periodic array.[11] A sequence of fluorescence photons therefore appears as a cascade of the dressed atom downwards its energy diagram. Such a picture allows us to interpret the signal here investigated as a radiative cascade signal,[12] where the cascading system is not the bare atom but the dressed one.

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[8] These experimental features might also result from a hyper Raman process bringing the atom from *g* to *e* through a virtual excitation in a Rydberg state (by the absorption of two laser photons) and the emission of a $2\omega_L - \omega_0$ fluorescence photon. But the rate of such a process, evaluated from the corresponding energy defects and oscillator strengths, is shown to be 6000 times smaller than the rate of the process studied in this paper. Moreover, we have experimentally verified that the ω_A photons are linearly polarized along the laser polarization, as expected from the diagram in Fig. 3(b). This would not be the case for the hyper Raman process which can bring the atom from *g* to any sublevel of *e*.

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[10] Furthermore, for the nonlinear process studied here, a multimode laser is more efficient than a single-mode laser with the same intensity by a factor $\langle I^2\rangle/\langle I\rangle^2$, which is equal to 2 for Gaussian fluctuations.

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[12] The picture of the dressed-atom cascade remains valid at resonance where a perturbative treatment would no longer be possible at high laser intensities. As shown in Ref. 4, the emissions in the sidebands remain strongly correlated. It must be noted, however, that the correlation signal becomes symmetric.

Observation of an Optical Stark Effect on Vibrational and Rotational Transitions

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(Received 27 May 1980)

Vibrational and rotational Raman transitions are shown to be shifted to lower frequencies in the presence of a nonresonant, high-intensity optical field. Experimental results using coherent anti-Stokes Raman spectroscopy for hydrogen and nitrogen are presented. The magnitude of the observed shift is in agreement with a calculation which considers the coupling of the optical field to the internuclear separation *via* the molecular electronic polarizability. The magnitude of the shift is predicted to be proportional to the optical field intensity.

PACS numbers: 33.55.+c, 33.20.Fb

We report the first observation of shifts in molecular vibrational and rotational frequencies induced by an optical field which is not resonant with molecular transition frequencies. The Stark shifts of rotational transitions in polar molecules have been studied extensively using low-frequency applied fields.[1] Changes in transition frequencies due to intermolecular fields have been studied extensively in matrices, liquids, and gases.[2] Apparent spectral shifts that did not involve actual changes in molecular frequencies also have been observed in coherent Raman experiments[3] with use of high-power lasers. The quadratic Stark effect on electronic transitions has been the subject of considerable research.[4] Stark shifts of vibrational frequencies driven near resonance have been investigated,[5] but shifts due to the presence of nonresonant fields have not been reported previously.

In the experiments described here, a frequency shift of a rotational transition in dynamic hydrogen is observed in coherent anti-Stokes Raman scattering (CARS) spectra obtained from a sample volume irradiated by the focused output of a pulsed 1.06-μm Nd:YAlG laser. The experiments were motivated by the observation of asymmetrically broadened line shapes in background-free CARS experiments designed to optimize the detection of minor species.[6,7] In this case, the broadening was induced by fields generated by the high-power pump laser used in the CARS experiment. The observed frequency shifts are interpreted by considering the time-independent coupling of the optical field to the molecule *via* the variation of the electronic polarizability with internuclear separation.

Figure 1 shows the change in frequency induced by a focused, pulsed laser field for the $S(3)$ rotational transition of molecular hydrogen. A shift of 0.12 cm^{-1} to lower frequency is observed for the perturbed spectrum (crosses in Fig. 1) compared to the unperturbed spectrum (circles in Fig. 1). The spectra were obtained near the exit of a 6-mm nozzle from which H_2 gas was flowing at 0.6 l/min. The hydrogen was then burned, forming a diffusion flame above the sample volume. Data were obtained using a high-resolution (0.1–0.2 cm^{-1}), time-averaged, crossed-beam CARS apparatus, which as been described previously.[5] Spatial resolution was obtained by crossing two focused 532.0-nm pump beams in the horizontal plane, such that they intersected a probe laser beam contained in the vertical plane. For each plotted datum point, 20 to 50 single-shot measurements were digitized, normalized, and then averaged. The perturbing optical field was provided by the 1.06-μm output "infrared" beam) of the Q-switched Nd:YAlG laser. By blocking alternate infrared laser pulses with a 5-Hz chopper, perturbed and unperturbed spectra were averaged simultaneously. This process essentially eliminated wavelength uncertainties between the two spectra. The infrared beam was directed onto the same 25-cm–focal-length lens used for the CARS lasers such that the infrared focal volume was spatially overlapped with the CARS signal generation volume. Assuming diffraction-limited focusing, the infrared laser beam waist (~ 80 μm) was approximately four times the diameter of the CARS sampling volume. Also, the infrared pulses were twice as long as the CARS laser pulses. As a result, relatively small spatial and temporal variations in the high-power infrared field intensity occurred during the generation of the CARS signal. For the measurements of Fig. 1, the infrared laser pulses were typically ~ 200 mJ, measured after the focusing lens, whereas the probe- and pump-laser pulses were 0.4 and 3 mJ, respectively. The infrared beam diameter at the lens was 0.4 cm, while that of the CARS lasers was 0.8 cm.

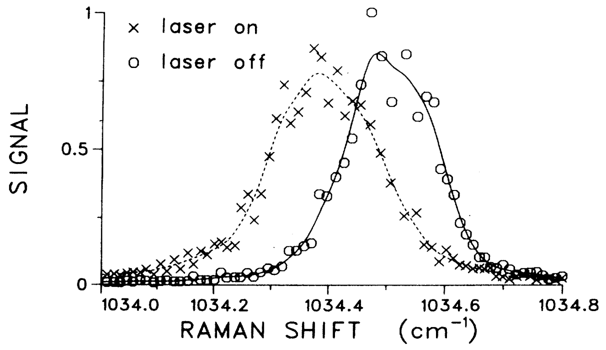

FIG. 1. The effects of high-intensity infrared radiation on the position and line shape of the $S(3)$ rotational transition of molecular hydrogen. Crosses represent CARS data obtained in the presence of 1.06-μm radiation from a Q-switched Nd:YAlG laser; circles show data in the absence of this field. The solid and dashed lines are smooth curves drawn through the data points.

The experiments on hydrogen (Fig. 1) employed a separate, nonresonant laser field to shift transition frequencies. However, the effect is also observable as an asymmetric broadening when high pump (or probe) intensities are used in a normal CARS measurement. Figure 2 compares the measured CARS line shapes of the rotational vibrational $S(6)$ line of nitrogen obtained using (a) 2-mJ and (b) 70-mJ pulses of 532.0 nm pump energy, with ~ 0.2 mJ of probe energy and with a 30-cm-focal-length lens. These spectra were obtained using a room-temperature optical cell at a pressure of 100 Torr. Because of variations in field intensity introduced by spatial variations in the crossed 532.0-nm beams and by the time-dependent laser output, the perturbed line shapes are inhomogeneously broadened rather than shifted uniformly as in Fig. 1. Since the spectra of Fig. 2 were measured in separate scans, the presence of small peak shifts (less than 0.1 cm^{-1}) could not be determined reliably. The presence of broadening due to stimulated Raman processes was investigated by varying the probe-laser energy, but was not detected.

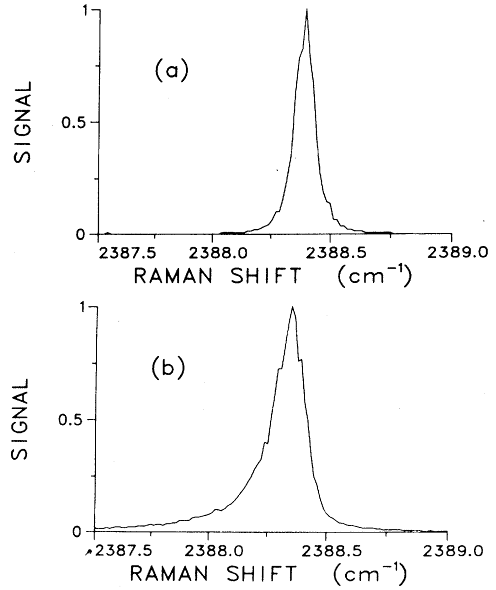

FIG. 2. A comparison of line shapes of the $S(6)$ rotational-vibrational line of molecular nitrogen, obtained using (a) 2-mJ and (b) 70-mJ 532.0-nm pump-laser pulses for the CARS measurements.

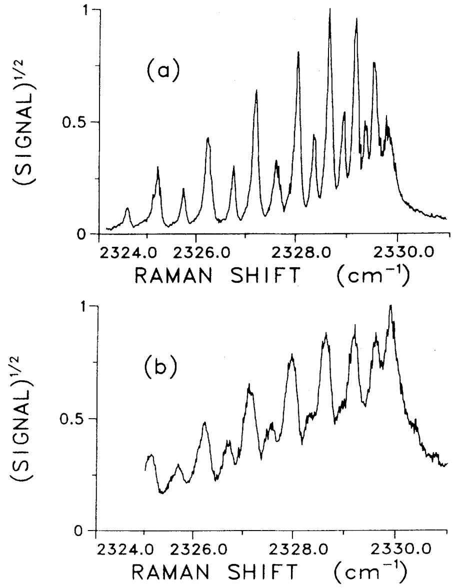

FIG. 3. A comparison of CARS spectra of the room-temperature nitrogen Q branch, obtained using (a) 0.25-mJ and (b) 70-mJ 532.0-nm pump-laser pulses. The square root of the CARS signal was averaged and plotted in order to display results linear in number density.

The consequences of this inhomogenous broadening for high-resolution spectroscopy measurements are illustrated in Fig. 3. The nitrogen Q-branch spectrum in (a) was obtained with 0.25-mJ pump-laser pulses, and in (b) with 70-mJ pulses, under the same conditions described previously. As a result of the broadening of individual vibrational lines, the weaker lines of Fig. 3(a) (odd-J transitions) are no longer resolved near the band head, and the relative peak heights of neighboring lines are strongly modified.

The magnitude of the optical Stark effect on molecular vibrational-rotational frequencies can be estimated by a simple classical-mechanics calculation. The vibrational Hamiltonian for a diatomic molecule (with no permanent dipole moment) in the presence of an applied optical field is

$$H=\tfrac{1}{2}\mu^{-1}p^2+V(q)-\tfrac{1}{2}\alpha(q)E_0^{\,2}(\tfrac{1}{2}+\tfrac{1}{2}\cos 2\omega_L t), \qquad (1)$$

where p and q are the canonically conjugate momentum and internuclear coordinate, μ is the reduced mass, $V(q)$ is the vibrational potential, $\alpha(q)$ is the polarizability (assumed to be isotropic), E_0 is the applied field amplitude, and the $\cos^2\omega_L t$ time dependence of the intensity has been rewritten. Since $2\omega_L$ is much larger than the vibrational frequency (by a factor of 5–10), the response of a molecule to the time-dependent perturbation will be small compared to the time-independent perturbation. Considering only the time-independent perturbation and introducing the Morse potential, Eq. (1) becomes

$$H=\tfrac{1}{2}\mu^{-1}p^2+D_e\{1-\exp[-\beta(q-q_e)]\}^2 -\tfrac{1}{4}\alpha(q)E_0^{\,2}, \qquad (2)$$

where D_e and β are the Morse parameters, q_e is the unperturbed equilibrium position, and E_0 is the electric field amplitude. The change in the equilibrium value of q is defined as $\delta q=q_e'-q_e$. The internuclear separation, q_e', at the minimum of the perturbed potential is given to the first order in δq by

$$q_e'=q_e+(E_0^{\,2}/8D_e\beta^2)d\alpha/dq, \qquad (3)$$

where $2D_e\beta^2$ is the harmonic force constant. Thus, the shift in the equilibrium internuclear separation is quadratic in the applied-laser-field amplitude, and results in an increase in the internuclear spacing for positive values of the polarizability derivative.

This change in internuclear spacing induces a shift in the vibrational and rotational frequencies. The change in rotational frequency can be calculated from the change in the moment of inertia, and is given to first order by

$$\delta\omega_r = -\,\omega_r^{\,0}(E_0^{\,2}/4D_e\beta^2 q_e)\,d\alpha/dq, \qquad (4)$$

where $\omega_r^{\,0}$ is the unperturbed frequency. Vibrational frequencies also will be shifted because of anharmonicities in $V(q)$. The magnitude of these shifts can be calculated from the change in the harmonic force constant, and is given to first order for the ground state by

$$\delta\omega_V = -\,\omega_V^{\,0}(3E_0^{\,2}/16D_e\beta)\,d\alpha/dq, \qquad (5)$$

where $\omega_V^{\,0}$ is the unperturbed vibrational frequency. The predicted frequency shifts are linear in the polarizability derivative and thus depend on the square root of the spontaneous Raman cross section.

From Eq. (4), the rotational-frequency shift is seen to be proportional to the perturbing laser intensity during the CARS measurement. An estimate of the peak intensity due to a 200-mJ, 1.06-μm Q-switched pulse, based on diffraction theory, gives $(8\pm 4)\times 10^{11}$ W/cm^2. With use of this value and a polarizability derivative for H_2 of 1.2 Å^2,[8] the predicted rotational shift is -0.11 ± 0.05 cm^{-1}. Thus, the observed -0.12-cm^{-1} line shift is consistent with the classical calculation. The increased width of the shifted peak in Fig. 1 can be attributed to the inhomogeneities in the 1.06-μm-laser intensity over the volume sampled by the crossed-beam CARS experiment. The observed shift is an order of magnitude larger than the estimated collisional width of hydrogen at 1 atm. Therefore, a consideration of this form of Stark shift is important for high-resolution spectroscopy, even at much lower power densities. An estimate of the 532.0-nm peak field intensity, used to obtain the data of Fig. 2(b), gives $\sim 8\times 10^{12}$ W/cm^2. For the $S(6)$ line considered, the vibrational Stark shift given by Eq. (5) must be added to the rotational Stark shift. The result for N_2 is a total shift of 0.6 cm^{-1}, consistent with the data of Fig. 2.

This type of Stark effect is general in nature, and will have important consequences for vibrational and rotational Raman and infrared spectroscopy using pulsed lasers. In particular, the effect represents a more serious limitation than stimulated Raman pumping on the ultimate sensitivity and spectral resolution of CARS and Raman gain techniques. It is also expected that this perturbation will be important in some infrared laser photolysis experiments and their application to isotope separation.

A modulation spectroscopy[9] based on this Stark effect promises to provide time- and space-resolved detection of molecules. We are also investigating the effects of anisotropy in the polarizability and time dependence of the perturbing field. Additional experiments are in progress to verify the linear dependence of the frequency shift on field intensity.

We are grateful to A. R. Van Hook and S. C. Gray for their invaluable assistance in these experiments. This research was supported by the U. S. Department of Energy.

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