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# Measurement of Methane Hyperfine Structure Using Laser Saturated Absorption

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With optical resolution above $10^{10}$, we study hyperfine structure in the methane vibration-rotation line at 3.39 $\mu$m. Doppler-generated crossing resonances were observed in addition to the resolved $\Delta F = 0$ and $-1$ lines. Splittings in both ground and excited states were determined. Differential saturation of such hyperfine structure will lead to an intensity-dependent shift in many molecularly stabilized lasers.

Fine structure in the methane spectrum has been investigated both theoretically and experimentally for some time.[1,2] Recently the magnetic hyperfine structure has become of interest, and transitions within the ground vibrational level have been studied.[3] In addition, for the last several years the infrared spectrum of methane has been actively studied for its possible application as a wavelength/frequency standard.[4,5] Studies in this laboratory[6] have shown that at low pressures the primary broadening mechanism for these saturated-absorption experiments is the molecule's finite residence time in the radiation field. Here we report studies of the methane hyperfine structure using a 5-cm-diam laser beam and a working resolution of about 6 kHz ($1.5 \times 10^{10}$). As this experiment is thought to represent the highest resolution yet achieved in coherent spectroscopy, we briefly discuss some experimental considerations.

The experimental principle of frequency offset-locked saturation spectroscopy is similar to that previously employed by us,[4,5] whereby the remarkable stability[6] of a reference laser servo stabilized to methane is transferred to a high-power laser through the use of frequency/phase-control servo electronics. The output of the power laser passes through an external 13-m-long absorption cell containing $^{12}CH_4$ and is retroreflected at the far end as required to produce the saturated-absorption peak. The return beam is finally steered away from the laser and into the cooled InSb photoreceiver by a $MgF_2$ Rochon prism. Additional isolation is provided by two 45° yttrium-iron-garnet Faraday isolators. Further details and frequency-stability results may be found in Ref. 6. Basically we generate a precise and stable correspondence between signal-averager channel number and absolute optical frequency. This long-term stability[7] is absolutely essential: The low frequency portion of Fig. 1 represents about 12 h integration!

Since the goal of these experiments is to minimize the uncertainty-principle broadening of the observed resonances and thus to maximize the resolution, we must require a coherent interaction during the entire transverse molecular flight across the 5-cm cell aperture. Equivalently stated, we must avoid excessive angular content of the radiation beyond that implied by diffraction from the (apodized) finite spatial extension of the laser spot—the larger angular content broadens the resonances through residual Doppler effect. Thus in the cell the wave-front radius of curva-

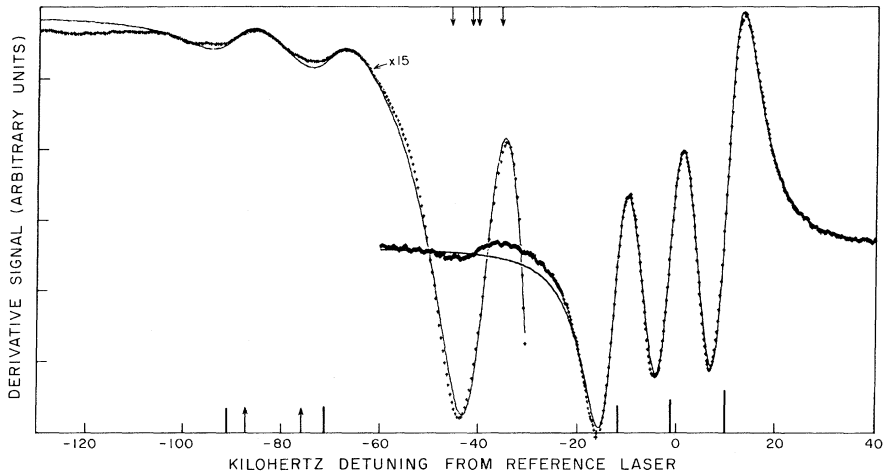


FIG. 1. Composite saturated-absorption hyperfine spectrum: experimental data and least-squares fit (solid curves). $T = 77°K$. Main triplet: methane pressure 70 $\mu$Torr, modulation 2 kHz peak-to-peak at 600 Hz. Fitted Lorentz width, 5.8 kHz. Low-frequency spectrum taken at lower resolution, ~9.8 kHz.

ture must exceed 1 km. The duality of transit-time/angular-content effects in nonlinear spectroscopy has been explored.[8]

The laser is 1.4 m long and uses rf excitation on the 3.5-mm-bore discharge tube. Although the laser emits single-frequency power in excess of 15 mW, it is found that only about 4 mW can be projected into one free-space spatial mode. The successive reflective telescopes expand the beam by a factor of 25 to a 25-mm mode radius thus overfilling the cell aperture. The total power loss is severe: Only about 500 $\mu$W enter the cell and only about 100 $\mu$W return to the detector.

The cell has been constructed of stainless steel with double walls and is surrounded with thermal insulation. Thus, we are able to reduce the methane average transverse velocity by a factor of about 2 through refrigeration of the cell to 77°K. The observed resolution increase is not quite proportionate because of additional broadening mechanisms such as pressure broadening, possible recoil structure,[9] second-order Doppler broadening, residual Zeeman effect after cancelation of the horizontal component of Earth's field, and natural lifetime, to which modulation and saturation broadening must be added. Even so, the structure is well resolved at room temperature, and at 77°K a resolution of 5.6 kHz half width at half-maximum (HWHM) was obtained.

In Fig. 1 we show a typical spectrum observed at 77°K for the methane $F_2^{(2)}$ component[10] at $33\,922.313\,76(12) \times 10^{-8}$ cm in the $P(7)$ line of the $\nu_3$ band.[5] The spectrum is seen to exhibit (a) three strong lines, of similar but not equal strengths; and (b) one weaker, broader "line" and two additional very weak lines (as shown in the 15× magnified left portion of the figure) all on the red side of the three main lines. The intensity ratios are approximately $1:\frac{1}{20}:(\frac{1}{20})^2$. The two levels of the observed $F_2^{(2)}$ transition have a total nuclear spin $I = 1$. Thus, there are three combinations to be formed coupling $\vec{I}$ and $\vec{J}$ to form $\vec{F} = \vec{I} + \vec{J}$. Corresponding to $J = 7$ in the ground state, the $F$ levels will be 6, 7, and 8. The vibrationally excited state, of $J = 6$, will have $F = 5$, 6, and 7.

The hyperfine structure studied here results from three magnetic interaction terms in the Hamiltonian[3]: a scalar and a tensor spin-rotation interaction, and a spin-spin interaction between the protons. For our transition the scalar spin-rotation term gives the major contribution, especially in the excited state. The resulting energy levels are indicated in Fig. 2.

From the theory of relative intensities of multiplet components[11] we expect three main diagonal lines $\Delta F = \Delta J = -1$ with intensities which increase with $F$. Thus, we are able to assign our high-frequency absorption line as $(J, F) = (7, 8) \rightarrow (6, 7)$. The central line is the $7 \rightarrow 6$ and the low-frequency main component is $6 \rightarrow 5$. These strong transitions are indicated in Fig. 2 and correspond to the "selection" rule $\Delta F = \Delta J = -1$. Besides these lines one expects two much weaker lines of $\Delta F = 0$, which are indicated on the low-frequency side of the spectrum of Fig. 1.[12] In addition to these usual components, saturated-absorption spectroscopy provides a new resonance each time

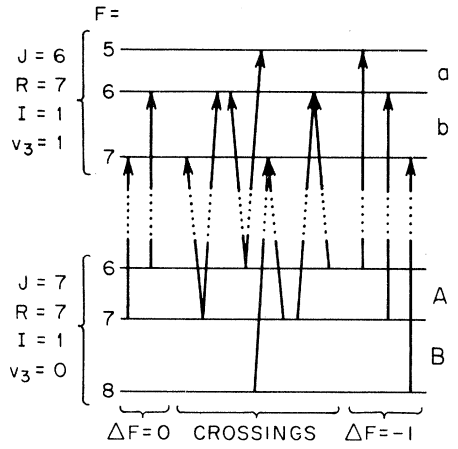


FIG. 2. Methane hyperfine-energy-level diagram. See text for values. The unobserved $\Delta F = +1$ line and its crossings are not illustrated.

two transitions share a common level.[13] These Doppler-generated level crossings occur at a frequency halfway between the two usual transitions and have an intensity proportional to the geometrical mean of the two parent lines.

One of the two assignments of the $\Delta F = 0$ pair leads to four overlapping crossing resonances (upper arrows in Fig. 1 indicate centers) which reproduce the observed spectrum near $-38$ kHz. The positions of the two crossing resonances using the $\Delta F = +1$ line are marked with lower arrows in Fig. 1, but the intensity of these resonances is too small to be observed at present.

The three main lines of Fig. 1 have been least-squares fitted with partially overlapping Lorentzian resonances, with the following result for center frequencies (in kilohertz): $f(8 \rightarrow 7) = +9.70 \pm 0.10$; $f(7 \rightarrow 6) = -1.70 \pm 0.10$; $f(6 \rightarrow 5) = -12.80 \pm 0.10$. The $\Delta F = 0$ lines were less well defined because of much lower signal-to-noise ratio and consequent choice of operating resolution. The results were $f(6 \rightarrow 6) = -72.0 \pm 1.5$ and $f(7 \rightarrow 7) = -91.2 \pm 1.5$.

Referencing the $7 \rightarrow 6$ transition as[14]

$$\nu_0 = 88.376\,181\,627(50)\ \text{THz},$$

we find the energy levels of Fig. 2 to be $E(v_3, F) = E(1, 5) = \nu_0 + 59.2$ kHz; $E(1, 6) = \nu_0 + 0$; $E(1, 7) = \nu_0 - 89.5$ kHz and $E(0, 6) = 0 + 70.3$ kHz; $E(0, 7) = 0 + 0$; $E(0, 8) = 0 - 100.9$ kHz. The uncertainty of the intervals is $\pm 1.5$ kHz. Thus, we have shown for the first time sufficiently high optical resolution and sensitivity to elucidate completely the hyperfine spectrum of both the ground and vibrationally excited states. It should be noted that the vibrationally excited states are not accessible with conventional molecular-beam techniques, because of the unfavorable Boltzmann factor (about $10^{-4}$).

The Hamiltonian which describes this structure has been presented by Yi, Ozier, and Ramsey,[3] and was used successfully to account for the transitions observed in their molecular beam experiments. Diagonalization of such a Hamiltonian under $T_d$ symmetry is somewhat unpleasant in view of the large number of states involved. Of course group theory and Racah algebra may be used to simplify the results considerably. But it is perhaps more attractive to take advantage of the computational power now available. Dr. J. Hougen of the National Bureau of Standards, Gaithersburg, Maryland, has been kind enough to use his computer programs to evaluate the ground-state energies of interest here, using as input data the three constants given by Yi, Ozier, and Ramsey.[3] The values obtained by Hougen are as follows: $F = 6$ at $+86.3$ kHz, $F = 7$ at $+17.9$ kHz, and $F = 8$ at $-81.8$ kHz.[15] Thus, the intervals as defined in Fig. 2 become $A = 68.4$ and $B = -99.7$ kHz, compared with our experimental values of $70.3 \pm 1.5$ and $-100.9 \pm 1.5$ kHz, respectively. These must be regarded as being in complete agreement, since the input data to the hyperfine-energy calculation have uncertainties of the same fractional magnitude as the 3% difference, not to mention our experimental uncertainty ~2%. Thus, the ground-state hyperfine energy, even of tetrahedral methane, now appears to be totally calculable from the known magnetic splitting constants. It would clearly be of interest to extend this kind of study to other Coriolis components within the $J = 7$ manifold. The $E$ component at $-3.0$ GHz may be readily reached by Zeeman tuning the helium-neon laser, as shown by Shimoda and by Gerritsen and Heller. Although this line has multiplicity 2 from group-theoretic arguments, it corresponds to nuclear spin $I = 0$ and consequently is free from hyperfine structure of the type studied in this paper. Estimates of its second-order hyperfine splitting range around 30 Hz, whereas the inversion frequency is estimated to be lower than 1 per day.[15] Thus, the $E$ line may be particularly attractive for quantum frequency-standards applications. It is a lucky accident that the magnetic field required (1.9 kG) to tune the neon is readily available with permanent magnets. On the other hand, the study of tetrahedral hyperfine interactions can be pursued

by the use of larger magnetic fields on the neon, approximately 3.76 kG to reach the $A$ component ($I=2$), and approximately 4.65 kG to reach the $F_1(I=1)$ transitions. We have observed the $E$ and $A$ transition resonances and, with the introduction of superconducting solenoids for atomic lasers,[16] presumably all six Coriolis components will soon be observed. Thus, in the near future it should be possible to test completely our understanding of the hyperfine coupling schemes in tetrahedral molecules such as methane. Using the frequency control methods discussed above and larger apertures (30 cm) it should be possible to observe the recoil effect on the sautrated-absorption resonance that should result in a doublet with a splitting of 2.4 kHz.[9]

We note that with increasing intensity the three allowed transitions will saturate differentially and before the crossing signals. Thus under lower resolution ($\Delta\nu \gtrsim 10$ kHz) an intensity-dependent "center" frequency will be observed.[4,17] Numerical synthesis gives an estimated fractional red shift of $10^{-12}$ for 10% intensity increase for our present reference device ($\Delta\nu \simeq 50$ kHz) at its usual operating point. We note that reported frequency-reproducibility results of Bagaev and Chebotayev[18] would require an intensity resetability of 0.2%.

The authors are indebted to Dr. Jon Hougen for a number of illuminating conversations on the properties of the $T_d$ group molecular spectra, and for communicating to us his numerical results prior to their publication. We are also grateful to Dr. R. L. Barger for his development of the "solid ingot" reference laser which provided the necessary short-term stability. We thank C. Kunasz for expert and cheerful assistance with the least-squares fitting program.

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[11]See for example, H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill, New York, 1934), p. 206.

[12]The $\Delta F=0$ line intensities are somewhat larger than expected from Ref. 11: A relative (saturation) signal of $(1/47)^2$ is expected and $\sim(1/20)^2$ is observed, perhaps because of second-order hyperfine mixing or a variation of the degree of saturation with transverse velocity of the observed molecules.

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