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COMMUNICATIONS

Observation of the infrared spectrum of methyl cation CH_3^+

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The polyatomic hydrocarbon cations CH_n^+ ($n = 2-5$) and C_2H_n^+ ($n = 1-7$) are fundamental ionic species which play important roles in chemical kinetics, in the laboratory, and in space. However, there has previously been no high resolution spectroscopic studies of these ions in any spectral region because their high reactivity makes it difficult to produce them in sufficient abundance. In this paper we report the first observation of such a spectrum, i.e., the ν_3 fundamental band of CH_3^+ .

The only available quantum mechanical information on CH_3^+ is the approximate frequency of the ν_2 vibration determined from the Rydberg spectrum of CH_3 by Herzberg¹ and from the photoelectron spectrum of CH_3 by Dyke *et al.*² Pople and his colleagues^{3,4} theoretically studied many simple carbocations and gave their geometrical structures and binding energies. Many more theoretical works on carbocations are quoted in these papers. More recently, Botschwina *et al.*⁵ and DeFrees and McLean⁶ calculated potential energy surfaces and predicted vibrational frequencies. In particular, the prediction by DeFrees and McLean⁶ of the ν_3 vibration frequency at 3090 cm^{-1} agreed very closely with our experimental value given later in this letter.

Our search for the infrared spectrum of hydrocarbon ions was conducted using the tunable radiation from our difference frequency laser system⁷ combined with the velocity modulation technique developed by Gudeman and Saylor.⁸ A specially designed ac discharge tube (the "tarantula") was used into which the gas mixture was introduced through many inlet ports. Initially, a $\text{He}:\text{H}_2:\text{C}_2\text{H}_2$ gas mixture of $\sim 700:20:1$ with a total pressure of ~ 7 Torr was used intending to detect protonated acetylene. Blue-green emission, probably due to CH , was noticed in the region of discharge around each inlet indicating that reactions are taking place vigorously in the optical path. Because of the low concentration of acetylene little carbon deposit was observed. Some 500 ion lines were found between $3250-2950\text{ cm}^{-1}$. Soon it was realized from the chemistry and the observed

linewidths that at least two hydrocarbon ions were present, one an asymmetric rotor with two carbon atoms and the other a symmetric rotor with one carbon atom. The former showed rather complicated patterns and is likely due to pro-

TABLE I. Observed frequencies of the ν_3 band of CH_3^+ (in cm^{-1}).

Transitions	Frequency ^a	Transitions	Frequency
<i>RR</i> (5,1)	3200.340(-2)	<i>RQ</i> (1,0)	3102.457(-1)
<i>RR</i> (5,2)	3190.144(-3)	<i>RQ</i> (3,0)	3101.620(6)
<i>RR</i> (4,1)	3182.899(13)	<i>RQ</i> (5,0)	3100.128(-2)
<i>RR</i> (5,3)	3180.043(-6)	<i>RQ</i> (2,1)	3091.692(-5)
<i>RR</i> (3,0)	3175.469(24)	<i>RQ</i> (3,1)	3091.175(1)
<i>RR</i> (4,2)	3172.673(12)	<i>RQ</i> (4,1)	3090.489(5)
<i>RR</i> (5,4)	3170.032(-2)	<i>RQ</i> (5,1)	3089.633(-1)
<i>RR</i> (3,1)	3165.211(21)	<i>RQ</i> (3,2)	3080.868(-8)
<i>RR</i> (4,3)	3162.533(1)		
<i>RR</i> (5,5)	3160.089(4)	<i>RQ</i> (4,2)	3080.199(-1)
<i>RR</i> (3,2)	3154.951(11)	<i>RQ</i> (5,2)	3079.369(3)
<i>RR</i> (4,4)	3152.480(-2)	<i>RQ</i> (4,3)	3069.975(-8)
<i>RR</i> (2,1)	3147.278(14)	<i>RQ</i> (5,3)	b
<i>RR</i> (3,3)	3144.778(-4)		
<i>RR</i> (1,0)	3139.492(16)		
<i>RR</i> (2,2)	3136.993(0)	<i>PP</i> (1,1)	3094.410(-1)
<i>RR</i> (1,1)	3129.125(6)	<i>PP</i> (2,2)	3086.113(-3)
		<i>PP</i> (3,3)	3077.738(-5)
<i>PQ</i> (5,5)	3153.345(-7)	<i>PP</i> (2,1)	3075.522(-2)
<i>PQ</i> (5,4)	3142.415(-9)	<i>PP</i> (4,4)	3069.285(-3)
<i>PQ</i> (3,3)	3133.332(4)	<i>PP</i> (5,5)	3060.755(10)
<i>PQ</i> (4,3)	3132.559(-10)	<i>PP</i> (4,3)	3058.528(1)
<i>PQ</i> (5,3)	3131.660(28)	<i>PP</i> (5,4)	3049.921(3)
<i>PQ</i> (2,2)	3123.186(6)	<i>PP</i> (4,2)	3047.877(-2)
<i>PQ</i> (3,2)	3122.627(7)	<i>PP</i> (5,3)	3039.188(-13)
<i>PQ</i> (4,2)	3121.888(7)	<i>PP</i> (4,1)	3037.325(-2)
<i>PQ</i> (5,2)	3120.967(-2)	<i>PP</i> (5,2)	3028.583(-2)
<i>PQ</i> (1,1)	3112.952(6)	<i>PP</i> (5,1)	3018.055(-4)
<i>PQ</i> (2,1)	3112.588(9)		
<i>PQ</i> (3,1)	3112.043(10)		
<i>PQ</i> (4,1)	3111.319(8)		
<i>PQ</i> (5,1)	3110.426(4)		

^a Observed minus calculated frequencies for the last digits are given in parentheses.

^b Overlapped with an H_3^+ line.

tonated acetylene $C_2H_3^+$; that spectrum will be discussed in a separate paper. When C_2H_2 was replaced with CH_4 , the latter spectrum increased in intensity by a factor of ~ 3 . Initially, protonated methane CH_5^+ was suspected to be the carrier of this spectrum because of the prominent series of lines separated by $\sim 8\text{ cm}^{-1}$, but the analysis revealed that it is CH_3^+ . With hindsight, the abundance of CH_3^+ in the methane discharge is not surprising because it does not react with H_2 to form CH_4^+ .

More than 100 lines were observed and assigned to the perpendicular ($\Delta K = \pm 1$) ν_3 fundamental band of CH_3^+ . Frequencies of low J (< 5) lines are listed in Table I. The spectrum fits well to a symmetric rotor Hamiltonian. The absence of transitions starting from the ($J = \text{even}, K = 0$) levels in the ground state together with the absence of any nearby group of lines and the stronger intensities for $K = 3n$ transitions clearly indicates that the geometrical structure of CH_3^+ is of D_{3h} symmetry as anticipated from theory. A least-squares fitting was carried out using up to quartic centrifugal distortion terms except for η_k which was found to be indeterminable. l doubling was taken into account for $K = l = 1$ levels, but l -resonance corrections have yet to be done. The determined molecular constants are listed in Table II. The constants of CH_3^+ are similar to those of its neutral analog CH_3 ⁹ except that the vibrational frequency is lower by 1.7% and the rotational constant by 2.3% showing that CH_3^+ is just slightly less bound than CH_3 although its bending vibrational potential is steeper.⁵ The zero-point CH distance was determined to be $r_0 = 1.091\ 51 \pm 0.000\ 09\ \text{\AA}$ as compared with $r_0 = 1.074\ 81\ \text{\AA}$ of CH_3 .⁹ The former value is in good agreement with the value $1.092\ \text{\AA}$ predicted by Botschwina *et al.*⁵

More detailed analyses of the CH_3^+ spectrum and other hydrocarbon cation spectra are in progress. We would like to thank G. Herzberg for discussions on the Rydberg state of

TABLE II. Molecular constants of CH_3^+ (in cm^{-1}).^a

$\nu_0 - (1 - \zeta) \zeta C' = 3107.8527$ (*†)	
$C' - C'\zeta - B' = -5.2244$ (18)	$(C' - B') - (C'' - B'') = 0.0530$ (16)
$B' = 9.2691$ (13)	$B'' = 9.3600$ (15)
$D_J = 6.57$ (29) $\times 10^{-4}$	$D_J'' = 7.25$ (34) $\times 10^{-4}$
$D_{JK} = -13.46$ (85) $\times 10^{-4}$	$D_{JK}'' = -14.5$ (11) $\times 10^{-4}$
$D_K - \eta_K/4 = 5.36$ (57) $\times 10^{-4}$	$D_K'' = 4.98$ (73) $\times 10^{-4}$
$\eta_J = -7.3$ (17) $\times 10^{-4}$	
$q = 9.94$ (99) $\times 10^{-3}$	$r_0 = 1.091\ 51$ (9) \AA

^aThe numbers in parentheses are one standard deviation.

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