopy with stimulated Raman pumping.

1. Introduction

In recent years measurements of trace greenhouse gases such as CO_2 and CH_4 have become important, as new schemes are devised to avoid environmental pollution problems. Continuous monitoring of the leakage of inflammable gases is also required, such as H_2, CH_4 and H_2S, in chemical plants and along gas pipe-lines for health and safety reasons. Laser spectroscopy provides sensitive detection techniques for a range of molecules in the gaseous phase. Absorption spectroscopy and photo-acoustic spectroscopy (PAS) in the infrared (IR) region are the methods that are most frequently performed. However, these techniques demand a tunable IR laser source. Photo-acoustic Raman spectroscopy (PARS) was first proposed by Barrett and Berry in 1979 [1]. In this method, two visible lasers with frequencies (ω_P) and (ω_S) are used instead of an IR laser, and the frequency differences ($\omega_P - \omega_S$) are tuned to be equal to the Raman shift frequency (ω_R). The thermal relaxation of the molecules from the upper vibrational state is detected as an acoustic wave.

Nonlinear Raman spectroscopy has the merit that it can excite the vibrational levels of gas molecules in the IR region without the use of a tunable IR laser [2–4]. However, traditional nonlinear Raman spectroscopy still requires two lasers whose frequency difference should coincide with the Raman frequency of the sample gas. Thus a fixed-frequency laser and a tunable laser are usually necessary for these experiments. Development of high power lasers has given rise to several nonlinear spectroscopic techniques based on non-linear Raman scattering such as coherent anti-Stokes Raman scattering (CARS) and stimulated Raman scattering (SRS) [2,3]. PARS has also been developed based on stimulated Raman spectroscopy. Fortunately, a scheme for nonlinear Raman spectroscopy without the requirement of a tunable laser and with only a single fixed-frequency laser and a Raman shifter has been proposed [2–4]. The various types of nonlinear Raman spectroscopy techniques have subsequently been performed using this method, such as CARS and PARS [4–9]. Further detailed experiments into the vibrational–vibrational transfer rates in the gas phase are then possible using SRP [10]. PARS and SRP–PARS were previously developed [11] with studies into the behaviour of H_2 molecules.

Aim of the present work to demonstrate and study combined photoacoustic Raman spectroscopy and coherent antistokes Raman spectroscopy with and without stimulated Raman pumping in selective vibrational levels of H_2 molecules. The signals to study in nonradiative and radiative transitions with efficiency of stimulated Raman pumping of H_2 molecule.

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2. Experimental

A combined technique using both PARS and CARS with SRP of gaseous hydrogen (H_2) molecules is demonstrated in the present paper. The $v'' = 1$ vibrational level is populated by using stimulated Raman pumping. The population fraction of molecules in the $v'' = 0$ and $v'' = 1$ vibrational levels have been calculated using PARS with and without SRP. The PARS signal was monitored using non-radiative transitions in the molecular sample with a sensitive microphone coupled to a preamplifier. Laser pulses with a wavelength of 532 nm were generated using secondary harmonics from a Nd:YAG laser, with a pulse width of 5–7 ns and a repetition rate of 10 Hz. The beam was divided into two parts with 80% of the radiation pumping a tunable dye laser. The bandwidth of the dye laser was 0.05 nm. The PARS setup was composed of two pulsed beams; one from a Nd:YAG laser at a wavelength of 532 nm with 16 mJ pulses and the other from a Nd:YAG laser pumped-dye laser emitting in the wavelength range 680–685 nm with 5–8 mJ pulses. Using a Dichroic mirror, both beams propagated along the same direction and were overlapped in time and space along the center of a photoacoustic cell. The 532 nm radiation was used as a pump beam (ω_P) and the tunable lasing beam from the dye laser was used as a Stokes beam (ω_S) for the photoacoustic Raman signal.

The two experimental setups are shown in Fig. 1a and b. In the first set up (Fig. 1a) a pyrex cell was made with four quartz windows arranged at the Brewster angle. The windows were 2.5 cm in diameter and the main tube was 15 cm in length. Two needle valves were connected to the sample cell. One valve was used to seal the sample reservoir, and the other was used to connect the sample cell to the vacuum pump. A sensitive microphone (Sennheiser KE-4-211-2) was fitted at the center of the Pyrex cell and proper shielding was made to minimize the external electrical pickup. The microphone was safely housed in a Teflon tube which was 2 cm in length and 1 cm in diameter. The photo-acoustic (PA) cell was found to be suitable for experiments in a free running mode in which the sample flow rate was carefully controlled by a needle valve. H_2 gas was introduced through the side-arms after evacuation of the PA cell.

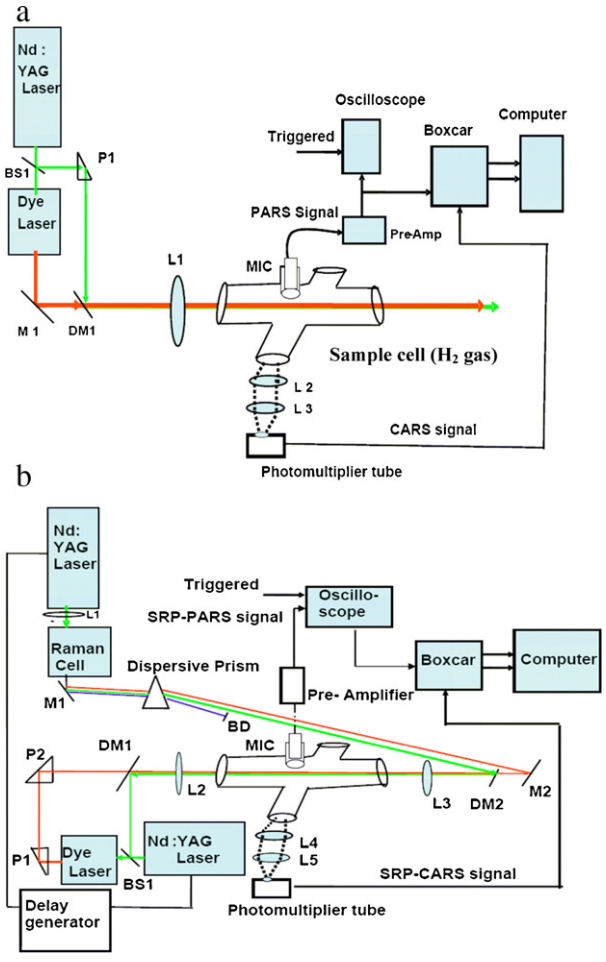

Fig. 1. (a) The experimental setup of PARS and CARS *without* SRP. (b) A combined setup of PARS and CARS *with* SRP. P1 and P2 are prisms, BS1, BS2, BS3 are beam splitters, L1, L2, L3 and L4 are lenses. BD is a beam dump, M1, M2 are mirrors, DM1 and DM2 are Dichroic mirrors. MIC is the microphone.

The photo-acoustic spectrum was recorded from the H_2 gas at a pressure of 2 Torr. In both PARS and CARS experiments the sample was illuminated by two pulsed laser beams which are temporally and spatially coincident. Selective population excitation occurs when transitions involve Raman active energy levels, i.e. the transition must involve a change in the molecular polarization. Therefore the frequency difference of the two incident laser beams had to be adjusted to equal the frequency of this Raman active transition ($\omega_P - \omega_S = \omega_R$). As the excited molecules in this energy level [4–9] relax non-radiatively by thermal collisions in the H_2 molecules, pressure fluctuations are generated that can be detected by a sensitive microphone and then fed into a boxcar averager to improve the signal to noise ratio. The stimulated Raman pumping (SRP) technique was employed as in the second experimental setup (Fig. 1b) to prepare the H_2 population in the excited vibrational $v'' = 1$ level. The second harmonic of the Nd:YAG laser at a wavelength of 532 nm was focused into a Raman cell which was 100 cm in length, 5 cm in diameter and filled with H_2 gas at nine atmospheres pressure (~6840 Torr). The gas then caused a strong first order Stokes and anti-Stokes Raman shift on the transmitted beam at wavelengths of 683 and 436 nm, respectively. The output beams at 532 and 683 nm were measured to be 14 and 17 mJ, respectively, prior to the pyrex cell, while the beam at 436 nm was removed using a filter. The 532 and 683 nm beams were focused on to the photoacoustic (PA) cell using a 50 cm focal length lens. A delay time of five ns was achieved between the two Nd-YAG lasers. The SRP technique was employed to prepare the H_2 population in the $v'' = 1$ level from the $v'' = 0$ vibrational level, using both the pump beam at 532 nm and the 683 nm Stokes beam. A schematic vibrational energy level diagram of SRP is shown in Fig. 2a for the gaseous H_2 molecules. The combined SRP–PARS technique was first employed to populate the $v'' = 1$ vibrational level (Fig. 2a) using both the pump beam ($\lambda = 532$ nm) and the Stokes beam ($\lambda = 683$ nm), which are generated from the Raman cell. Next after 5 ns the pump beam ($\lambda = 532$ nm) from the second Nd-YAG laser and the tunable Stokes beam from the tunable dye laser ($\lambda = 680$–685 nm) were focused onto the photoacoustic cell. The energy level diagram of SRP–PARS is given in Fig. 2b.The non-radiative transitions in the combined technique SRP–PARS were monitored using a sensitive microphone and amplified by a pre-amplifier. The signal was processed using a boxcar averager to improve the signal to noise ratio.

3. Results and discussion

Standard PARS spectra were recorded in the frequency range 3880–3936 cm^{-1} (Fig. 3a) without using the SRP technique. The frequency of the pump beam was fixed (ω_P) and the frequency of Stokes beam (ω_S) was tunable. The pump (ω_P) was excited from the $v'' = 0$ vibrational level of the H_2 molecules. The spectrum was recorded as a function of the frequency difference ($\omega_P - \omega_S = \omega_R$). The frequency difference (ω_R) is Raman active in non-radiative transitions. A PARS spectrum was recorded in the frequency range 3880–3936 cm^{-1} using the SRP technique and is shown in Fig. 3b. In this case, the $v'' = 1$ vibrational level is populated by the SRP method. The delay time was so short that the population of H_2 ($v'' = 1$) vibra-