LASER MAGNETIC RESONANCE DETECTION OF ROTATIONAL TRANSITIONS IN CH₂

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Laser magnetic resonance spectra observed at 163.0 μm have been identified as pure rotational transitions in the ground electronic state (3B₁) of the methylene radical. The identification was based on the observation of hyperfine spin triplets and by isotopic substitutions involving deuterium and 1³C, 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 CH₂ radicals.

The methylene biradical, CH₂, 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 (3B₁). The available rotational constants of CH₂ 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 singlet–triplet splitting (1A₁ → 3B₁) 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 CH₂ 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 CH₂. Fig. 1 shows an LMR spectrum identified with CH₂. Although the quantum states are not yet assigned, the large signal-to-noise ratio indicates the sensitivity of LMR for detecting CH₂. 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 CO₂ laser. First-derivative presentation was effected using 1 kHz magnetic field modulation with an amplitude of about 0.0004 T (10⁻⁶ T = 1 G) and phase-sen-
The 0-0.2 T portion of the 163.0 μm laser magnetic resonance spectrum of CH₂ (¹B₁) in perpendicular (σ) polarization. The + or − signs designate transitions which shift to higher or lower field respectively when the laser frequency is increased.

The observation of rotational spectra in this wavelength region agrees with Bernheim's estimates [9] of the rotational energy levels of CH₂ based on optical [2] and EPR [11,10-12] 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 CH₂ 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 NH₂ [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 CH₂ 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: CH₂ 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 CH₂ 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
<table>
<thead>
<tr>
<th>Source</th>
<th>Isotopic purity (%)</th>
<th>Signal intensity (arb. units)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>observed</td>
<td>predicted a)</td>
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<tr>
<td></td>
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<tr>
<td>¹²CH₄ + F</td>
<td>99</td>
<td>100 ± 5</td>
</tr>
<tr>
<td>CH₂N₂ + N</td>
<td></td>
<td>20 ± 5</td>
</tr>
<tr>
<td>C₂H₂ + O</td>
<td></td>
<td>20 ± 5</td>
</tr>
<tr>
<td>C₂H₄ + F</td>
<td></td>
<td>20 ± 5</td>
</tr>
<tr>
<td>CH₃F + F</td>
<td></td>
<td>10 ± 5</td>
</tr>
<tr>
<td>¹³CD₄ + F</td>
<td>99</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>¹²CH₄ + F</td>
<td>90</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>¹⁵CD₂H₂ + F</td>
<td>99</td>
<td>18 ± 2</td>
</tr>
</tbody>
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a) Prediction based on the abstraction mechanism: CH₄ + 2F → CH₂ + 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 $\mu$m $\sigma$ 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 expected for a molecule containing two hydrogen atoms and one carbon atom, assuming an abstraction mechanism. However, subsequent observation of the ethynyl radical (C$_3$H) in the methane-fluorine flame [17], as well as CH$_2$F [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 $\mu$m from CH$_3$OH, and 100, 157.9 and 171.8 $\mu$m from $^{13}$CH$_3$OH) 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 $^3$B$_1$ and $^1$A$_1$ states and the HCH bending frequency in the $^3$B$_1$ 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$_2^3$B$_1$ 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.

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References