

## LETTER TO THE EDITOR

Detection of the Infrared Spectrum of  $\text{CH}_2^+$ 

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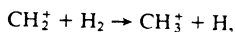
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The spectroscopy of carbo-ions (ions composed of carbon atoms or carbon and hydrogen) has been a special challenge because of their high reactivities, especially toward polymerization. We have overcome this difficulty by using discharges with a large amount of He mixed with small amounts of hydrocarbon and hydrogen. Not only does the chemical inactivity of He make it an ideal buffer, but also the high ionization potential (which leads to Penning ionization) and the low proton affinity (which prevents the depletion of positive charge in the form of  $\text{HeH}^+$ ) allow us to produce plasmas which are rich in carbo-ions. By using such plasmas, we have been able to observe and characterize infrared spectra of  $\text{CH}_3^+$  (1, 2),  $\text{HCCH}^+$  (3, 4),  $\text{C}_2^-$  (5),  $\text{C}_2\text{H}_3^+$  (6, 7), and their deuterated species (8, 9). In this paper we report our detection of the  $\nu_3$  band of  $\text{CH}_2^+$ .

Although  $\text{CH}_2^+$  has been well known to mass spectroscopists since its early detection by Hogness and Kvalness (10), and many chemical kinetic papers have been published (11), experimental studies of its quantum-mechanical properties are almost nonexistent. We have not been able to find any spectroscopic paper related to this ion apart from Herzberg's early study on high Rydberg states of  $\text{CH}_2$  in which he reported the ionization potential of  $\text{CH}_2$  (12). Our study will fill this void.

There have been quite a few theoretical reports on this fundamental ion. The early ab initio theory by Lathan, Hehre, and Pople (13) predicted the  $\text{C}_{2v}$  equilibrium structure of  $r_e = 1.132 \text{ \AA}$ ,  $\theta_e = 136^\circ$  (STO-3G) and  $r_e = 1.079 \text{ \AA}$ ,  $\theta_e = 141.8^\circ$  (4-31G). DeFrees and McLean (14) predicted the vibrational frequencies to be  $\nu_1 = 2901 \text{ cm}^{-1}$ ,  $\nu_2 = 948 \text{ cm}^{-1}$ , and  $\nu_3 = 3118 \text{ cm}^{-1}$ . This molecular ion is of special theoretical interest because of its quasilinearity (the barrier to linearity  $\leq 1000 \text{ cm}^{-1}$ ) and the expected Renner-Teller effect. There have been an extensive ab initio potential calculation by Bartholomae, Martin, and Sutcliffe (15) and the treatment of intramolecular dynamics by Sutcliffe and Tennyson (15-18) and by Carter and Handy (19-21). The  $\nu_3$  value is predicted to be  $3162 \text{ cm}^{-1}$  (15),  $3271 \text{ cm}^{-1}$  (16, 17, 19, 20), and  $3267 \text{ cm}^{-1}$  (21).

We have observed the spectrum of  $\text{CH}_2^+$  using the difference frequency spectrometer and velocity modulation with unidirectional multiple reflection and noise subtraction. More details will be found in Refs. (7) and (9). The new multiple-inlet multiple-outlet discharge cell (9) has been used. The new arrangement of gas inlets which introduces the gas mixture in pairs of diametrically opposed jets was essential in enhancing the intensities of the  $\text{CH}_2^+$  lines. The  $\text{CH}_2^+$  lines are stronger relative to  $\text{CH}_3^+$  lines in the gas mixture of  $\text{CH}_4:\text{He} = 0.12:7$  Torr than that of  $\text{CH}_4:\text{H}_2:\text{He} = 0.12:0.10:7$  Torr. Evidently, this is due to the hydrogen abstraction reaction



which has the Langevin rate of  $10^{-9} \text{ cm}^3\text{sec}^{-1}$  (11).

The *P*- and *R*-branch series with  $K_a = 0$  are listed in Table I. The series shows the 3:1 intensity alternation for  $K_a + K_c = \text{odd}$  and even, respectively, as expected from the  $\text{C}_{2v}$  geometry and the  ${}^2A_1$  symmetry of the ground electronic state (12). The spin-rotation doublet is not split but makes the lines slightly broader than those of  $\text{CH}_3^+$ ; this helps us assign the  $\text{CH}_2^+$  lines, which appear amidst much stronger  $\text{CH}_3^+$  lines. The spectrum has been fitted to the asymmetric rotor pattern with the standard deviation of  $\sigma = 0.004 \text{ cm}^{-1}$  with the following molecular constants:

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TABLE I

Observed Transitions of the  $\nu_3$  Band of  $\text{CH}_2^+$  (in  $\text{cm}^{-1}$ )

$N'_{Ka, Kc} \leftarrow N_{Ka, Kc}$	$\nu_{\text{obs}} (\Delta\nu \times 10^3)$
$12_{0,12} \leftarrow 11_{0,11}$	3286.093(2)
$11_{0,11} \leftarrow 10_{0,10}$	3275.030(-3)
$10_{0,10} \leftarrow 9_{0,9}$	3263.621(2)
$9_{0,9} \leftarrow 8_{0,8}$	3251.850(2)
$8_{0,8} \leftarrow 7_{0,7}$	3239.726(1)
$7_{0,7} \leftarrow 6_{0,6}$	3227.249(-8)
$6_{0,6} \leftarrow 5_{0,5}$	3214.454(-2)
$5_{0,5} \leftarrow 4_{0,4}$	3201.340(7)
$4_{0,4} \leftarrow 3_{0,3}$	3187.906(4)
$3_{0,3} \leftarrow 2_{0,2}$	3174.176(0)
$2_{0,2} \leftarrow 1_{0,1}$	3160.169(-2)
$2_{0,2} \leftarrow 3_{0,3}$	3086.428(-5)
$3_{0,3} \leftarrow 4_{0,4}$	3071.036(-2)
$4_{0,4} \leftarrow 5_{0,5}$	3055.459(2)
$5_{0,5} \leftarrow 6_{0,6}$	3039.703(3)
$6_{0,6} \leftarrow 7_{0,7}$	3023.786(5)
$7_{0,7} \leftarrow 8_{0,8}$	3007.704(-2)
$8_{0,8} \leftarrow 9_{0,9}$	2991.479(-5)

$$\nu_0 = 3131.373(14) \text{ cm}^{-1}$$

$$\text{ground state } (B + C)/2 = 7.38131(57) \text{ cm}^{-1}$$

$$\nu_3 \text{ state } (B' + C')/2 = 7.26281(103) \text{ cm}^{-1}.$$

The spectrum could be fitted nearly equally well to the linear molecule, in which case  $\sigma = 0.014 \text{ cm}^{-1}$ . Compared with the  $\nu_3$  band of  $\text{H}_2\text{O}^+$ , for which only high  $J$ ,  $R$ -branch lines for  $K_a = 0$  are unsplit and which requires a definite asymmetric rotor pattern even for  $K_a = 0$  (22, 23), the quasilinear nature of  $\text{CH}_2^+$  is evident in the spectrum.

Obviously much more extensive measurements and analysis are needed to fully characterize the spectrum. Together with the spectrum of  $\text{NH}_2^+$  (24) it presents a fascinating example of quasilinearity.

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