

NOTES

Infrared spectra of carboions. II. ν_3 band of acetylene ion $C_2H_2^+$ (${}^2\Pi_u$)

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Carboions (here defined as molecular ions composed of carbon and hydrogen atoms) are well known in mass spectrometry but spectroscopic information about them has been extremely limited. The most fundamental series of polyatomic carbocations CH_n^+ ($n \geq 2$) and $C_2H_n^+$ ($n \geq 1$) have been discussed much by organic chemists as reaction intermediates, but their spectra had never been directly observed in any spectral region until the recent discovery of the ν_3 fundamental infrared band of CH_3^+ (Ref. 1, hereafter called I). In the present paper we report our observation of the infrared spectrum of another important carbocation, $C_2H_2^+$.

The only previous experimental information available on this molecular ion has been through studies of the Rydberg spectrum,²⁻⁵ photoionization,⁶ and photoelectron spectroscopy⁷ of acetylene. The frequency of the ν_2 vibration of $C_2H_2^+$ has been determined (1830 cm^{-1} in Ref. 7 and $1860 \pm 27 \text{ cm}^{-1}$ in Ref. 6) and its molecular structure was calculated [$r_{CH} = 1.070 \text{ \AA}$ and $r_{CC} = 1.257 \text{ \AA}$ and $r_{CH} = 1.06(1) \text{ \AA}$ and $r_{CC} = 1.25_5(1) \text{ \AA}$ in Ref. 8]. *Ab initio* theory⁹ predicts $r_{CH} = 1.102 \text{ \AA}$ and $r_{CC} = 1.247 \text{ \AA}$.

Our infrared spectrum has been obtained using a difference frequency laser system¹⁰ and the velocity modulation method¹¹ using an ac discharge (6 kHz) of a $C_2H_2:H_2:He$ (1:20:700) gas mixture at a total pressure of ~ 7 Torr. We have observed a great many spectral lines in the $3.2 \mu\text{m}$ region, most of which are believed to be due to the vinyl cation $C_2H_3^+$, but a definite assignment has yet to be made. The lines of $C_2H_2^+$ were identified in this bush of hydrocarbon ion transitions from their spectral pattern and different chemical behavior. The intensities of the spectral lines of $C_2H_2^+$ were reduced with respect to the rest of the lines when the H_2 concentration was increased.

Observed frequencies of $C_2H_2^+$ are listed in Table I. The strongest *P* and *R* branch lines have been observed with a signal to noise ratio of ~ 20 . As expected for a $\Pi \leftarrow \Pi$ transition, the *Q* branch lines are very weak.

The Hamiltonian for ${}^2\Pi$ molecules originally given by

Hill and Van Vleck¹² and later studied by Brown and Watson^{13,14} has been adapted to our problem in the form

$$H = B N^2 - D N^4 + [(A + A_D N^2), L_z S_z]_+ / 2 \quad (1)$$

and used to fit the spectrum. In Eq. (1), $N = J - S$ where J is the total angular momentum and S is the electron spin angular momentum, L_z and S_z are the z components of the orbital and spin angular momentum, respectively, and the $[]_+$ indicates anticommutator; B is the rotational constant, D is the centrifugal distortion constant, and A and A_D are the spin-orbit coupling constant and its centrifugal con-

TABLE I. Observed frequencies of $C_2H_2^+$ (${}^2\Pi_u$) in cm^{-1} .

Transitions	F_1	F_2
<i>R</i> (9)		3156.705
<i>R</i> (8)	3156.087	3154.574
<i>R</i> (7)	3154.013	3152.420
<i>R</i> (6)	3151.942	3150.253
<i>R</i> (5)	3149.862	3148.063
<i>R</i> (4)	3147.781	3145.860
<i>R</i> (3)	3145.690	3143.636
<i>R</i> (2)	3143.594	3141.402
<i>R</i> (1)	3141.491	3139.150
<i>Q</i> (1)	3136.177	3135.753
<i>Q</i> (2)	3136.148	3135.727
<i>Q</i> (3)	3136.118	3135.690
<i>Q</i> (4)	3136.068	3135.658
<i>Q</i> (5)	3136.009	3135.601
<i>P</i> (2)	3130.838	3132.321
<i>P</i> (3)	3128.675	3130.023
<i>P</i> (4)	3126.493	3127.711
<i>P</i> (5)	3124.300	3125.395
<i>P</i> (6)	3122.097	3123.068
<i>P</i> (7)	3119.872	3120.733
<i>P</i> (8)	3117.642	3118.390
<i>P</i> (9)	3115.396	3116.045
<i>P</i> (10)	3113.136	3113.678
<i>P</i> (11)		3111.310

TABLE II. Molecular constants of $C_2H_2^+$ (in cm^{-1}).^a

$\nu_0 = 3135.975(5)$	
$B_0 = 1.104\,56(7)$	$B' = 1.098\,95(13)$
$D_0 = 1.44 \times 10^{-6}$	$D' = 1.44 \times 10^{-6}$
$A_0 = -30.1(15)$	$A' = -29.6(15)$
$A_{D_0} = 1.7(34) \times 10^{-3}$	$A'_D = 3.3(35) \times 10^{-3}$

^aNumbers in parentheses are 3σ . Values of D_0 and D' were fixed at the calculated values.

stant, respectively. The small Λ doubling terms and the sextic centrifugal distortion terms are not included at this stage, and the spin-rotation interaction $\gamma N \cdot S$ is omitted because of the inherent indeterminacy^{13,14} between A_D and γ . Using $|\Omega\Sigma\Lambda\rangle$ as the basis set we obtain 2×2 secular equations from Eq. (1). It was realized in the process of the least squares fitting that the spin-orbit coupling constant A cannot be determined accurately from the $\Pi \leftarrow \Pi$ transition. In particular two sets of solutions with opposite signs of A fit the spectrum equally well. We take the solution with negative A value because isoelectronic species such as CN, C_2 , N_2^+ , CO^+ , etc., all have negative A values in their lowest ${}^2\Pi$ states. Values of D 's were fixed at the calculated values.¹⁵ The observed 46 lines provided 34 combination differences in the ground state which were also used in the least-squares fitting to improve ground state constants. The $C_2H_2^+$ lines with J values higher than 10 deviate considerably from the calculated pattern. The standard deviation of the fit is $0.0036\,cm^{-1}$.

The determined molecular constants are listed in Table II. The magnitude of the spin-orbit coupling constant $A = -28.4(15)\,cm^{-1}$ is much smaller than $126\,cm^{-1}$ initially suggested by Price² but is close to the estimate of $50\,cm^{-1}$ given by Herzberg.¹⁶ Accurate determination of the structure awaits the study of isotopic species, but the observed ground state rotational constant $B = 1.104\,56(7)\,cm^{-1}$ is close to that of the Rydberg G state [$1.1023(1)\,cm^{-1}$]³ and the H state [$1.104(1)\,cm^{-1}$]³ of acetylene. The

higher Rydberg spectra gave lower rotational constants [$B = 1.0932(7)\,cm^{-1}$ for the $\tilde{M}(8R)$ state and $B = 1.1006(6)\,cm^{-1}$ for the $\tilde{N}(10R)$ state]⁴ although the analysis was noted uncertain by the authors. The theoretical structure of Pople and his colleagues⁹ gives $1.0996\,cm^{-1}$. The present results confirm the earlier estimate by Hollas and Sutherberg that the C-C bond length is increased by about $0.04\text{--}0.05\,\text{\AA}$ upon ionization of acetylene.

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