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PRECISION INFRARED STARK SPECTRA OF $N^{14}H_2D$ USING LAMB DIP*

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By Stark tuning the $N^{14}H_2D$ molecule into optical resonance with a standing-wave laser field, which is intense and monochromatic, it has been possible to obtain a unique vibration-rotation line assignment and its transition matrix element, and to probe ground- and excited-state Stark splittings with precision. Stark splittings as narrow as 1.5 MHz (within a Doppler width of 82 MHz) are observed for the first time in an optically excited state using the Lamb dip.

In this Letter, we present a new spectroscopic technique based on the Lamb dip,[1] which yields extraordinarily high-resolution optical Stark spectra. The principal feature involves Stark tuning a molecule into optical resonance with an intense monochromatic laser field which is in the form of a standing wave. The resulting spectrum consists of a series of Stark lines, each exhibiting a Lamb dip which approximates the natural line shape. It will become evident that many of the attractive advantages inherent in microwave spectroscopy such as tunability, high resolution, and unique line assignment are available here as well. Linewidths of about 1.6 MHz have been achieved in these preliminary studies, and it appears that this width can be reduced by at least one order of magnitude in the immediate future. Notice that this width rivals that encountered in high-resolution microwave spectroscopy, but when resolution is compared, there is at least a two order of magnitude difference in favor of our optical result. With the present resolution, it has been possible to observe for the first time molecular Stark splittings of about 1.5 MHz in an optically excited state.

Other nonlinear optical schemes[2,3] have been reported previously, and in a few instances, hfs[4-6] or isotope shift[7] have been resolved as well as the natural line shape.[8-10] However, these methods tend to be less general in application to resonances other than the laser transitions.[11]

We will now elaborate on these general comments by considering the molecule $N^{14}H_2D$ as an example. Its vibration-rotation spectrum is examined here in the region of the ν_2 vibration[12] (inversion-type mode) using as a source the $P(20)$ line of a cw CO_2 laser at a frequency of 944.191 cm^{-1}.[13] This transition has been identified as $4_{04}(a) \rightarrow 5_{14}(s)$ in asymmetric rotor notation where the symmetry operation is that of inversion. Ordinarily this CO_2 line would not be absorbed by NH_2D, but by application of a uniform electric field, each NH_2D Stark line can be tuned into resonance as indicated in Fig. 1. It will be shown that this spectrum provides an unambiguous transition assignment even though the coarse spectrum of this molecule has not been reported and even though our initial gas sample of ordinary NH_3 contained only 0.045% $N^{14}H_2D$ by natural abundance.

For our initial experiments, the CO_2 laser was free running and was not stabilized in any way; it operated cw on a single longitudinal mode with $c/2L = 75$ MHz, with linear polarization, and with

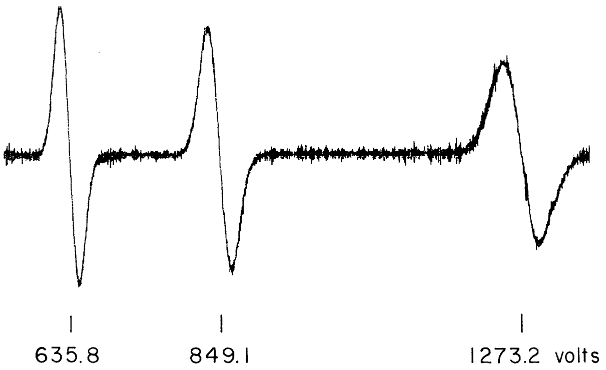

FIG. 1. Stark spectrum for the case of a traveling wave. The selection rule is $\Delta M = \pm 1$, the overall pressure of the deuterium-enriched ammonia is 50 μ, and the Stark plates of 50-cm length are separated by 0.1928 cm. All lines have essentially the same Doppler width, but the apparent linewidth in field increases in successive lines because M decreases.

an output power of a few W/cm^2 or less. The $P(20)$ line at 10.6-μ wavelength was selected by properly orienting a Fabry-Perot interferometer[14] located inside the laser cavity. This beam passed through a cell containing the gas sample and two Stark plates made of glass and vacuum-coated with aluminum on the inner surfaces. The narrowest lines were observed with plates 12.5 cm long×2.5 cm wide and separated by polished ($\lambda/10$) quartz spacers 0.1519 cm thick. These plates were oriented so that the Stark field was either parallel or perpendicular to the optical field direction corresponding to the selection rules $\Delta M = 0$ or $\Delta M = \pm 1$. Either selection rule could be studied conveniently merely by passing the exciting laser beam through a properly oriented half-wave retardation plate. To form a standing wave in the Stark cell, the emerging beam was directed backward upon reflection by a 95% dielectric flat mirror, slightly misaligned to avoid interference with laser operation. The remaining fraction transmitted by the mirror was detected by a gold-doped germanium detector. Sample gas pressures of ammonia were in the range 1-300 μ.

Low-noise Lamb-dip signals were only obtained in the later stages of this work through the use of an exceptionally stable free-running cw laser,[15] which was kindly made available to us by Dr. C. Freed of the Massachusetts Institute of Technology Lincoln Laboratory. This gave 0.9 W output at the $P(20)$ line in a single linearly polarized mode with $c/2L = 300$ MHz; its stability characteristics have been given elsewhere.[15]

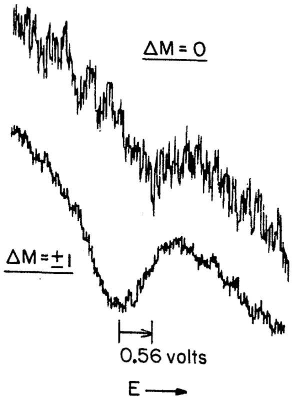

FIG. 2. Stark spectrum for the case of a standing wave. The transitions are $M_J = \pm 3 \rightarrow \pm 3$ (upper spectrum) and $M_J = \pm 3 \rightarrow \pm 4$ (lower spectrum) where the field strength corresponds to the second line of Fig. 1. Note that the upper spectrum is shifted to a higher frequency by 1.56 ± 0.05 MHz and that its greater noise is the result of a smaller transition matrix element and a higher gain setting. Total pressure of the deuterium-enriched ammonia is 80 μ, and the Stark plates of 12.5-cm length are separated by 0.1519 cm. The linewidth, full width at half-maximum, is ~2.9 MHz.

Phase-sensitive detection of the optical signal using small-amplitude Stark modulation, typically 0.1-V peak-to-peak square-wave at 20 kHz, gave readily observable first derivative amplitude-field line shapes when plotted on an X-Y recorder.

In Fig. 1, it will be noticed that there is a coarse Stark pattern[16, 17] consisting of Doppler-broadened lines separated by large intervals. In turn, each of these lines decomposes into a much narrower line (or lines) due to the Lamb dip as shown in Fig. 2. The former splittings, as will be seen, are the result of a first order Stark effect in the lower state, while the excited state exhibits a small quadratic Stark effect, both being in the strong-field regime. For both cases, $\pm M_J$ remain degenerate. In agreement with expectation, the narrow line structure disappears when the standing-wave optical field is replaced by a traveling wave as in Fig. 1.

The particular vibration-rotation transition investigated here is shown in Fig. 3, and its assignment was settled in the following way. First, the M quantum numbers of the lower state are readily obtained from the large splittings by their inverse voltage ratios of 4:3:2, which are integral ratios to an accuracy of 1 part in 1300. The fourth line, lower level $M = \pm 1$, has also been observed at the expected field strength but using 0.1-cm Stark spacing to avoid breakdown. Hence,

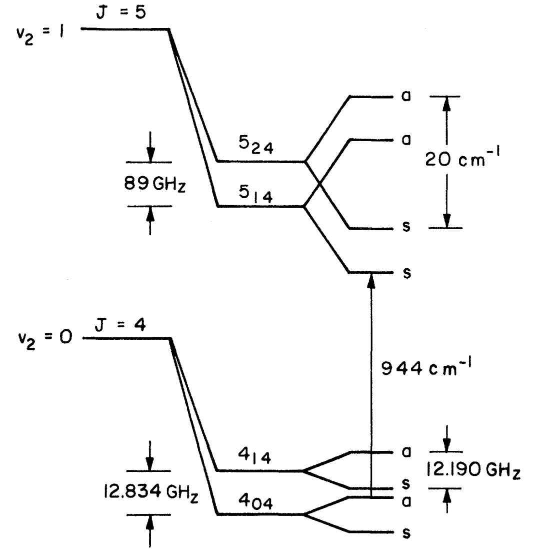

FIG. 3. Schematic energy level diagram for $N^{14}H_2D$ showing the transition observed (not to scale). Note the disparity of the inversion splitting in ground and excited states, which yields at the operating fields a weak second order and a large linear Stark effect in the excited and ground levels, respectively.

the lower state is $J=4$. Since the $\Delta M=0$ spectrum yields the same number of Doppler-broadened lines located at the same positions as the $\Delta M=\pm1$ spectrum (Fig. 1), the excited state cannot be $J=3$, and finally, the relative line intensities in both spectra favor a $J=4\rightarrow5$ transition.

This assignment is incompatible with the known ν_2 transitions for NH_3[18, 19] or ND_3.[20] The possibility of the lower state being a thermally excited vibrational level (hot band) can be rejected because the line intensity remains unchanged upon heating the Stark cell to 150°C. However, enrichment[21] of the deuterium content in NH_3 increases the signal strength by about two orders of magnitude, thus providing definitive evidence that a deuterated ammonia species is involved.

In Fig. 3, it will be seen that the NH_2D energy-level diagram is that of an asymmetric rotor with inversion doubling. The ground-state splittings are known accurately from microwave spectroscopy,[22] while the excited state is based on rigid-rotor energies[23] and a rough experimental value of the inversion splitting from earlier infrared data.[20] As a further test of assignment, one of the two NH_2D band origins can be obtained simply from the transition frequency and rigid-rotor energies, calculable from the molecular structure.[22] This gives a value of 869 cm^{-1} which compares favorably with Migeotte and Barker's NH_2D value of 874 cm^{-1} $(0_a \rightarrow 1_s)$,[20] whereas the band origin originating in the other inversion level $(0_s \rightarrow 1_a)$ and for the other isotopic species are much too distant to be considered. The possibility of $N^{15}H_2D$ can be excluded since the N^{15} abundance is 0.365% and the content in ordinary NH_3 would give a much weaker signal than observed. (Ultimately, the hyperfine splitting will also test this point.)

The Stark effect in the lower level results from the mixing of the two rotation-inversion levels, $4_{04}(a)$ and $4_{14}(s)$, which are separated by only 644 MHz.[22] At the present field strengths, these levels yield a first order Stark shift

$$\Delta\nu\ (\mathrm{MHz}) = \pm 42.6\mathcal{E}|M|,$$

where $\mathcal{E}$ is in esu/cm and the minus sign applies specifically to the $4_{04}(a)$ state. This frequency scale, unlike that for other pairs of $J=4$ rotational states, gives an observed Doppler linewidth of 84 MHz at full width and is in excellent agreement with the expected value of 82 MHz. The perturbing levels in the ground state are thus confirmed as well as the frequency scale.

The only possible allowed transitions become $4_{04}(a)\rightarrow5_{14}(s)$ and $4_{14}(s)\rightarrow5_{24}(a)$. However, because of the large inversion splitting in the excited state, only the former transition can be resonant with the CO_2 line as indicated in the band origin calculation. Thus, the sign of the ground-level Stark shift is established as being negative (transition frequency increases with field), and in zero field, the $4_{04}(a)\rightarrow5_{14}(s)$ transition will lie at 944.128 cm^{-1} or 1900 ± 25 MHz to the low-frequency side of the $P(20)$ CO_2 line. Here, we have utilized the exact expression for the Stark effect of two nearby levels.[23] There appears to be little doubt that this is the same line reported by Garing, Nielsen, and Rao[18] at 944.14 cm^{-1}, which was instead assigned as a hot band of NH_3, and which further verifies the sign of the Stark shift. As will be shown, the sign of the excited state Stark shift also supports this assignment.

In Fig. 2, the Lamb-dip spectrum is shown for the selection rules $\Delta M=0$ and $\Delta M=\pm1$ where each spectrum exhibits a single narrow line on a Doppler background. In this instance, the full width at half-maximum is about 2.9 MHz and is due partly to gas collisional processes (ammonia pressure 80 μ) and partly to a nonuniform electric field distribution. This derivative line shape exhibits 180° phase reversal relative to the Doppler curve because of the heightened transparency at the Doppler peak. We note that this behavior is described by the gain or attenuation expression for the Lamb dip[1,2] but with a normal population distribution. For this strong-field case, the principal transitions are $M_J = \pm 3 \to \pm 3$ and $M_J = \pm 3 \to \pm 4$. Note that the $M_J = \pm 3 \to \pm 2$ transition will be exceedingly weak since the Lamb-dip power signal varies as the fourth power of the transition matrix element. With additional resolution, each Lamb dip would split into two lines separated by about 1 MHz and with intensity ratio 4/1. This corresponds to the expected N^{14} hyperfine interval of 0.25 MHz in the excited state and 1.34-MHz splitting of the ground state. It has not been possible to resolve this hfs as yet.

However, it has been possible to measure a small excited-state Stark splitting by comparing the Lamb-dip transition frequency in two transitions which share a common lower level. This shift is indicated in Fig. 2 and gives the result that the $M_J = \pm 4$ level is 1.56 ± 0.05 MHz below the $M_J = \pm 3$ level, i.e., the upper-state M_J levels are inverted, as in the ground state. (For this purpose, the laser frequency stability was sufficient that essentially no drift could be detected over the period of the measurement.) The shift agrees quantitatively with our assignment, both in sign and magnitude, that the excited state is $5_{14}(a)$ and mixes with the $5_{24}(s)$ level. The observed second-order Stark shift for the $5_{14}(a)$ state is

$$\Delta\nu\ (\text{kHz}) = -1.03\mathcal{E}^2 M^2,$$

with $\mathcal{E}$ in esu/cm. Additional accuracy in this measurement would allow a precision determination of the excited-state dipole moment once the excited-state inversion splitting is accurately known. Our result serves to illustrate that narrow molecular Stark (or hfs) splittings are now accessible in the infrared spectral region even though the Doppler width may be two orders of magnitude larger.

At present, it has not been possible to reduce the Lamb-dip linewidth below 1.6 MHz by further reduction of either the gas pressure (below 30 μ) or the light intensity. The molecular transit time across the Stark-plate gap contributes perhaps ~300 kHz but the dominant effect is apparently due to a nonuniform field distribution, which might include possible fringe effects. This might also cause some asymmetry in the line shape.

Measurements of the amount of absorption of $N^{14}H_2D$ in natural ammonia, where the isotopic composition is accurately known, yield a preliminary value for the electric dipole matrix element

$$\mu_{12} = 0.33 \pm 0.10\ \text{D}$$

for the transition $(v_2, J_\tau, M) = (0, 4_{04}, \pm 4) \to (1, 5_{14}, \pm 5)$. [See Eq. (57) of Feld and Javan, Ref. 3.] (A rotational partition function of 289 has been utilized here.) This corresponds to an absorption coefficient at the Doppler peak of $\gamma = 2.4 \times 10^{-5}\ \text{cm}^{-1}$ in natural ammonia at a total pressure of 36 μ. By combining the relative spontaneous-emission rates from the upper level (see Ref. 23 for relative line strengths), the above result leads to a 0.60-msec radiative lifetime for the $5_{14}(s)$ state in zero field. It is to be noted that these matrix elements are easily obtained here and can be made considerably more accurate (by reducing the uncertainty in the pressure), in contrast to previous infrared studies where this resolution is lacking. This particularly large matrix element compares to a similarly large ground-state dipole moment of about 1.468 D.[24]

We wish to point out an additional nonlinear effect[2] which can arise in studies of this type in cases where two closely spaced levels are simultaneously coupled to a third common level by optical transitions. Each transition will give rise to a Lamb dip but in addition, a third dip midway between the other two will also occur with an intensity equal to the geometric mean of the two Lamb-dip intensities. This effect was predicted some time ago; see Eq. (33c) of Ref. 2 and the accompanying discussion. Consider the standing-wave frequency to lie exactly midway between the two transition frequencies. When a molecule with appropriate velocity Doppler-shifts one of the traveling waves into resonance with one of the transitions, the other traveling wave will be simultaneously Doppler shifted in the opposite direction and into resonance with the second transition. This effect may be responsible for some of the resonances observed in the I_2 spectrum, obtained with a 6328-Å He-Ne laser, and interpreted as Lamb dips of various hyperfine transitions.[6] In the present experiment, the three-level dip is not observed because the second transition is too weak.

In the future, it will be desirable to extend many of the points touched on here, as this appears to be a generally useful spectroscopic technique applicable to a wide variety of molecular systems. Thus, in addition to reducing the inhomogeneous line broadening, we plan to examine the pressure-broadening problem, and the hfs, as well as obtain accurate values for the excited-state inversion splitting and the dipole moments for ground and excited states.

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[11] Unlike the Lamb dip, other optical saturation effects such as "level or mode crossing" are more restrictive in their use as a general spectroscopic technique. This is because two resonance conditions must simultaneously be met: (1) The absorbing molecule (or atom) must be coincident with the laser frequency to within its Doppler width and (2) the crossing condition must be satisfied to within the natural width. These resonance conditions are easily satisfied in laser systems where these effects have been demonstrated, but in the more general case where the source and absorber are different systems, these conditions will usually be incompatible with one another. On the other hand, beyond the standing-wave condition, the Lamb dip requires only that (1) be realized.

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[24] This is actually the dipole moment for NH_3 (see Townes and Schawlow, Ref. 23) in its ground state and should closely approximate that for NH_2D as well.