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Frequency Measurement of the $K = 6$ Asymmetry Splittings in CH_3OH[1]

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Tunable far-infrared spectroscopy was applied to the study of small asymmetry doublings in the ground vibrational, ground torsional state of CH_3OH. For the first time splittings of $K = 6$ states were measured. The splitting constant was found to be $S(6) = 9(1) \times 10^{-19}$ MHz, corresponding to a splitting of 360(35) KHz for $J = 29$ and 240(25) kHz for $J = 28$.

INTRODUCTION

Methanol is one of the simplest asymmetric molecules displaying internal torsional rotation. The understanding of its spectrum has thus been a challenge to molecular quantum mechanics and has resulted in the formulation of theoretical treatments of steadily increasing sophistication during the last 40 years. A very clear and straightforward presentation of the methanol Hamiltonian is that given by Kwan and Dennison (*1*). At present the general features of the spectrum are quite well understood. However, the quantitative agreement between computed spectra and experimental measurements is good only in the vibrational (CO-stretch) ground state and for transitions involving low angular moments only ($J < \approx 10$). The agreement is much less satisfactory when the levels involved in the transitions are affected by high centrifugal distortions or by Fermi interactions, even if small. Fermi interactions are often observed between low torsional states of the CO-stretch fundamental and high torsional states of the CO-stretch ground state. There is, thus, still a need for experimental information. The most widely used techniques fall into roughly two categories: (i) Fourier transform spectroscopy (FTS) (*2*), in which a single experiment provides the frequencies of several thousands of transitions, with a resolution of the order of 40 MHz and an accuracy of the order of 5 MHz for the center of unblended lines (*3*) and (ii) coherent methods, such as microwave or laser spectroscopy. Tunable far infrared (TuFIR) (*4*) in the present work uses coherent radiation synthesized from laser radiation. The drawback

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of this method is that very small spectral intervals, each tuning range containing a maximum of 4 ~ 5 nearby lines, are investigated in single measurements.

A systematic investigation of the methanol spectrum requires a combination of both techniques. In fact, FTS is best suited to follow patterns of unblended lines all over the spectrum. A very large amount of information, relative to a large number of lines, is provided by a single measurement. The information about the molecular Hamiltonian is then extracted from the experimental data, and the poorer accuracy for the individual line positions is compensated by treating many lines simultaneously.

On the other hand, higher resolution methods, like TuFIR, are essential for the investigation of small spectral regions where the lines are so dense that overlapping occurs in FTS. Disregarding casual coincidences, which are relatively common in the methanol spectrum, this is the case for the origins of many Q branches and for practically all of the $\Delta J = 0$ bands. Another very interesting case is the measurement of the spacing of very narrow line doublets which correspond to small asymmetry splittings occurring at high K values. This is the subject of the present work.

THE ASYMMETRY SPLITTING OF CH_3OH

Because of the threefold torsional potential, the energy levels of methanol can be classified into the three symmetry species A, E_1, and E_2. The selection rules are that transitions can occur only between levels belonging to the same symmetry. Because of the asymmetry, produced by the unbalanced OH group, K is not a rigorous quantum number, and levels that belong to the same symmetry species and have the same J but different K are mixed (the asymmetry Hamiltonian has matrix elements between $|J, K\rangle$ and $|J, K \pm 1\rangle$, $|J, K \pm 2\rangle$). This results in a small shift of all the levels, whichever symmetry species they belong to. For A-type symmetry, where $+K$ and $-K$ would be degenerate in the absence of asymmetry, an asymmetry doubling, similar to the case of the rigid asymmetric top, also appears.

The experimental values of the asymmetry splittings are described very well by the formula

$$\Delta E = \frac{(J+K)!}{(J-K)!}[S(K) + J(J+1)T(K)], \tag{1}$$

where the S and T coefficients decrease dramatically in absolute value with increasing K (see, for instance, Ref. (*2*)). T is a correction coefficient which is much smaller than S, usually by a factor of 10^4, and is required for large splittings at high J only.

Because of the small energy difference between the partners of an asymmetry doublet, the observation of a transition between the two members of the asymmetry doublet is extremely difficult. Thus, most asymmetry splittings have been measured as differences between two members of line doublets. At low K the asymmetry splittings are observable for low J, allowing microwave measurements with their inherent high precision. At higher K, J must be high to observe the splittings because of the smallness of S and T. As a consequence, the line doublets tend to fall in the far infrared rather than in the microwave region. Since wavelength measurements are easier to perform than frequency measurements in the far infrared, the data on higher K splittings are usually affected by the lower accuracy of wavelength measurements. Often wavelength measurements do not even allow the resolution of the doublet.

Lees and Baker (*5*) were able to apply frequency measurement techniques to the asymmetry splittings for K values up to 5 in the ground vibrational state. They multiplied the frequency of a klystron using a Gordy-type multiplier, and detected using a phosphorus-bombarded, silicon-multiplier crystal. More recently, Sastry *et al.* (*6*) have measured CH_3OH frequencies up to 400 GHz with an accuracy of the order of 50 KHz, obtaining submillimeter radiation from a harmonic multiplier driven by a 50-GHz klystron. However, they could find no evidence for asymmetry splittings for $K = 6$ or 7. In fact, we shall see later that the splittings of the $K = 6$ levels become observable, with a 50-KHz resolution, only for transitions above about 2.5 THz, since high values of J are needed.

A technique for the direct measurement of the splittings inside the cavity of a CH_3OH laser has been introduced in Pisa (*7*). This technique exploits the nonequilibrium distribution caused by the presence of the laser cycle by means of a triple (IR–FIR–RF) resonance. Splittings for $K = 4$ have thus been directly measured both in the ground and in the first excited, CO-stretch state (*8*). The limit to this technique results from the need for coincidence of a transition of the investigated level with a pump-laser frequency (in order to break thermal equilibrium).

A technique of wider applicability is tunable far-infrared spectroscopy (*4*), used in the present work. The application of TuFIR to the investigation of asymmetry splittings offers two advantages: the elimination of the requirement for an optical pumping cycle and the higher precision of frequency measurements.

EXPERIMENTAL DETAILS

The TuFIR technique has been described in previous works (*4, 9, 10*). Here we shall confine ourselves to a brief description of the experimental apparatus used for the present work. Tunable cw–FIR radiation is generated by nonlinear mixing of radiation from two CO_2 lasers in a metal–insulator–metal (MIM) diode. The resultant difference frequency radiation is tuned by varying the output of one of the lasers over its pressure-broadened gain profile. The fixed frequency CO_2 laser is frequency locked to its saturated fluorescence signal in low-pressure CO_2. The tunable laser is frequency offset locked to a third, fluorescence-stabilized, CO_2 laser. The CO_2 difference frequency has an absolute uncertainty of 35 KHz. The FIR radiation is frequency modulated at 1 KHz and the signal is detected at this frequency; therefore, a derivative absorption signal is observed.

The FIR radiation passes through a 50-cm-long absorption cell containing CH_3OH at a pressure of 6.67 Pa and is then detected by a gallium-doped germanium bolometer which is cooled to the λ point of ^{4}He. The NEP of the bolometer is about 10^{-12} W/$\sqrt{\text{Hz}}$. The bolometer signal is fed into a computer-controlled data acquisition system via a lock-in amplifier. The time constant of this amplifier was set to 125 msec. The main advantages of the TuFIR system compared to the FTS system are high resolution (see Fig. 1) and frequency accuracy.

We have used the TuFIR technique to measure line doublets connecting asymmetry levels with $K = 4$, 5, and 6 in the ground vibrational, ground torsional state of CH_3OH. The diagram of the investigated transitions is shown in Fig. 2. For each of the investigated doublets the corresponding CO_2 laser pair is indicated in Table I.

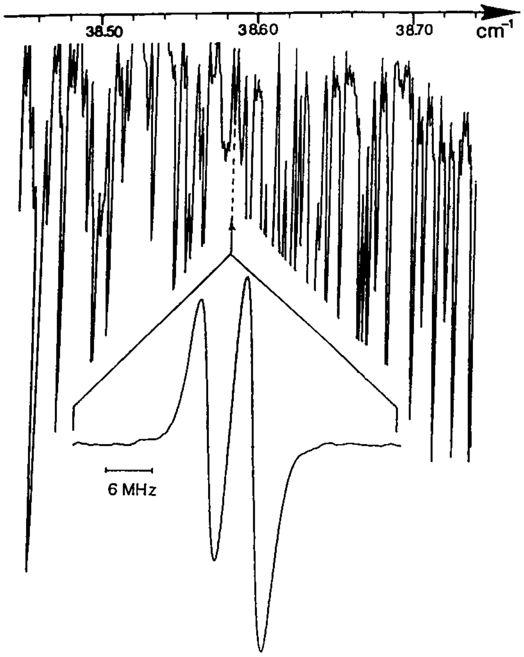

FIG. 1. Resolution of TuFIR vs a Fourier transform spectrum. The doublet corresponding to the (26, 6)–(26, 5) transition, which is collapsed into a single line in the FTS spectrum, is still clearly resolved.

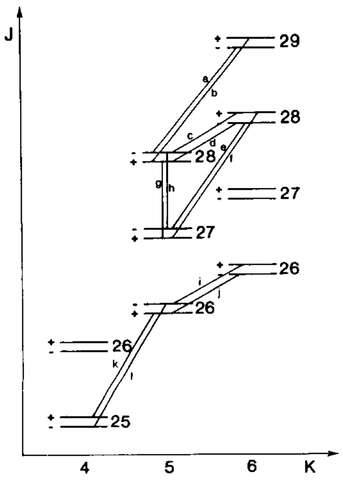

FIG. 2. The Asymmetry CH_3OH transitions investigated in the present work. The energies of the levels are not to scale. + and −, The asymmetry split sublevels following the notation used in Ref. (*5*).

TABLE I

CO_2 Laser Line Pairs Used for the Measurements

Assignment	lines	laser I	laser II
(29,6)-(28,5)	a,b	$^{12}C^{16}O_2$ 10R(24)	$^{13}C^{16}O_2$ 10P(24)
(28,6)-(28,5)	c,d	$^{12}C^{16}O_2$ 10P(8)	$^{13}C^{16}O_2$ 9P(28)
(28,6)-(27,5)	e,f	$^{12}C^{16}O_2$ 10R(16)	$^{13}C^{16}O_2$ 10P(28)
(28,5)-(27,5)	g,h	$^{12}C^{16}O_2$ 10P(32)	$^{13}C^{16}O_2$ 10P(30)
(26,6)-(26,5)	i,j	$^{12}C^{16}O_2$ 9P(32)	$^{12}C^{16}O_2$ 9P(24)
(26,5)-(25,4)	k,l	$^{12}C^{16}O_2$ 10R(24)	$^{13}C^{16}O_2$ 10P(20)

EXPERIMENTAL RESULTS

The experimental results are shown in Table II. The larger experimental errors for lines *g* and *h* are due to a partial overlapping of the dispersion-shaped signals corresponding to the doublet partners, as seen in Fig. 3. Due to the selection rules (the initial and final states of an electric dipole transition must have opposite parity, and the parity of an $A\pm$ state is $\pm(-1)^{J+n}$, where n = torsional quantum number), the separation of the *g*–*h* doublet equals the difference between the splittings of the level pairs (28, 5) and (27, 5). Since these two splittings are of the same order of magnitude,

TABLE II

Frequencies of the Investigated Lines Measured by TuFIR Spectroscopy Illustrated in Fig. 2

line	(J′,K′)-(J″,K″)	frequency, MHz
a	(29,6−)-(28,5−)	2551161.010 (50)
b	(29,6+)-(28,5+)	2551173.316 (50)
c	(28,6+)-(28,5−)	1154173.612 (50)
d	(28,6−)-(28,5+)	1154185.212 (50)
e	(28,6−)-(27,5−)	2504420.116 (50)
f	(28,6+)-(27,5+)	2504428.416 (50)
g	(28,5+)-(27,5+)	1350243.200 (300)
h	(28,5−)-(27,5−)	1350246.400 (300)
i	(26,6+)-(26,5−)	1156219.245 (50)
j	(26,6−)-(26,5+)	1156225.006 (50)
k	(26,5+)-(25,4+)	2444957.467 (50)
l	(26,5−)-(25,4−)	2445388.911 (50)

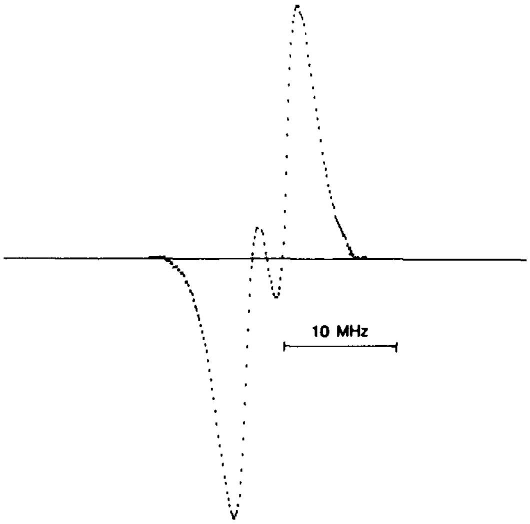

FIG. 3. The line doublet corresponding to the (28, 5)–(27, 5) transition. A partial overlapping of the dispersion-shaped curves decreases the accuracy of this measurement.

a somewhat unfavorable experimental condition exists. For this particular doublet a lock-in time constant of 400 msec and a modulation depth of about 1.5 MHz have been used.

The situation is definitely better for all the other measurements in Table II. As an example, Fig. 4 reports the signal for the (29, 6)–(28, 5) doublet. Here the central zero crossings of the dispersion-shaped curves are practically unaffected by overlap and can be determined with a relative uncertainty of less than 15 kHz. The error for the measurements of Table II can thus be obtained by the quadrature sum of this uncertainty with the CO_2 difference uncertainty ($\approx$35 kHz). This results in an overall uncertainty of less than 50 kHz.

This accuracy is high enough to provide the first experimental evidence for the asymmetry splittings of $K = 6$ states. In fact, the difference between the separation of the *a–b* doublet (12.306 MHz) and the separation of the *c–d* doublet (11.600 MHz)

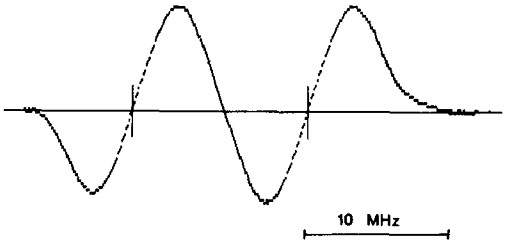

FIG. 4. The line doublet corresponding to the (29, 6)–(28, 5) transition. The central zero crossings of the dispersion-shaped curves, corresponding to the line centers, are indicated.

is larger than the propagated experimental error (70 kHz) and must be due to the splittings in the (29, 6) and (28, 6) levels. It is thus possible to get a first estimate of the S coefficient for $K = 6$, neglecting the small correction T, by solving the equation

$$12.306 - 11.600 = S(6)\left[\frac{(29+6)!}{(29-6)!} + \frac{(28+6)!}{(28-6)!}\right],$$

and we obtain $S(6) = 1.0(2) \times 10^{-18}$ MHz. A somewhat more precise estimate can be obtained by inserting the TuFIR measurements of Table II into the fit program of Ref. (*2*), together with the available microwave measurements for the splittings of $K = 5$ and with the available FTS data of Ref. (*11*). Thus, we take advantage of the information contained in all of the measurements of Table II simultaneously with the information contained in the microwave and FTS measurements. The result is

$$S(6) = 9(1) \times 10^{-19}\,\mathrm{MHz}.$$

By means of the same fit we have also obtained a value for the $K = 5$ splitting constant: $S(5) = -3.52(5) \times 10^{-14}$ MHz, which is in good agreement with, and should be somewhat more precise than, the value of Ref. (*7*). The experimental accuracy is also good enough to prove the consistency of the assignments by following transition loops; for instance, $h + c - e - \Delta E(28, 6) = -0.2(3)$ MHz; $g + d - f + \Delta E(28.6) = +0.2(3)$ MHz. Unfortunately, the uncertainty, due to mainly the g–h doublet, is too large to obtain an accurate estimate for the (28, 6) splitting from the loop which exploits the microwave measurements of Ref. (*5*) for the splittings of (28, 5) and (27, 5).

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