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Far-Infrared Laser Magnetic Resonance Spectrum of CH_2F

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Laser magnetic resonance rotational spectra of the free radical CH_2F have been obtained using far-infrared laser lines at 301.3, 393.6, 513.0, and 567.9 μm. The radical was prepared under fast-flow conditions by fluorine atom abstraction of a hydrogen from methyl fluoride and by fluorine atom addition to diazomethane. The spectra obtained are too crowded and overlapped to permit significant spectroscopic analysis, but they do support a planar C_{2v} structure for CH_2F and lead to a value of $(B + C) = 1.953 \pm 0.015$ cm^{-1}.

In the course of a series of investigations of gas-phase free radicals using a newly constructed CO_2-pumped far-infrared magnetic resonance spectrometer (*1*), a spectrum attributable to CH_2F has been observed. Identification of the carrier rests partly on chemical evidence, partly on observed hyperfine patterns, and partly on spectroscopic analysis.

A relatively thorough search for laser lines exhibiting CH_2F absorption resonances was carried out using the reaction

$$F + CH_3F \rightarrow CH_2F + HF, \tag{1}$$

where the F atoms were generated in a microwave discharge of flowing He + CF_4, and the CH_3F was introduced 25 cm downstream, just above the center of the magnet pole pieces. Pressures, as measured in the absorption section of the far-infrared laser cavity, somewhat removed from the reaction zone, were in the neighborhood of 90 μ of He, 40 μ of CF_4, and 30 μ of CH_3F for optimum yield of CH_2F. (1 μ corresponds to 0.133 Pa.) In all, 25 far-infrared laser lines were examined in the wavelength region 300–890 μm (as shown in Fig. 1), but absorptions were found only for the four lines (and gain media) at: 301.3 μm (N_2H_4), 393.6 μm (HCOOH), 513.0 μm (HCOOH), and 567.9 μm (CH_2CHCl). All four of these observed spectra were reproduced when the He + CF_4 source of F atoms was replaced by He + SF_6. The four spectra were also obtained from the reaction

$$CH_2N_2 + F \rightarrow CH_2F + N_2, \tag{2}$$

where the source of F atoms was again the He + CF_4 discharge (*2*). The observations in this paragraph constitute the chemical evidence for the carrier identification.

The isotropic hyperfine coupling constants for CH_2F are known from a matrix isolation electron spin resonance study (*3*) to have the values $a_F = 64$ G and $a_H = 21$ G (1 G = 100 μT). Our spectra, although badly overlapped, exhibit a small number of

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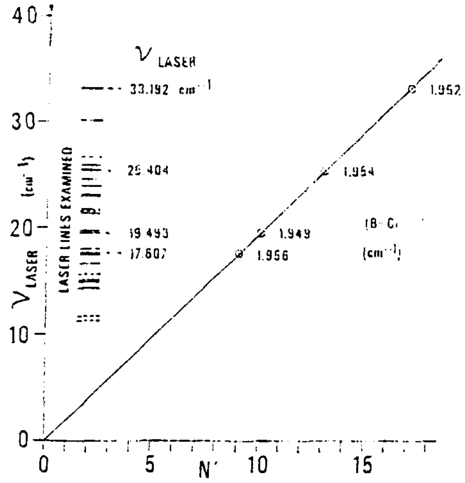

FIG. 1. A plot of laser wavenumber against upper state quantum number N. All 25 laser lines examined are shown along the ordinate, the four dashed lines having somewhat uncertain wavelengths. Points corresponding to the four laser lines showing absorption resonances are plotted along the straight line. Values of $(B + C)$ obtained from these points by dividing ν_{laser} (sho lefwn on thet) by N' are indicated to the right of the points.

hyperfine patterns consisting of six equally intense, equally spaced lines with a separation of about 20 G, and a small number of patterns consisting of pairs of equally intense lines with a separation of about 60 G. Precisely such hyperfine splittings of individual M_J lines are expected in the high magnetic field limit for even (odd) and odd (even) K_a values, respectively, if the CH_2F molecule has C_{2v} symmetry and is in a ${}^2B_1$ or ${}^2B_2$ (${}^2A_1$ or ${}^2A_2$) vibronic state. Unfortunately, these hyperfine pattern arguments supporting identification of the carrier as planar CH_2F are weakened somewhat by the fact that the simple patterns described above are the exception rather than the rule in our spectra, a situation presumably arising because of the overlapping and because at low magnetic fields intermediate coupling effects give rise to less simple patterns.

Because all four spectra obtained are severely overlapped and crowded essentially into the 0–2 kG portion of the 20-kG scanning range of the spectrometer, they are all rather unsuitable for complete spectroscopic analysis. Nevertheless, we can draw from these spectra a qualitative conclusion concerning spin-rotation splittings and a quantitative conclusion concerning the rotational constant $(B + C)$.

The laser magnetic resonance spectra observed for CH_2F are in general quite strong in the region from 0 to 2 kG, quite weak from 2 to 4 kG, and absent above 4 kG. (These tuning ranges in kilogauss can be approximately correlated with tuning ranges in cm^{-1} by noting that tuning rates for CH_2F transitions are expected to be less than $2\mu_B \cong 0.1$ cm^{-1}/kG.) This very small usable tuning range of 2 kG is consistent with the fact that no trace of the spectra observed with the lines at 393.6 and 567.9 μm, respectively, can be seen with lines at 392.1 and 570.6 μm. Since the usable tuning range in laser magnetic resonance spectroscopy terminates when the electron spin is uncoupled from the molecular framework, and since this uncoupling becomes appreciable when the interaction energy of the spin with the external magnetic field ($\sim 2\mu_B H$) is greater than the largest spin splittings in the molecule, we conclude that spin splittings in CH_2F (i.e., spin-rotation splittings) are in general 0.2 cm^{-1} or smaller.

The spectrum observed in this work is very sparse in the sense that only 4 out of 25 laser lines showed absorption resonances, but it is very dense in the sense that severe overlapping occurs whenever absorption resonances are actually found. From these observations we conclude that the molecule responsible for the spectrum is a near prolate rotor exhibiting only a μ_a rotational spectrum ($\Delta K_a = 0$.) For then, rotational transitions (apart from the small spin splittings mentioned above) occur only at the wavenumbers:

$$[(B + C) - 2D_{NK}K^2 - 4D_N(N + 1)^2](N + 1) \cong (B + C)(N + 1), \qquad (3)$$

but exhibit at each of these wavenumbers a complexity associated with the $(2N + 1)$ values of K allowed for the $(N + 1) \leftarrow N$ transition. (Note that because $S \neq 0$ in this molecule, the rotational angular momentum is represented by the quantum number N, the symbol J being reserved for the sum of N and S.) A near prolate rotor exhibiting only μ_a rotational transitions is consistent with a CH_2F molecule of C_{2v} symmetry (i.e., planar), as deduced by Fessenden and Schuler (*3*) from the magnitudes of the hyperfine coupling constants, and as supposed above from the appearance of sextet and doublet hyperfine patterns.

If we neglect corrections due to magnetic field, spin splittings, and centrifugal distortion effects, we can determine an approximate value for the rotational constant $(B + C)$ simply by plotting the wavenumber of each laser line (*4*) exhibiting absorption resonances against an assigned upper state rotational quantum number N', as shown in Fig. 1. Since the neglected corrections are expected to be less than 0.2 cm^{-1}, and since N' is of the order of 15, we believe that the value of $(B + C) = 1.953$ cm^{-1} determined from these observations has an uncertainty of ± 0.015 cm^{-1}. It seems unlikely that further consideration of the present data can reduce this uncertainty. Note that a value of $(B + C) = 1.960$ cm^{-1} may be obtained from the not unreasonable structure of r(C–H) = 1.09 Å, r(C–F) = 1.32 Å, and $\angle$HCH = 118°.

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2. The diazomethane used in these experiments was kindly supplied by Dr. G. B. Ellison.

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