PHYSICAL REVIEW LETTERS

VOLUME 25 | 14 DECEMBER 1970 | NUMBER 24

Precision Determination of CH_3F Dipole Moment by Nonlinear Infrared Spectroscopy

Richard G. Brewer
IBM Research Laboratory, San Jose, California 95114
(Received 26 October 1970)

An optical double-resonance effect, requiring two optical frequencies, is demonstrated in the infrared for the molecule CH_3F, and provides high-precision dipole-moment values for both the ground and an excited vibrational state. The method is a particularly convenient and precise means for probing optically excited molecular levels.

A nonlinear spectroscopic technique is described in this Letter which is capable of a high-precision determination of narrow Stark, Zeeman, or hyperfine splittings in molecular infrared transitions. For the molecule CH_3F, we have achieved a spectral resolution of $\sim 10^8$ at an optical wavelength of 9.55 μm. This result corresponds to an observed linewidth of 100 kHz, and is about 300 times narrower than the Doppler width, the limiting linewidth in conventional molecular infrared spectroscopy. At this resolution, the infrared Stark spectrum of CH_3F yields dipole moments precise to about one part in 2000 and as a function of the rotational and vibrational state. We note that previous dipole-moment measurements have not been derived from infrared spectroscopy because of insufficient resolution, nor have these excited states been generally accessible by microwave or molecular-beam resonance spectroscopy. Furthermore, other recent optical saturation methods[1,2] have not yielded precise molecular dipole moments as yet.

The optical resonances to be described have also been observed in CH_3F and other molecules in this laboratory using a multimode 3.39-μm He-Ne laser, permitting other vibrational excitational excitations such as the C-H stretch mode to be examined; this will be reported subsequently.[3]

The nonlinear optical effect utilized here, which may be called "optical-optical double resonance," was demonstrated some time ago in Xe by Schlossberg and Javan[4] using a Zeeman-tuned Xe laser. A theoretical review of this subject and other references are presented elsewhere.[5] As in all double-resonance effects, two transitions sharing a common level are excited simultaneously by two radiation fields. For the case of two overlapping Doppler-broadened transitions, a molecule will only interact strongly and nonlinearly with both radiation fields when it Doppler shifts each field equally, or $\Omega_1-\omega_1=\Omega_2-\omega_2$.[6] Here the radiation frequencies are Ω_1 and Ω_2 and the corresponding molecular-level intervals are ω_1 and ω_2. Thus, if the molecular-level splitting $\omega_1-\omega_2$ can be tuned by the Stark or Zeeman effect, a nonlinear absorption response will appear for the resonance condition $\Omega_1-\Omega_2=\omega_1-\omega_2$ as illustrated in Fig. 1. Since the linewidth will usually be limited by the interaction time with the radiation field, this nonlinear resonance may be orders of magnitude narrower than the Doppler width.

Our experimental arrangement consists of two CO_2 laser beams which are collinear and which propagate in the same direction through a precision Stark cell, containing the gas sample, before detection. The radiation is provided by two independent CO_2 lasers[7] with identical construc-

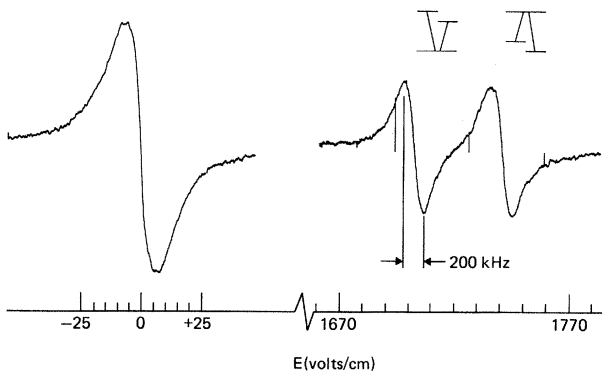

FIG. 1. Stark-tuned optical-optical double-resonance spectrum of the $^QQ(J=12, K=2)$ CH_3F line in the ν_3 band. The CH_3F pressure is 4 mTorr. Field markers shown on the high-field resonances occur in 33.2-V/cm intervals. Excitation is provided by two CO_2 lasers oscillating on the $P(20)$ line (9.6-μm band) and with a frequency difference of 41.67 MHz.

tion for frequency stability. Each operates cw with single-frequency output but without feedback stabilization, the power is about 1 W in each line, and oscillation on any one of 70 lines in the 9- and 10-μm bands is controlled by a rotatable grating at one end of the laser cavity. In this experiment, both lasers oscillate on the same line, the $P(20)$ of the 9-μm band, and their frequency difference is set within the range 0-50 MHz by piezoelectric tuning of the optical cavity lengths. Measurements of this beat frequency, which provide a frequency scale for the spectrum, indicate a 20- to 30-kHz acoustic jitter over a 1-sec interval; this, at present, limits the accuracy of the dipole measurement. Because the polarizations of these lasers are linear and parallel to one another but perpendicular to the Stark field, the selection rules $\Delta M = \pm 1$ apply.

The Stark cell is made of components with optical tolerances and includes two fused-quartz disks which are 4 in. diam $\times \frac{3}{4}$ in. thick, flat to $\pm 10^{-5}$ cm, and coated on the inner surfaces with vacuum-deposited chromium. Separating the flats are fused-quartz spacers whose thickness as determined by gage blocks is $0.602\,56 \pm 0.000\,01$ cm. Measurements of the Stark voltage are made with a digital voltmeter, checked against a standard, and accurate to 0.008 %.

The molecule CH_3F is particularly convenient in these initial studies as its ν_3 band at 9.5 μm (C-F stretch mode) has been analyzed[8] and one of its lines, the $^QQ(J,K) = {}^QQ(12, 2)$, coincides within its Doppler width of 66 MHz with the $P(20)$ CO_2 laser transition (001-020 band) at 1046.8543 cm^{-1}.[9,10] In addition, being a symmetric top, CH_3F exhibits a simple first-order Stark effect without hyperfine structure so that the nonlinear resonance condition becomes $\Omega_1 - \Omega_2 = 2\mu EK/J(J+1)\hbar$. This condition permits a determination of the permanent molecular dipole moment μ. It should be noted that the M states can combine in a superposition of appropriate three-level resonances which satisfy this condition.

An optical-optical double-resonance absorption spectrum for CH_3F is shown in Fig. 1. Here the Stark voltage is swept but the beat frequency of the two lasers is held fixed at 41.67 MHz. The lines are derivatives due to small-amplitude Stark modulation (1-V square wave at 10 kHz) and are observed with phase-sensitive detection. The first line to appear is the zero-field level-crossing signal,[2] which is the "zero beat" signal or degenerate case of optical-optical double resonance. The next two lines correspond to the resonance condition with finite level splitting. Since the dipole moments of ground and excited vibrational states are different, there are two such resonances. These lines, which are separated by only ~1 MHz, are clearly resolved as the linewidth is but 100-kHz half width at half-maximum. The cause of this width appears to be the molecular transit time through the laser beam's cross section and the second-order Stark effect. Furthermore, if the beat frequency is reduced, the appearance of these two lines on a voltage scale changes correspondingly, as expected.

The magnitude of the Stark tuning rate is, of course, a critical test of transition assignment. In the present instance, these nonlinear resonances confirm that the observed line is indeed $(v_3 = 0 \to 1, J = 12 \to 12, K = 2 \to 2)$ or $^QQ(12, 2)$, a parallel ν_3 transition. A search for other subbranch lines of $Q(12)$ with[10] different K was not successful even though the two lasers were scanned over an ~30-MHz range with a beat between them of 1 MHz.

From these results we derive the first measurement of the dipole moment for CH_3F in its excited vibrational state $v_3 = 1$. A summary of existing dipole-moment measurements for CH_3F is shown in Table I. The entries from this work are an average of eight independent determinations. Note that the high-precision microwave studies of the ground state[11-13] are in good agreement with the laser results and thus support this work. It now becomes evident that the second of the high-field resonances corresponds to the ground-state dipole moment whereas the first

Table I. Dipole moments of CH_3F.

v_3	J	K	CH_3F dipole moment (Debye)	Reference
0	1,2	0,1	1.8555 ± 0.0015	Larkin and Gordy, Ref. 11
0	1,2	0,1	1.8572 ± 0.0010	Steiner and Gordy, Ref. 12
0	0,1	0	1.8580 ± 0.0010	Muenter and Laurie, Ref. 13
0	12	2	1.8549 ± 0.0010	This work
1	12	2	1.9009 ± 0.0010	This work

high-field line is that of the excited state as indicated in the M level structures of Fig. 1. We can also conclude from these results that the variation of dipole moment with rotational quantum numbers J and K is a small effect. These measurements are of current theoretical interest in this laboratory and are to be compared with ab initio calculations of these quantities, especially the increase in dipole moment with vibrational excitation.

It should be emphasized here that the present technique offers at least two unique advantages beyond that of resolving the homogeneous width. First, it separates excited- and ground-state Stark or Zeeman splittings so that both can be observed in a single spectrum as in Fig. 1. Second, the spectrum contains a frequency scale, which is not true, for example, with the zero-field level-crossing line[2] or with some Lamb-dip spectra.[1]

Another property of these resonances is that the linewidth is determined by the average relaxation rate of the Stark split levels in (a) the excited state or (b) the ground state (but not both). Consequently, when the lines are pressure broadened, they could exhibit different widths, depending on the nature of the relaxation mechanisms in the two vibrational states. This aspect of the problem is now being examined in CH_3F.

The expert technical assistance of K. L. Foster and P. Hoff added greatly to the success of this study and is gratefully acknowledged. Conversations with C. Freed, A. Luntz, J. D. Swalen, P. Hoff, R. M. Macfarlane, and K. Eisenthal were instructive and are also appreciated.

[1]R. G. Brewer, M. J. Kelly, and A. Javan, Phys. Rev. Lett. 23, 559 (1969).

[2]A. C. Luntz, R. G. Brewer, K. L. Foster, and J. D. Swalen, Phys. Rev. Lett. 23, 951 (1969).

[3]A. C. Luntz, J. D. Swalen, and R. G. Brewer, to be published.

[4]H. R. Schlossberg and A. Javan, Phys. Rev. Lett. 17, 1242 (1966).

[5]M. S. Feld and A. Javan, Phys. Rev. 177, 540 (1969).

[6]Actually $(\Omega_1-\Omega_2)(1-v/c)=\omega_1-\omega_2$ but $v/c \sim 10^{-6}$ so that it can be dropped for the precision required here.

[7]C. Freed, IEEE J. Quantum Electron. 4, 404 (1968), and 3, 203 (1967); the design is similar to that described in this reference.

[8]W. L. Smith and I. M. Mills, J. Mol. Spectrosc. 11, 11 (1963).

[9]T. Y. Chang, C. H. Wang, and P. K. Cheo, Appl. Phys. Lett. 15, 157 (1969).

[10]T. Y. Chang and T. J. Bridges, Opt. Commun. 1, 423 (1970).

[11]D. M. Larkin and W. Gordy, J. Chem. Phys. 38, 2329 (1963).

[12]P. A. Steiner and W. Gordy, J. Mol. Spectrosc. 21, 291 (1966).

[13]J. S. Muenter and V. W. Laurie, unpublished; however, see J. S. Muenter, J. Chem. Phys. 48, 4544 (1968).