Optical Stark Splitting of Rotational Raman Transitions

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The first observation of optical Stark splitting of a molecular Raman transition is reported. The splitting is observed in inverse Raman rotational spectra of diatomic nitrogen, measured in the presence of a pulsed 1.06-μm laser field. The line positions and intensities of the Stark-split multiplets are in good agreement with calculations of the quadratic Stark effect associated with the optical polarizability anisotropy.

The use of high-peak-power, narrow-bandwidth pulsed lasers for molecular spectroscopy is rapidly expanding. An important consideration in these measurements is the possibility of perturbations in spectra due to laser-induced Stark effects. The significance of these effects has been recognized for laser frequencies near resonance with the transitions under study, e.g., in spectroscopies utilizing laser absorption.[1] However, little attention has been given to the analysis of such perturbations in high-resolution, coherent Raman spectra. For these experiments, a detailed understanding of Stark effects on rovibrational transitions due to higher frequency, nonresonant fields is required.

In the past, studies of Stark effects on rovibrational states have involved the use of perturbing frequencies near resonance with the measured transitions,[2] or the use of low-frequency perturbing fields.[3] These results, however, are not easily applied to the analysis of effects associated with nonresonant optical fields. Recently, Stark shifts induced by visible and near-infrared frequencies far above rovibrational transitions were reported for molecular CARS (coherent anti-Stokes Raman spectroscopy) spectra.[4] These shifts were interpreted in terms of the interaction of time-averaged optical fields with molecules via the isotropic polarizability derivative. The effect later formed the basis for new optical Stark-modulated absorption spectroscopies.[5]

In this Letter, we report the first observation of optical Stark splitting of (pure) rotational Raman transitions. These splittings are described by the interaction of a molecule with the mean square component of an optical field via the molecular polarizability anisotropy. This mechanism gives rise to observable Stark splittings in the rotational spectra of molecules without permanent dipole moments. The results reported here are fundamentally different from those of Ref. 4, since the interaction is with the polarizability

anisotropy, instead of the polarizability *derivative*. In general, both effects must be considered to account for the total Stark splitting.

High-resolution rotational Raman spectra were measured in a crossed-beam, "quasi-cw" inverse Raman experiment (IRS).[6] The IRS pump radiation was generated by using a frequency-doubled Nd-doped yttrium aluminum garnet (Nd:YAlG) laser (532 nm) to give pulse amplification of the output of a cw ring dye laser. The resulting $\simeq$ 10-nsec (full width at half maximum) pulses were nearly Fourier-transform limited, with a spectral bandwidth of $\simeq 0.003$ cm^{-1}. The probe laser was a single-frequency, cw krypton ion laser operating at 568.2 nm. Stark splitting induced by the pump laser alone was observed to cause asymmetric line broadening in the spectra for pump-laser energies greater than $\simeq 1.5$ mJ ($\simeq 7.6$ GW/cm^2). Consequently, the data reported here were typically obtained with pump energies below this value.

The Stark field was provided by residual 1.06-μm infrared (IR) output from the Nd:YAlG laser. This laser was operated in a single mode to obtain a smooth, near-Gaussian pulse of $\simeq$ 20 nsec duration. The spatial and temporal resolutions of the IRS technique were exploited to obtain maximum uniformity of the Stark field applied to the sample. Spatial uniformity was achieved by centering the Raman sampling volume (a cylinder $\simeq$ 3 mm in length $\times$ 50 μm in diameter) within the focused IR beam ($\simeq$ 140 μm diam). Optical path lengths were adjusted so that the measurement laser pulse arrived at the sample during the peak of the IR pulse, thereby maximizing the temporal uniformity of the Stark field during measurements.

The dependence of Stark splitting on applied field was investigated by varying the IR beam energy with polarization rotators and analyzers. However, because of variations in beam pointing and optical alignment, the Stark-field intensity in the Raman sampling volume could not be deter-

mined accurately. An estimate of this parameter was obtained by adjusting the optical alignment for maximum Stark effect and measuring the IR pulse energy for each scan.

Measurements were performed on the $S(2)$ and and $S(6)$ pure rotational lines of nitrogen in a cell at 25 Torr and room temperature. The data shown in Figs. 1(a)–1(c) summarize results for the $S(2)$ transition with the IR field polarized parallel to the polarizations of the measurement lasers (also parallel). The $S(2)$ line is observed to split into a triplet, with components that shift linearly with IR energy. Both positive and negative shifts with respect to the unperturbed line position (27.852 cm^{-1}) are observed. In addition, an increase in the linewidth of individual transitions is observed to occur with increasing Stark shift. This effect is believed to result from inhomogeneous broadening due to residual temporal and spatial nonuniformities in the optical Stark field.

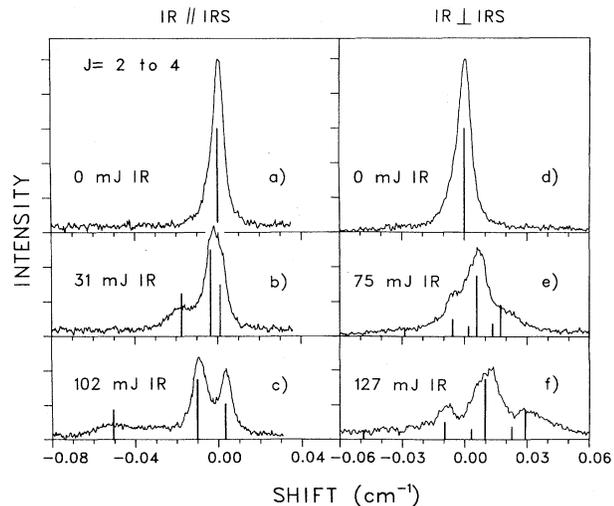Spectra obtained with the Stark-field polarization rotated perpendicular to the measurement fields are shown in Figs. 1(d)–1(f). In comparison with the previous data, broader linewidths and splittings of different signs and magnitudes are observed. In addition, most of the integrated intensity shifts above, rather than below, the unperturbed transition frequency.

The Stark effect on the $S(6)$ transition at 59.67 cm^{-1} is shown in Fig. 2. The Stark field is parallel to the fields of the measurement lasers. For this transition, splittings are not resolved even at the highest attainable fields. It is apparent, however, that the integrated intensity shifts to lower frequency, with the largest splittings occurring for the weakest transitions.

The experimental results can be understood in detail by considering the quadratic Stark effect associated with the optical polarizability anisotropy. (The polarizability-derivative–induced Stark effect is neglected here because of the small Raman shifts of the pure rotational transitions.[4]) In this approach, the energy of a homonuclear molecule due to an electric field is

$$H = -\tfrac{1}{2}\vec{E}(t) \cdot \vec{\alpha} \cdot \vec{E}(t), \tag{1}$$

where $\vec{\alpha}$ is the optical polarizability tensor. The time-dependent term in Eq. (1) is omitted for fields with frequencies much greater than molecular rotational frequencies, as in the present case. For a state with rotational and magnetic quantum numbers J and M, the lowest-order energy-level
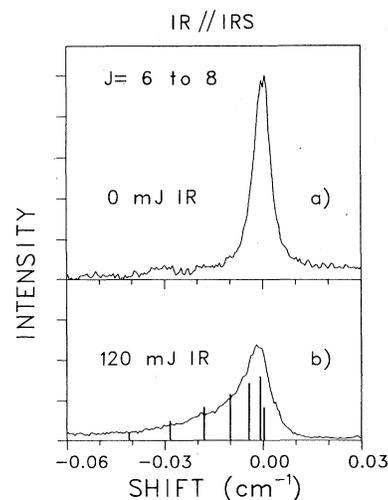

FIG. 1. Inverse Raman spectra of the $S(2)$ pure rotational line of nitrogen, obtained during irradiation by a pulsed 1.06-μm (IR) optical field at several energies. The IR intensity at the measurement probe volume was not measured directly, being extremely dependent on optical alignment. However, total IR energy per 20-nsec pulse was measured, and the IR beam waist was approximately 140 μm. (a)–(c) Spectra obtained with the IR field polarized parallel to the measurement laser polarizations, and (d)–(f) spectra with IR field polarized perpendicular to measurement laser polarizations. Bars represent line and intensities calculated from polarizability theory using time-averaged fields (see text).

FIG. 2. Inverse Raman spectra of the $S(6)$ pure rotational nitrogen transition, obtained as in Fig. 1, for parallel polarizations of the Stark and measurement laser fields.

shifts obtained using Eq. (1) are

$$\Delta E_{J,M} = \frac{1}{6} E_0^2 \left\{ \frac{3M^2 - J(J+1)}{(2J-1)(2J+3)} \right\} \gamma \qquad (2)$$

for a diatomic molecule.[7] Here, γ is the polarizability anisotropy[8] and E_0 is the field amplitude. Note that J states are predicted to split into $J+1$ levels since the degeneracy of M levels with opposite sign is not removed (see Fig. 3).

Selection rules and intensities for Raman transitions between J multiplets can be calculated from matrix elements of the polarizability tensor. With all field polarizations parallel, the selection rule $\Delta M = 0$ is obtained from direct integration of the rotational wave functions (spherical harmonics). For transitions with $J \to J+2$, the M-dependent intensities are

$$I_{J,M;J+2,M} = D\gamma^2 \frac{[(J+1)^2 - M^2][(J+2)^2 - M^2]}{(2J+5)(2J+3)^2(2J+1)}, \qquad (3)$$

where D is a proportionality constant. Similarly, the selection rule for transitions with the Stark field polarized perpendicular to the measurement fields is found to be $\Delta M = 0, \pm 2$. The corresponding expression for intensities is lengthy and will be reported elsewhere.[9]
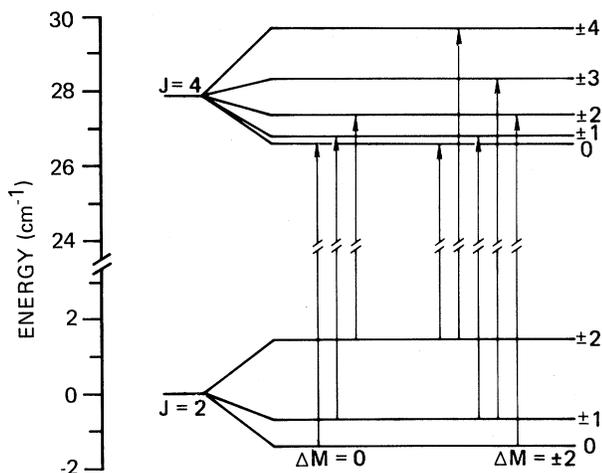
To facilitate a detailed comparison between the predicted and observed splittings, an absolute Stark-field intensity was inferred by fitting theory to experiment for the spectra measured in the highest fields [Figs. 1(c), 1(f), and 2(b)]. (The field intensities thus obtained were consistent with experimental estimates.) Once calibrated in this manner, Stark fields for the remaining spectra were assumed proportional to the measured IR energy.

The predicted transition frequencies are indicated by vertical bars in Figs. 1 and 2. Where resolvable, the signs and relative magnitudes of shifts of individual transitions are well described [e.g., Fig. 1(c)]. This agreement verifies the use of Eq. (2) to predict relative shifts of transitions from a particular J state. The quadratic nature of the Stark effect is evidenced by the results of Figs. 1(b), 1(c), 1(e), and 1(f): The observed splittings agree with calculated shifts which varied linearly in the field intensity.

The calculated integrated intensities are indicated by the relative bar heights in the figures. When we take into account the linewidth variation due to the inhomogeneous broadening effect mentioned above, the measured intensities are in good agreement with theory [see, e.g., the resolved triplet in Figs. 1(b) and 1(c)]. The line shapes shown in Figs. 1(e), 1(f), and 2(b) are also consistent with calculations: The observed asymmetry and widths are seen to arise from closely spaced, unresolved transitions.

The Stark shifts described in Ref. 4 and the splittings reported here both affect transitions involving rotations; the relative importance of the two mechanisms depends on a number of factors. Stark shifts via the polarizability derivative[4] are determined by the vibrational and rotational frequencies, the molecular potential, and $d\alpha/dq$. Stark splittings due to polarizability anisotropy depend on J, the magnitude of γ, and the polarization of applied and measurement fields. Recently, we have observed that splittings decreased with the use of circularly polarized Stark fields. These observations may explain the near absence of anisotropy splittings in the low-resolution measurement of the $S(3)$ hydrogen line[4] using elliptically polarized Stark fields. However, splitting did contribute to the asymmetric broadening of the nitrogen $S(6)$ line shape of Fig. 2(b) of Ref. 4.

Theory indicates that for pure vibrational tran-

FIG. 3. Energy-level diagram for $J = 2$ and $J = 4$ calculated from Eq. (2). With IR and measurement laser polarizations parallel, transitions with $\Delta M = 0$ are allowed, giving rise to three lines. With the IR field polarization perpendicular to the measurement fields, transitions with $\Delta M = 0$ and ± 2 are allowed, resulting in seven different lines. Numerical values for the Stark splittings were obtained from Eq. (2) assuming a polarizability anisotropy of 7.1×10^{-25} cm^3 from Ref. 8, and an electric field intensity of 1 TW/cm^2 ($E_0^2 = 8.38 \times 10^9$ erg/cm^3). Thus, a realistic optical intensity of 35 GW/cm^2 (5.1 MV/cm) produces a maximum splitting of 0.073 cm^{-1} for the $\Delta M = 0$ manifold; this is a factor of $\simeq 10$ greater than the perturbed linewidth at 25 Torr.

sitions (Q branch), anisotropy splittings cannot occur. This has been verified by our recent high-resolution measurements of the $Q(1)$ line shape of hydrogen (4155.2 cm^{-1}) in an applied field. The line was not split, but was shifted toward lower frequency in accordance with Eq. (5) of Ref. 4.

In summary, optical Stark splittings of rotational Raman transitions have been observed in high-resolution inverse Raman spectra. The results are described well by calculations employing the optical polarizability anisotropy and time-averaged optical fields. Measurements show that the magnitudes of the splittings are significant even at moderate pulsed-laser powers. Thus, these laser-induced Stark effects are an important new consideration in high-resolution, nonlinear spectroscopy involving rotational transitions.

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Measurement of the Lamb Shift in Hydrogenic Cl^{16+}

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The Lamb-shift splitting in hydrogenic chlorine is measured to be 31.19(22) THz. The experiment was performed on a relativistic beam of chlorine ions using a CO_2 laser resonance method. The result agrees with one of the two existing calculations and is the most sensitive test to date of QED in high-Z systems.

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The $2s_{1/2}$-$2p_{1/2}$ Lamb-shift splitting, $\mathcal{S}$, in the hydrogenic system Cl^{16+} has been measured in a laser resonance experiment using a relativistic beam of chlorine ions. The result is 31.19 ± 0.22 THz, in agreement with one of the two quantum electrodynamics (QED) calculations in the literature.[1,2] This result is one of the most sensitive tests to date of QED in bound systems because of the scaling of $\mathcal{S}$ with $(\alpha Z)^n$, $n \geqslant 4$, and is important for interpreting the result of the recently reported Lamb-shift measurement in atomic hydrogen,[3] for assessing relativistic calculations of energy levels in heavy atoms, and for predicting QED effects in the limit of short distances and high field strengths.

The only previously reported high-Z Lamb-shift resonance measurement has been for the $Z = 9$, F^{8+} system.[4] However, nonresonance measurements of $\mathcal{S}$ have been reported for several systems[5] of which hydrogenic argon has the highest atomic number.[6] Other experiments on high-Z hydrogenic systems are in progress or are