Multiplex CARS Study of Infrared-Multiphoton-Excited OCS

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Coherent anti-Stokes Raman spectroscopy (CARS) is a sensitive and efficient technique to monitor molecular vibrational and rotational distributions. This paper reports on the application of CARS to study the dynamics of OCS after infrared multiphoton excitation. The OCS molecule has three widely separated fundamental modes (ν_1 = 859 cm^{-1}, ν_2 = 527 cm^{-1}, ν_3 = 2079 cm^{-1}). The overtone of the ν_2 mode can be excited with CO_2 laser frequencies between the $P(10)$ and $P(26)$ lines of the 9.6 μm branch. The experiments were carried out both in bulk samples and in a supersonic molecular jet.

1. Setup

The experimental setup is shown in Fig. 1. The important features of the CARS spectrometer, described previously,[1] are summarized here. The main improvement to the setup is the addition of a supersonic molecular jet described below.

The infrared pulses from a TEA CO_2-laser have a 150-ns duration and a maximum energy of 200 mJ. The beam is focused into the interaction region with a 15-cm focal length cylindrical lens down to a beam waist of 110 μm by 18 mm.

Frequency-doubled Nd:YAG laser pulses with a 10-ns duration and 200-mJ average energy are used to generate the CARS signals. The bandwidth of these pulses is reduced with an intracavity line-narrowing etalon to 0.1 cm^{-1}. About 25 mJ of the doubled Nd:YAG laser output is used for each of two beams at ω_1 = 532 nm, while the remainder serves to pump a broad band prism-tuned dye laser at ω_2 = 557 nm. After amplification, 6-ns, 20-mJ pulses of 60-cm^{-1} linewidth are obtained. This linewidth is sufficient to generate multiplex CARS signals[2] over the entire region of interest.

The ω_1 and ω_2 beams are aligned parallel to each other and focused in a folded BOXCARS geometry by a 25-cm focal length lens. The beam waist in the interaction region where the infrared laser beam, the CARS laser beams and the molecular jet cross at right angles is 80μm.

The CARS signal passes through an aperture which spatially rejects the ω_1 and ω_2 beams. The signal is dispersed using an 1-m spectrograph, and the dispersed CARS signal

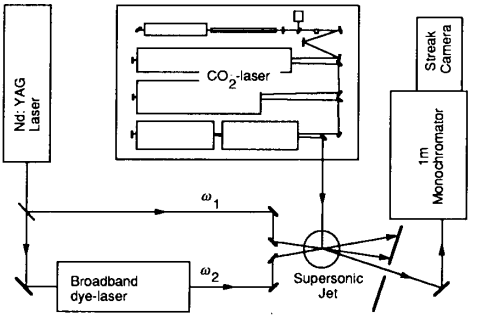

Fig. 1. The experimental setup.

is then recorded on a streak camera system with a detector array. The resolution of the entire system is 0.012 nm (0.46 cm^{-1}). To obtain a good signal-to-noise ratio each spectrum is averaged over 50 shots.

The molecular jet apparatus consists of a nozzle mounted on an *XYZ* translational manipulator, and a high vacuum chamber pumped by a 700-liter/s diffusion pump. Without molecular jet the chamber pressure was 4×10^{-7} Torr; with a back pressure on the nozzle of about 3 atm, and 1-ms molecular pulses at a 10-Hz repetition rate, the chamber pressure increases to 7×10^{-4} Torr.

The supersonic jet system has several advantages over the static cell: First, it greatly reduces the number of collisions between molecules and thus allows one to study molecules under collisionless conditions. Second, because of the adiabatic expansion the translational, rotational and vibrational temperatures of the sample are drastically reduced. This reduces the total number of populated molecular states and increases the population of individual states, thereby improving the CARS signal which is proportional to the square of the number of molecules in that state.

The density in the supersonic jet was determined by comparing the integrated intensity of ground state peak in the CARS spectrum obtained in the jet with the one in bulk samples at various pressures. For OCS at $x/D = 3$, with x the distance from the nozzle and $D = 1$ mm the diameter of the nozzle aperture, the density in the jet was found to be 5×10^{22} m^{-3}.

The temperature of the supersonic jet was determined using both vibrational and pure rotational[3] CARS. From the integrated line intensities of the CARS spectrum it follows that the vibrational temperature of OCS after expansion is 200 K. Because of rotational cooling, the linewidth of the lines in the vibrational CARS spectrum in the jet is 0.5 cm^{-1}, or about one third of that observed in the bulk. It was not possible to determine the rotational temperature for OCS because the individual rotational lines could not be resolved. For nitrogen, however, the pure rotational spectrum can easily be resolved, showing a rotational temperature of 5 K.

2. Results and Discussion

Results from the measurements carried out in the bulk have been reported previously,[1] and can be summarized as follows. At high excitation, the temperature of the ν_2 mode rises up to 2000 K, and hot bands are observed up to the $v_2 = 4$ state. Because of the small anharmonicity and the fast collisional relaxation within the ν_2 mode, the bulk measurements always show an equilibrium distribution for the ν_2 mode, despite the fact that only the even-numbered states are populated by the CO_2 laser. The time-dependence of the spectra provides information on *V-V* energy transfer rates. In particular, the measurements put a lower limit of $k_{\nu_2 \rightarrow \nu_2} = 1$ μs^{-1} $Torr^{-1}$ on the vibrational relaxation rate within the ν_2 mode.

Collisions increase the infrared multiphoton excitation because of collisional broadening and rotational hole-filling during the excitation. In the bulk it may be possible to study infrared multiphoton excitation under nearly collisionless conditions by reducing the density of the sample and the duration of the laser pulses. In a supersonic jet it is much easier to obtain collisionless conditions; as the distance from the nozzle, x, is increased, the translational temperature of molecules decreases, and the mean free time between collisions is greatly increased.

Close to the nozzle the spectra obtained in the jet (see Fig. 2) are similar to the ones obtained in the bulk. The right-most peak is the ground state peak for the ν_2 mode, and corresponds to the vibrational transition between the $(v_1,v_2,v_3) = (0,0,0)$ and $(1,0,0)$ states. The other transitions, which are shifted because of the 6 cm^{-1} cross-anharmonicity between

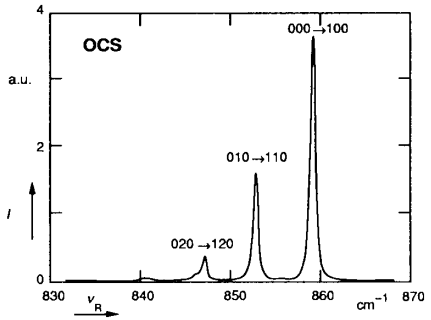

Fig. 2. CARS spectrum of OCS in a supersonic jet 500 ns after 7.2 J/cm^2 infrared excitation .

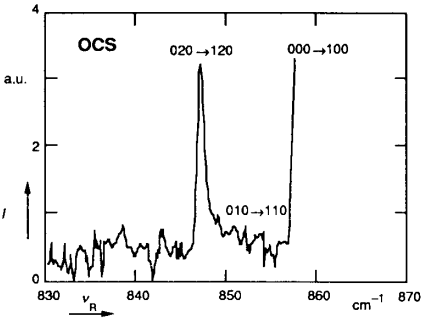

Fig. 3. CARS spectrum of OCS in a supersonic jet 30 ns after 7.2 J/cm^2 infrared excitation, for x/D = 3.2.

the ν_1 and ν_2 modes, are labeled correspondingly in the Figure. As in the bulk, odd-numbered states are populated because of collisions occurring in the jet during the laser pulse. As the distance x to the nozzle is increased, the excitation decreases because of the reduced collision rate. This clearly shows that even in a supersonic expansion collisions contribute to the excitation close to the nozzle. However, at distances $x/D > 3$, the excitation no longer decreases. At this distance, where the temperature reaches its lowest point, about 10% of the molecules are still excited under collisionless conditions. A spectrum obtained in this regime at a delay of 30 ns is shown in Fig. 3. As expected, the spectrum here only shows a single peak corresponding to the excited overtone transition.

At a delay of 60 ns the spectra show that the v_2=1 state begins to be populated. At x/D = 3 the density determined from CARS measurement is 5×10^{22} m^{-3}. Assuming a translational temperature of 10 K, one obtains a gas-kinetic mean-free-time between collisions of 40 ns for OCS. Therefore, collisional energy transfer occurs within 1.5 gas-kinetic collisions, which corresponds to an energy transfer rate of $k_{v2\rightarrow v2} = 5.4\ \mu s^{-1}\ Torr^{-1}$ at room temperature.

In the supersonic jet the OCS could only be vibrationally excited by the $P(22)$ and $P(18)$ lines of the 9.6 μm CO_2 laser. This is because only a few rotational states are populated and there is virtually no collisional broadening. The Rabi frequency for OCS is given by $\omega_R = 1.3 \times 10^{-5}\sqrt{I}$, with ω_R in cm^{-1} and where I is the peak CO_2 laser intensity in W/cm^2.[4] In this experiment one has $\omega_R = 0.08$ cm^{-1}, and only the $P(22)$ and $P(18)$ CO_2 laser lines have a frequency mismatch below the Rabi frequency. These lines pump the P_5 and R_3 transitions of OCS, respectively. This is quite different from the situation in the bulk, where excitation was observed for all CO_2 lines between the $P(10)$ to $P(26)$ lines of the 9.6 μm CO_2 laser branch. In the bulk, the broader rotational distribution and rotational hole filling by collisions assist the excitation.

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