Stark spectroscopy using tunable far-infrared radiation

L. R. Zink, D. A. Jennings, and K. M. Evenson

Time and Frequency Division, National Bureau of Standards, Boulder, Colorado 80303

A. Sasso and M. Inguscio

Dipartimento di Fisica N.S.M.F.A., University of Naples, Naples, Italy

We report on an experimental demonstration of molecular Stark spectroscopy based on the use of tunable far-infrared radiation at 0.91 THz. The radiation was generated by the nonlinear mixing of the radiation from two CO_2 lasers in a point-contact metal–insulator–metal diode. The technique is used to make the first reported measurement of the permanent dipole moment of $^{13}CH_3OH$; $\mu_a = 0.883(25)$ D.

INTRODUCTION

The generation of tunable far-infrared (TuFIR) radiation from the nonlinear mixing of the radiation of two CO_2 lasers in a metal–insulator–metal (MIM) diode[1] has been demonstrated to be an excellent source of coherent radiation for spectroscopy.[2] As summarized in Ref. 3, the technique has been used to make highly accurate measurements of FIR frequencies of molecules that serve as frequency- and wavelength-calibration standards and as highly accurate frequencies for astronomical searches. It is also used to study line-broadening and line-shape parameters needed for atmospheric measurement analysis. Furthermore, the technique has been extended to make measurements at sub-Doppler resolution,[4] to measure directly the frequency of lasing gases,[5] and to measure the K doubling frequencies in $^{13}CH_3OH$.[6]

In the present work, Stark spectra of $^{13}CH_3OH$ were obtained by using the National Bureau of Standards TuFIR spectrometer. In this case the source is broadly tunable, and Stark or Zeeman effects are not necessary to bring the sample transitions into coincidence, as in the case of laser magnetic resonance.[7] Nevertheless, the application of external fields, which removes the degeneracy of the levels, is in general a valuable help in the assignment of molecular transitions. This is especially true for small polyatomic molecules in which internal rotational degrees of freedom or slight asymmetries can cause crowded and complex spectra. In these cases, the precise frequency determination of a single transition is not sufficient by itself for an unambiguous assignment of the transition.

Our results demonstrate that TuFIR spectroscopy can be advantageously applied with the Stark effect. The sensitivity is sufficient for the resolution of the Stark components with good signal-to-noise ratio, and the high accuracy of the knowledge of the frequency produces a high accuracy for the determination of permanent dipole moments.

EXPERIMENTAL APPARATUS

The complete TuFIR spectrometer is described elsewhere.[1,3] Here we summarize the general features. The arrangement for these experiments employed two stabilized fixed-frequency CO_2 lasers and a tunable waveguide laser. The two fixed-frequency lasers are locked to saturated fluorescence signals that use a 2.5-MHz amplitude modulation at a frequency of 1 kHz to stabilize the laser frequency at the sub-Doppler fluorescence minima. The waveguide laser and one of the fixed-frequency lasers are combined with a beam splitter and focused on a MIM diode. The second fixed-frequency laser is offset locked to the waveguide laser to provide a servocontrolled sweep of the waveguide laser's frequency over the desired frequency range. The waveguide CO_2 laser provides a tunability of about ±120 MHz. Optoacoustic modulators operating at 90 MHz isolate the lasers from the MIM diode and provide an additional 180 MHz of tunability. By selecting different pairs of CO_2 laser lines, we can cover about 80% of the spectrum between 0.3 and 6 THz. The FIR frequency is known with an accuracy of about 35 kHz and has a spectral purity of about 10 kHz. After making a single pass through an absorption cell, the radiation is detected with a liquid-helium-cooled germanium bolometer. The FIR radiation is frequency modulated (as a result of the stabilized-CO_2-laser modulation), and phase-sensitive demodulation of the bolometer signals approximates the first derivative of the cell absorption.

For carrying out Stark spectroscopy, we constructed a simple rectangular absorption cell. The two parallel metal sides, serving as Stark electrodes, were made of polished stainless steel, while the dielectric sides were made of acrylic plastic. The cell is 200.4 mm long, 69.5 mm wide, and 5.8 mm high (the electrodes are at this 5.8-mm spacing). As we discuss below, the distance between the electrodes was calibrated using a reference molecular transition. The design of the cell permitted the application of electric fields up to several kilovolts per centimeter, without breakdown, and spatial inhomogeneities did not seriously affect the observed line shapes.

In order to provide nearly linearly polarized radiation to improve the sensitivity of the spectrometer, we explored different optical geometries for the coupling of the radiations to and from the diode. A section of an off-axis parabola collimates the FIR radiation and reflects the beam down the absorption cell. The intensity of the FIR radiation is
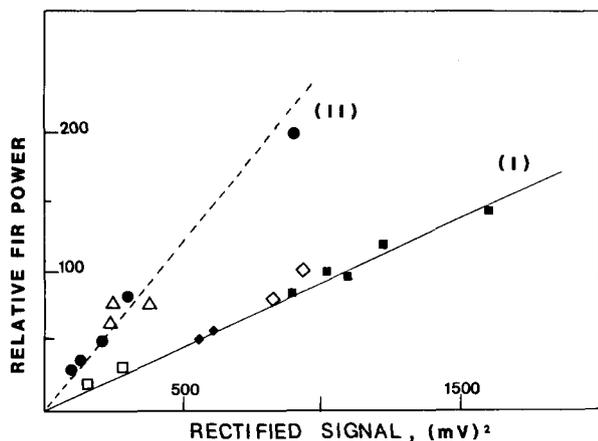
Fig. 1. Dependence of the detected FIR (1.2-THz) signal on the rectified signals from the CO_2 lasers. As explained in the text, different optical geometries were tested in I and II. The improved efficiency and near-linear-polarization is obtained by adding a corner reflector mirror, as is shown in II.

proportional to the product of the rectified voltages (on the MIM diode) from each of the two CO_2 lasers. The CO_2 laser beams were superimposed and focused on the MIM diode by means of a short-focal-length lens. This is shown in line I of Fig. 1. The measurements were performed at a FIR frequency of 1.2 THz, and different symbols in the figure correspond to different diode contacts. The diode impedance was adjusted to maximize the FIR power, and the dc resistance was approximately 110 Ω for most contacts. For the measurements in line II of Fig. 1, we added a corner reflector to be used as roof mirror on the antenna. With this configuration, originally introduced to improve FIR detection,[8] the efficiency was higher, the radiation was linearly polarized, and the beam was much better collimated.

EXPERIMENTAL RESULTS

In a first experiment we performed measurements on a CH_3OH transition already known and assigned from Fouri-

er-transform spectroscopy,[9] namely, the E_2 transition (n, J, K):(0, 3, 3) $\leftarrow$ (0, 2, 2) at 30.425 cm^{-1}. The frequency determined in this experiment is 912,108.568(50) MHz, or 30.424 667(2) cm^{-1}. By applying a static electric field orthogonal to the FIR polarization, we completely resolved two symmetric groups of five components each, corresponding to $\Delta M = \pm 1$ selection rules. A typical recording with 300 V of electricity applied to the electrodes is shown in Fig. 2. For this measurement we averaged two sweeps, one of increasing and the other of decreasing frequency.

By using the standard formulas for a first-order Stark effect on a slightly asymmetric rotor[10] and the available precise values of the parallel component of the dipole moment,[11,12] $\mu_a(^{12}CH_3OH)$ = 0.8956 D, we obtained d = 5.787(30) mm for the electrodes spacing in our cell. Here the uncertainty was due to the uncertainty of the voltage measurement.

We then performed measurements on a previously measured transition[13] of $^{13}CH_3OH$ in which the absorption was brought into resonance with a fixed-frequency laser by means of Stark tuning. The zero-field transition frequency was extrapolated to be 81.657 334(50) cm^{-1}, with the assignment E_1 symmetry, (n, J, K):(1, 4, 2) $\leftarrow$ (1, 3, 1). We directly observed the transition at zero electric field, as shown in curve a of Fig. 3. The frequency is 2,448, 024.644(35) MHz, or 81.657 312 7 (15) cm^{-1}, in good agreement with the previous measurement of lower accuracy.

The accuracy permitted the investigation of a small pressure shift, shown in Fig. 4. The solid line represents a shift of +10.7(2.6) kHz/Pa, in agreement with that expected for methyl alcohol[5,14] from the predictions of the Anderson model.[15]

As discussed in Ref. 13, the knowledge of the FIR absorption spectrum of $^{13}CH_3OH$ is incomplete, and, using the molecular constants that are available,[16] we can compute several transitions with a frequency consistent with the observed one. However, the observed Stark pattern (curves b and c of Fig. 3) confirms the assignment unambiguously. The Stark shift for this transition is, to first order, given by
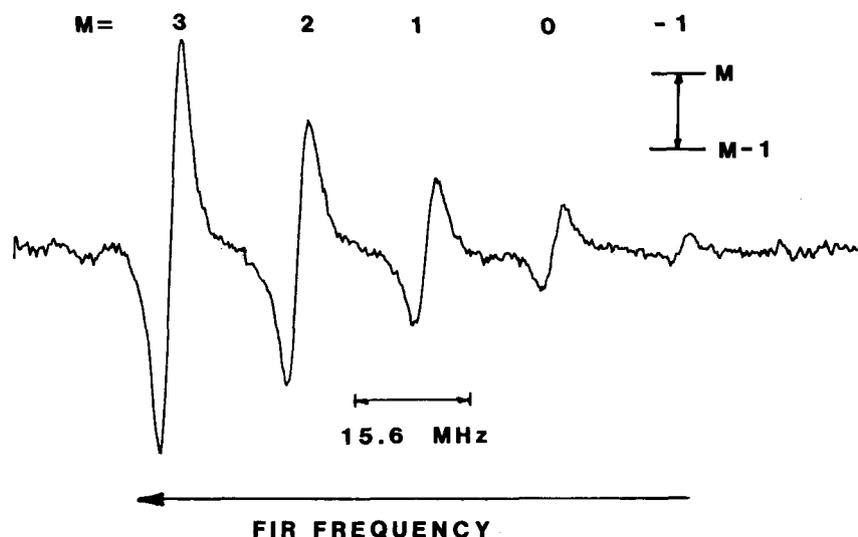

Fig. 2. Stark effect on the CH_3OH transition E_2, (n, J, K):(0, 3, 3)–(0, 2, 2). (ν_0 = 912,108.568(50) MHz at zero electric field.) The gas pressure during the measurement was 16 Pa. The applied voltage was 300 V, and the observed pattern is used for the calibration of the distance between electrodes. Only the $\Delta M = +1$ components are shown.
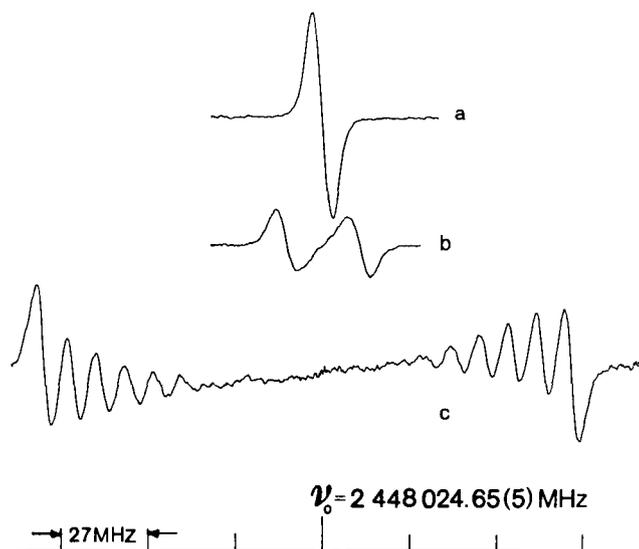
$$\mathcal{V}_0 = 2\ 448\ 024.65(5)\ \text{MHz}$$

Fig. 3. Measurements on the $^{13}CH_3OH$ transition E_1 (n, J, K):(1, 4, 2)–(1, 3, 1). a, The frequency at zero field is measured to be 2,448,024.650(50). A static electric field orthogonal to the FIR polarization is applied: in b, 211 V/cm, and in c, 1230 V/cm. The gas pressure during these measuresments was 2.5 Pa.
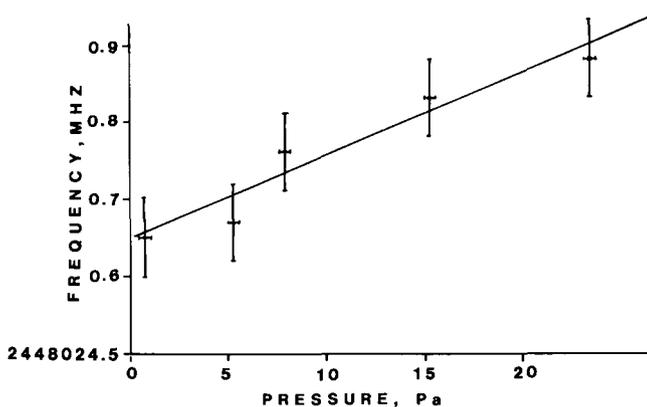

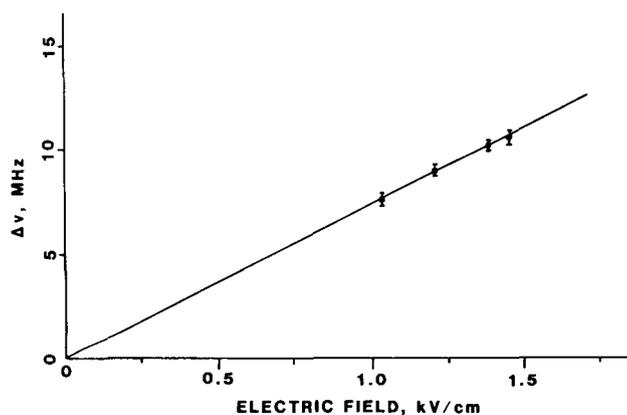Fig. 4. Frequency shift on the same transition as in Fig. 3 at zero electric field.

Fig. 5. Frequency separation of the resolved Stark components of the transition of Fig. 3 versus the applied electric field. From the slope, a value of 0.883(25) D is obtained for the parallel component of the permanent dipole moment of $^{13}CH_3OH$.

$$V(M, \Delta M), = [\mu_a E/J(J + 1)] \times [(2K - J - 1)m/(J + 1)$$

$$\pm (K - 1) \Delta M].$$

In curve b of Fig. 3 the electric field is sufficient to resolve the doublet originating from $\Delta M = \pm 1$ selection rules. In Fig. 3 the higher electric-field value permits the resolution of the single M components. The total frequency scan in curve c of Fig. 3, about 200 MHz, is a direct display of the continuous tunability of the FIR radiation generated by two CO_2 lasers.

We measured the frequency separation of the components at different field values, calibrated as previously described. The averages of the frequency separations of the components at all these fields are plotted in Fig. 5. We have used each single separation independently and obtained the value $\mu_a(^{13}CH_3OH) = 0.883(25)$ D for the parallel component of the dipole moment of $^{13}CH_3OH$. Within the accuracy of the present measurements, this value is the same as that of normal methyl alcohol.

DISCUSSION

We have demonstrated that TuFIR Stark spectroscopy can be performed with good signal-to-noise ratios. The sensitivity is about the same as that of the conventional TuFIR spectrometer, with a minimum-detectable absorption of about 0.01% (1-sec time constant).[17] This sensitivity is still about 100 times lower than that for optimized intracavity spectrometers[3,7] but, in any case, significantly higher than for spectrometers using room-temperature detectors. For example, in a direct comparison, we were able to measure the same[13]CH_3OH transition at a gas pressure 1 order of magnitude less than that used in a recent intracavity optically pumped experiment.[13] At the higher pressures, we observed a deviation of the relative intensities of resolved components from the theoretical values. These deviations are suggestive of possible mixing of M sublevels through collisions and could complicate line-shift measurements at high pressures.

Futhermore, in our apparatus the absorption cell is not only external but is also compact. This means that there are no constraints or limitations to the use of cells especially designed for very-high-voltage breakdown and high-field accuracy and homogeneity. On the contrary, laser geometries always impose constraints to the operation with intracavity devices.

The accuracy of our measurements is essentially determined by the electric-field calibration. The limitations are not intrinsic in the apparatus but instead come from the quick and simple design that we have adopted for the absorption cell in this experiment. At the present level of accuracy, no contribution to the uncertainty comes from uncertainty of the frequency of the CO_2 lasers. In fact, the absolute accuracy of 1.3 parts in 10^7 at 3 THz is about 100 times better than for state-of-the-art interferometers.

We believe that the present results demonstrate the possibility of investigating the Stark effect over a broad frequency range. Previously, fixed-frequency lasers could be used to study only a small region of the spectrum. The Stark line shape can be investigated with high accuracy.

Stark and Zeeman Spectroscopy

ACKNOWLEDGMENTS

REFERENCES

1. K. M. Evenson, D. A. Jennings, and F. R. Petersen, Appl. Phys. Lett. **44,** 576 (1984).
2. K. M. Evenson, D. A. Jennings, K. R. Leopold, and L. R. Zink, in *Laser Spectroscopy VII*, T. W. Hänsch and Y. R. Shen, eds., Vol. 49 of Springer Series in Optical Sciences (Springer-Verlag, Berlin, 1985), p. 366.
3. K. M. Evenson, D. A. Jennings, L. R. Zink, and K. R. Leopold, in *Digest of the 11th International Conference on IR & MM Waves*, G. Moruzzi, ed. (ETS Editrice, Pisa, Italy, 1986), p. 267.
4. M. Inguscio, L. R. Zink, K. M. Evenson, and D. A. Jennings, in *Digest of the 11th International Conference on IR & MM Waves*, G. Moruzzi, ed. (ETS Editrice, Pisa, Italy, 1986), p. 289.
5. M. Inguscio, L. R. Zink, D. A. Jennings, and K. M. Evenson, in *Digest of the 11th International Conference on IR & MM Waves*, G. Moruzzi, ed. (ETS Editrice, Pisa, Italy, 1986), p. 98.
6. L. R. Zink, K. M. Evenson, D. A. Jennings, G. Moruzzi, and M. Inguscio, in *Digest of the 11th International Conference on IR & MM Waves*, G. Moruzzi, ed. (ETS Editrice, Pisa, Italy, 1986), p. 392.
7. K. M. Evenson, Faraday Discuss. Chem. Soc. **71,** 7 (1981).
8. E. Sauter and G. V. Schultz, IEEE Trans. Microwave Theory Tech. **MTT-25,** 468 (1977).
9. G. Moruzzi, F. Strumia, C. Conetti, B. Carli, F. Mencaraglia, M. Carlotti, G. Di Lonardo, and A. Trombetti, J. Mol. Spectrosc. **105,** 24 (1984).
10. F. Strumia and M. Inguscio, *Infrared and Millimeter Waves* (Academic, New York, 1983), Vol. 5, Chap. 3, p. 129.
11. T. Amano, J. Mol. Spectrosc. **88,** 194 (1981).
12. K. V. L. N. Sastry, R. M. Lees, and J. van der Linde, J. Mol. Spectrosc. **88,** 228 (1981).
13. N. Ioli, A. Moretti, P. Roselli, and F. Strumia, J. Opt. Soc. Am. B. **3,** 867 (1986).
14. M. Inguscio and K. M. Evenson, Opt. Lett. **9,** 443 (1984).
15. G. Buffa, G. Moruzzi, and G. Tarrini, in *Digest of the 11th International Conference on IR & MM Waves*, G. Moruzzi, ed. (ETS Editrice, Pisa, Italy, 1986), p. 388.
16. J. C. Petersen and J. O. Henningsen, in *Review of Infrared and Millimeter Waves*, K. J. Button, M. Inguscio, and F. Strumia, eds. (Plenum, New York, 1984), p. 151.
17. L. R. Zink, Ph.D. dissertation (University of Colorado, Boulder, Colo., 1986).