LASER MAGNETIC RESONANCE DETECTION OF ROTATIONAL TRANSITIONS IN CH_2

J.A. MUCHA [*], K.M. EVENSON, D.A. JENNINGS
National Bureau of Standards, Boulder, Colorado 80303, USA

G.B. ELLISON
Department of Chemistry, University of Colorado, Boulder, Colorado 80309, USA

and

C.J. HOWARD
*Aeronomy Laboratory, National Oceanic and Atmospheric Administration,
Boulder, Colorado 80303, USA*

Laser magnetic resonance spectra observed at 163.0 μm have been identified as pure rotational transitions in the ground electronic state ($^3B_1$) of the methylene radical. The identification was based on the observation of hyperfine spin triplets and by isotopic substitutions involving deuterium and ^{13}C, as well as other chemical and spectroscopic evidence. A low-pressure flame produced by reacting discharged fluorine with methane was found to be an excellent new spectroscopic source of ground-state CH_2 radicals.

The methylene biradical, CH_2, observed with electron paramagnetic resonance [**] and optical [2] spectroscopic techniques, continues to be an extremely important species for experimentalists and theoreticians [†] alike. After several years of uncertainty about its ground state, there is now general agreement that it is a bent triplet state ($^3B_1$). The available rotational constants of CH_2 are calculated from low-resolution optical data [2] and EPR data [1] and are accurate to about 30%. By comparison, the extremely sensitive technique of far-infrared laser magnetic resonance (LMR) spectroscopy [4] provides rotational constants and structural information with 100 times greater accuracy. Because of the present controversy about the sin-

glet–triplet splitting ($^1A_1 \leftarrow\ ^3B_1$) in methylene [5–7], a direct determination of its ground-state geometry is very desirable. Furthermore, an accurate structural determination would provide frequencies which could serve as the basis for astronomical searches for CH_2 in interstellar gas clouds.

This communication reports the observation of several LMR absorptions which are attributed to rotational transitions in the ground electronic state of CH_2. Fig. 1 shows an LMR spectrum identified with CH_2. Although the quantum states are not yet assigned, the large signal-to-noise ratio indicates the sensitivity of LMR for detecting CH_2. In this experiment, the optically pumped far-infrared (FIR) laser spectrometer [8] was oscillating on the 163.0 μm laser line of methanol, with its electric vector polarized perpendicular to the magnetic field (σ polarization). The methanol transition was pumped with the 10 μm R(38) line of a cw CO_2 laser. First-derivative presentation was effected using 1 kHz magnetic field modulation with an amplitude of about 0.0004 T (10^{-4} T = 1 G) and phase-sen-
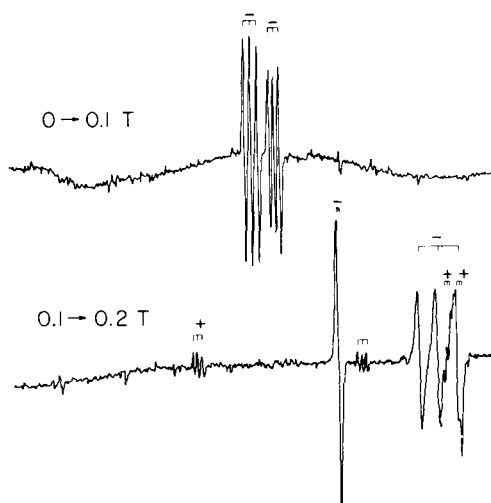

Fig. 1. The 0–0.2 T portion of the 163.0 μm laser magnetic resonance spectrum of CH_2 ($^3B_1$) in perpendicular (σ) polarization. The + or – signs designate transitions which shift to higher or lower field respectively when the laser frequency is increased.

sitive detection. In all, eleven sets of hyperfine triplets were observed at this frequency in σ polarization; eight triplets are shown in fig. 1, centered at 0.0472, 0.0520, 0.1384, 0.1687, 0.1728, 0.1900, 0.1922, and 0.1952 T. Three additional triplets were observed at 0.2829, 0.6620 and 0.7550 T. In the other polarization (π), three triplets were observed at 0.0851, 0.1261 and 0.2288 T. The uncertainty is about 0.0002 T.

The observation of rotational spectra in this wavelength region agrees with Bernheim's estimates [9] of the rotational energy levels of CH_2 based on optical [2] and EPR [1,10–12] data. Although these estimates do not permit identification or assignment of the observed transitions, they do indicate this spectral region to be particularly dense in B-type rotational transitions. Hyperfine triplets and singlets are both expected in CH_2 LMR spectra; however, both are not likely to occur with the same laser line. No attempt was made to analyse hyperfine singlet spectra in these preliminary studies since they could well be due to other free radicals. The lack of recognizable patterns in this observed spectrum precludes an assignment at present; however, the small number of widely spaced lines indicate transitions involving low rotational quantum numbers. Both the ratio of the hyperfine splitting

to observed linewidth and the direction of the magnetic field shift with laser frequency vary for these lines, indicating that the observed spectrum may be due to transitions involving different spin or vibrational states.

The observed hyperfine triplets could be attributed to other radicals containing an I = 1 nucleus such as nitrogen or two I = 1/2 nuclei such as fluorine. Our measurements indicate fluorine-containing radicals can be disregarded since sources lacking fluorine also duplicated the spectrum. Ammonia was substituted for methane in order to determine whether the triplets were a result of a nitrogen impurity. Well-known NH [13] and NH_2 [14] spectra resulted; however, none of the features of fig. 1 was reproduced. Similarly, mixtures of oxygen and nitrogen passed through the microwave discharge failed to generate the observed spectrum.

The identification of CH_2 as the carrier responsible for the transitions shown in fig. 1 rests on the previously mentioned spectroscopic evidence as well as the following chemical evidence: CH_2 was formed by the reaction of fluorine atoms with methane inside the laser cavity. Helium and fluorine at pressures of 126 and 0.4 Pa (7.52 mTorr = 1.0 Pa), respectively, were passed through a microwave discharge and mixed with 0.4 Pa of methane in a nozzle located 30 mm from the axis of the laser. A blue flame resulted and its intensity maximized under approximately the same conditions as the CH_2 signal. CH spectra, also observed in this flame [15], maximized under very similar conditions. A number of other sources, summarized in table 1,

Table 1
Effect of source chemistry and isotopic substitution upon the relative LMR signal intensities in the 163 μm σ spectrum between 0 and 0.2 T

Source	Isotopic purity (%)	Signal intensity (arb. units)	
		observed	predicted [a]
$^{12}CH_4$ + F	99	100 ± 5	100
CH_2N_2 + N	–	20 ± 5	–
C_2H_2 + O	–	20 ± 5	–
C_2H_4 + F	–	20 ± 5	–
CH_3F + F	–	10 ± 5	–
$^{12}CD_4$ + F	99	< 2	0
$^{13}CH_4$ + F	90	7 ± 2	10
$^{12}CD_2H_2$ + F	99	18 ± 2	17

[a] Prediction based on the abstraction mechanism: CH_4 + 2F $\rightarrow CH_2$ + 2HF.

also produced the spectrum in fig. 1; however, the methane source was significantly stronger than any other. It should be noted that the reaction of atomic oxygen with acetylene listed in table 1 is a known source of methylene [16]. Attempts to detect CH_2 by photolysis or pyrolysis of diazomethane and ketene in the flow apparatus were not successful, possibly due to the lack of intensity of the mercury lamp used, or to the formation of methylene in its singlet state. The transitions in the 163 μm σ spectrum were also tested using isotopically substituted methanes as precursors and these results are also summarized in table 1. Each of the triplets exhibited identical variation in intensity, indicating that all of the observed lines originate from a single species. The intensity variations are as expected for a molecule containing two hydrogen atoms and one carbon atom, assuming an abstraction mechanism. However, subsequent observation of the ethynyl radical (C_2H) in the methane—fluorine flame [17], as well as CF [17], and CH_2F [18] suggests, the chemistry of radical formation in this flame is more complex. Searches made with thirteen other FIR laser lines (95.6, 118.8, 165.5, 170.5, 232.9, 251, 392, 469, 570.5 and 699.5 μm from CH_3OH, and 100, 157.9 and 171.8 μm from $^{13}CH_3OH$) failed to produce spectra attributable to hyperfine triplets of CH_2.

The evidence discussed above indicates the presence of the electronic ground state of CH_2 in the fluorine—methane flame. A detailed spectroscopic fitting and analysis of the spectra obtained thus far has not been possible; however the observation of further spectra with other laser lines should provide sufficient data for an accurate fit and a determination of accurate rotational constants of CH_2. When the LMR spectra of CH_2 is assigned it will be possible to deduce an accurate molecular structure for the radical. It is also possible that knowledge of the spin—orbit interaction, coupling the $^3B_1$ and $^1A_1$ states and the HCH bending frequency in the $^3B_1$ state will be obtained. This will be an important contribution toward the interpretation of the CH_2 photoelectron spectra [5]. LMR detection has been used to study the reaction kinetics of HO_2 [19] and HO [20] in flow reactors and similar studies of the chemistry of CH_2 $^3B_1$ may also be possible. Finally, and perhaps most importantly, the discovery of this new source of triplet CH_2 should provide other experiments with a valuable means to perform additional new studies on this radical.

References

[1] R.A. Bernheim and S.H. Chien, J. Chem. Phys. 66 (1977) 5703.

[2] G. Herzberg and J. Shoosmith, Nature 183 (1959) 1801; G. Herzberg, Proc. Roy. Soc. A 262 (1961) 291; G. Herzberg and J.W.C. Johns, J. Chem. Phys. 54 (1971) 2276.

[3] J.F. Harrison, Accounts Chem. Res. 7 (1974) 378.

[4] P.B. Davies and K.M. Evenson, in: Lecture notes in physics, Vol. 43: Laser Spectroscopy, Proceedings of the 2nd International Conference, eds. S. Haroche, J.C. Pebay Peyroula, T.W. Hänsch and S.E. Harris (Springer, Berlin, 1975) p. 132.

[5] P.F. Zittel, G.B. Ellison, S.V. O'Neil, E. Herbst, W.C. Lineberger and W.P. Reinhardt, J. Am. Chem. Soc. 98 (1976) 3731.

[6] J. Danon, S.V. Filseth, D. Feldmann, H. Zacharias, C.H. Dugan and K.H. Welge, Chem. Phys. 29 (1978) 345; R.K. Lengel and R.N. Zare, J. Am. Chem. Soc., to be published.

[7] R.R. Lucchese and H.F. Schaefer III, J. Am. Chem. Soc. 99 (1977) 6765; B. Roos and P.M. Siegbahn, J. Am. Chem. Soc. 99 (1977) 7716; L.B. Harding and W.A. Goddard III, J. Chem. Phys. 67 (1977) 1777; C.W. Bauschlicher Jr. and I. Shavitt, J. Am. Chem. Soc. 100 (1978) 739; S.-K. Shih, S.D. Peyerimhoff, R.J. Buenker and M. Perić, Chem. Phys. Letters 55 (1978) 206; L.B. Harding and W.A. Goddard III, Chem. Phys. Letters 55 (1978) 217.

[8] K.M. Evenson, D.A. Jennings, F.R. Petersen, J.A. Mucha, J.J. Jimenez, R.M. Charlton and C.J. Howard, IEEE J. Quantum Electron. QE-13 (1977) 442.

[9] R.A. Bernheim, private communication.

[10] E. Wasserman, R.S. Hutton, V.J. Kuck and W.A. Yager, J. Chem. Phys. 55 (1971) 2593.

[11] R.A. Bernheim, T. Adl, H.W. Bernard, A. Songco, P.S. Wang, R. Wang, L.S. Wood and P.S. Skell, J. Chem. Phys. 64 (1976) 2747.

[12] B.R. Bicknell, W.R.M. Graham and W. Weltner Jr., J. Chem. Phys. 64 (1976) 3319.

[13] H.E. Radford and M.M. Litvak, Chem. Phys. Letters 34 (1975) 561; F.D. Wayne and H.E. Radford, Mol. Phys. 32 (1976) 1407.

[14] P.B. Davies, D.K. Russell, B.A. Thrush and F.D. Wayne, J. Chem. Phys. 62 (1975) 3739; P.B. Davies, D.K. Russell, B.A. Thrush and H.E. Radford, Chem. Phys. Letters 42 (1976) 35.

[15] J.T. Hougen, J.A. Mucha, D.A. Jennings and K.M. Evenson, J. Mol. Spectry. 72 (1978) 463.

[16] J.R. Kanofsky, D. Lucas, F. Pruss and D. Gutman, J. Phys. Chem. 78 (1974) 311;
I.T.N. Jones and K.D. Bayes, 14th Symposium International on Combustion (Combustion Institute, Pittsburg, 1973) p. 277.

[17] R.J. Saykally and K.M. Evenson, paper FB-8, Thirty-Third Symposium on Molecular Spectroscopy, The Ohio State University, Columbus, Ohio, June 12–16, 1978.

[18] J.A. Mucha, D.A. Jennings, K.M. Evenson and J.T. Hougen, J. Mol. Spectry. 68 (1977) 122.

[19] C.J. Howard and K.M. Evenson, Geophys. Res. Letters 10 (1977) 437.

[20] C.J. Howard and K.M. Evenson, J. Chem. Phys. 61 (1974) 1943.