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Microwave Spectra of Vinylacetylene and Monodeutero Vinylacetylene in Ground and Excited Vibrational States

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The microwave spectra of vinylacetylene, CH_2CHCCH, and monodeutero-vinylacetylene, CH_2CHCCD, have been observed in the ground state and several vibrational excited states. The vibration-rotation constants $\alpha_1^{(a)}$, $\alpha_1^{(b)}$, $\alpha_1^{(c)}$, $\alpha_2^{(a)}$, $\alpha_2^{(b)}$, and $\alpha_2^{(c)}$, have been obtained as 1 370, −18.32, −7.73, −907, −2.78, and −8.97 MHz for CH_2CHCCH, and 2 010, −16.66, −7.05, −1 640, −2.18 and −7.84 MHz for CH_2CHCCD, respectively, the error limits being ±50 MHz for $\alpha^{(a)}$'s and ±0.03 MHz for $\alpha^{(b)}$'s and $\alpha^{(c)}$'s. Electric dipole moments obtained are 0.223±0.020 and 0.206±0.008 Debye for CH_2CHCCH and CH_2CHCCD, respectively, which are quite different from the values reported previously.

The present study was begun with the purpose of getting the rotational constants of normal- and monodeutero-vinylacetylene. The values obtained have been used by Fukuyama *et al.* in their research on the structure of a series of molecules with conjugated carbon-carbon multiple bonds.[1]

The study of vibration-rotation interactions of the molecule presents another interesting theme, since infrared spectroscopy gives relatively poor information, especially below 550 cm^{-1}, where three or five fundamentals, one overtone, and one combination-tone are known to exist,[2] and some perturbations on the energy levels are supposed to exist. The data on vibrational frequencies are listed in Table 1.[*1] The author has investigated the rotational spectra in the above-mentioned vibrational states and found that strong resonances among the levels take place.

TABLE 1. LOW-LYING VIBRATIONAL LEVELS[a] (in cm^{-1})

Mode of vibration		CH_2C-$HCCH$	CH_2C-$HCCD$
ν_1 (A')	C≡C–C in plane deformation	225	212
ν_2 (A'')	C≡C–C out of plane deform.	307	287
ν_3 (A')	C=C–C bending	539	541
ν_4 (A'')	C≡C–H out of plane deform.	624	489
ν_5 (A')	C≡C–H in plane bending	667	494
ν_6 (A'')	CH_2 twisting	673[b]	676
$2\nu_1$ (A')[c]		450	424
$\nu_1+\nu_2$ (A'')[c]		532	499
$3\nu_1$ (A')[c]		675	636

a) Observed and assigned by Abe.[2]
b) Calculated by Abe.[2]
c) Sum of the corresponding fundamentals.

The electric dipole moment of the molecule has been reported by Sobolev *et al.* to be 0.43 Debye, which is obtained by analyzing the Stark effect of the transition $1_{0,1}\leftarrow 0_{0,0}$ on the assumption that $\mu_b=0$.[3] The author has tried to obtain the electric dipole moment without this assumption by analyzing transitions $J=1\leftarrow 0$ and $J=2\leftarrow 1$.

Experimental

Normal vinylacetylene, CH_2CHCCH, was supplied by Denki Kagaku Co. and was used without further purification. Impurities were checked using infrared and microwave spectra and believed to be less than 10%. Monodeutero-vinylacetylene, CH_2CHCCD, synthesized by reacting the normal species with D_2O, was contaminated with a few percent of normal vinylacetylene but was used without purification.

The rotational spectra were observed using a conventional microwave spectrometer with 110 kHz Stark modulation. Most lines were observed by cooling the waveguide cell with dry ice. The rotational transitions were assigned from the Stark effects of the lines. The relative intensities of the lines which had nearly the same Stark effect were the principal means for vibrational assignments.

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[1] T. Fukuyama, K. Kuchitsu and Y. Morino, This Bulletin, **42**, 379 (1969).

[2] K. Abe and T. Shimanouchi, *Spectrochim. Acta*, to be published.

[*1] For the sake of simplicity, subscripts for the vibrational modes start from the lowest frequency ignoring the symmetry properties.

[3] G. A. Sobolev, A. M. Scherbakov and P. A. Akishin, *Optics and Spectry.*, **12**, 78 (1962).

TABLE 2. OBSERED TRANSITIONS FOR GROUND AND LOW-LYING VIBRATIONAL STATES (in MHz)

CH$_2$CHCCH Transition	G. S. Obsd	ν_1 Obsd	ν_2 Obsd
$0_{0,0}\rightarrow 1_{0,1}$	9 074.74±0.02	9 100.73±0.02	9 086.3 ±0.02
$1_{0,1}\rightarrow 2_{0,2}$	18 146.58±0.02	18 198.58±0.02	18 169.97±0.02
$1_{1,1}\rightarrow 2_{1,2}$	17 734.53±0.02	17 776.05±0.02	17 763.05±0.02
$1_{1,0}\rightarrow 2_{1,1}$	18 564.91±0.02	18 627.64±0.02	18 582.16±0.02
$2_{0,2}\rightarrow 3_{0,3}$	27 212.62±0.02	27 290.06±0.02	27 248.22±0.02
$2_{1,2}\rightarrow 3_{1,3}$	26 599.93±0.02	26 662.18±0.02	26 644.19±0.02
$2_{1,1}\rightarrow 3_{1,2}$	27 845.38±0.02	27 939.32±0.02	27 871.38±0.02
$2_{2,1}\rightarrow 3_{2,2}$	27 225.99±0.02	27 303.86±0.02	27 261.07±0.02
$2_{2,0}\rightarrow 3_{2,1}$	27 237.27±0.02	27 316.07±0.02	27 271.76±0.03

CH$_2$CHCCH Transition	$\nu_1+\nu_2$ Obsd	$2\nu_1$ Obsd	$2\nu_2$ Obsd.
$0_{0,0}\rightarrow 1_{0,1}$	9 113.0 ±0.1	9 127.5 ±0.1	
$1_{0,1}\rightarrow 2_{0,2}$	18 221.1 ±0.1	18 429.1 ±0.1	
$1_{1,1}\rightarrow 2_{1,2}$	17 806.5 ±0.1	17 816.5 ±0.1	17 794.0 ±0.3
$1_{1,0}\rightarrow 2_{1,1}$	18 643.0 ±0.2	18 689.3 ±0.1	18 600.3 ±0.3
$2_{0,2}\rightarrow 3_{0,3}$		27 365.77±0.05	
$2_{1,2}\rightarrow 3_{1,3}$	26 707.0 ±0.1	26 723.00±0.05	26 688.0 ±0.3
$2_{1,1}\rightarrow 3_{1,2}$	27 961.70±0.05	28 031.60±0.05	27 898.0 ±0.3
$2_{2,1}\rightarrow 3_{2,2}$		27 380.29±0.05	
$2_{2,0}\rightarrow 3_{2,1}$		27 392.95±0.05	

CH$_2$CHCCD Transition	G. S. Obsd	ν_1 Obsd	ν_2 Obsd
$0_{0,0}\rightarrow 1_{0,1}$	8 441.80±0.01	8 465.51±0.01	8 451.79±0.02
$1_{0,1}\rightarrow 2_{0,2}$	16 881.20±0.02	16 928.58±0.02	16 901.31±0.03
$1_{1,1}\rightarrow 2_{1,2}$	16 517.60±0.02	16 555.46±0.02	16 543.22±0.03
$1_{1,0}\rightarrow 2_{1,1}$	17 249.87±0.02	17 307.00±0.02	17 264.30±0.03
$2_{0,2}\rightarrow 3_{0,3}$	25 316.27±0.01	25 386.83±0.02	25 346.73±0.03
$2_{1,2}\rightarrow 3_{1,3}$	24 774.82±0.01	24 831.33±0.02	24 813.36±0.03
$2_{1,1}\rightarrow 3_{1,2}$	25 873.50±0.01	25 958.95±0.02	25 895.14±0.03
$2_{2,1}\rightarrow 3_{2,2}$	25 326.13±0.01	25 397.10±0.02	25 357.46±0.03
$2_{2,0}\rightarrow 3_{2,1}$	25 334.49±0.01	25 406.26±0.02	25 365.29±0.03
$3_{0,3}\rightarrow 4_{0,4}$	33 745.50±0.01		33 776.6 ±0.1
$3_{1,3}\rightarrow 4_{1,4}$	33 030.31±0.01	33 105.75±0.01	33 082.04±0.02
$3_{1,3}\rightarrow 4_{1,3}$	34 495.38±0.01	34 609.02±0.01	34 524.30±0.02
$3_{2,2}\rightarrow 4_{2,3}$	33 767.46±0.01	33 862.11±0.01	33 800.70±0.02
$3_{2,1}\rightarrow 4_{2,2}$	33 789.54±0.01	33 885.69±0.01	33 821.56±0.02
$3_{3,1}\rightarrow 4_{3,2}$ $3_{3,0}\rightarrow 4_{3,1}$	33 776.76±0.05	33 870.98±0.07	33 812.07±0.08

CH$_2$CHCCD Transition	$2\nu_1$ Obsd	$3\nu_1$ Obsd	$2\nu_2$ Obsd
$0_{0,0}\rightarrow 1_{0,1}$	8 489.0 ±0.1	8 512.0 ±0.1	
$1_{0,1}\rightarrow 2_{0,2}$	16 975.5 ±0.2	17 019.5 ±0.2	16 922.0 ±0.3
$1_{1,1}\rightarrow 2_{1,2}$	16 592.5 ±0.2		16 569.0 ±0.3
$1_{1,0}\rightarrow 2_{1,1}$	17 362.3 ±0.3	17 418.7 ±0.3	17 279.5 ±0.3
$2_{0,2}\rightarrow 3_{0,3}$			
$2_{1,2}\rightarrow 3_{1,3}$	24 886.5 ±0.3	24 942.1 ±0.3	24 853.1 ±0.3
$2_{1,1}\rightarrow 3_{1,2}$	26 043.3 ±0.3	26 125.3 ±0.5	25 918.3 ±0.3
$2_{2,1}\rightarrow 3_{2,2}$	25 468.3 ±0.5	25 536.8 ±0.5	
$2_{2,0}\rightarrow 3_{2,1}$	25 476.5 ±0.5	25 546.0 ±0.5	
$3_{0,3}\rightarrow 4_{0,4}$			
$3_{1,3}\rightarrow 4_{1,4}$	33 179.8 ±0.3	33 251.7 ±0.3	
$3_{1,2}\rightarrow 4_{1,3}$	34 720.0 ±0.3	34 831.0 ±0.3	34 554.0 ±0.3
$3_{2,2}\rightarrow 4_{2,3}$	33 955.0 ±0.5		
$3_{2,1}\rightarrow 4_{2,2}$	33 980.3 ±0.5		
$3_{3,1}\rightarrow 4_{3,2}$	33 964.0 ±0.5		
$3_{3,0}\rightarrow 4_{3,1}$	33 964.0 ±0.5		

Results

The transitions assigned are listed in Table 2. No b-type transition was observed in spite of a careful search. Because of this and a slight asymmetry of the molecule, it was impossible to obtain the exact value of the rotational constant A. Table 3 lists the derived constants B_0 and C_0 for the ground vibrational state and vibration-rotation constants $\alpha_i^{(b)}$ and $\alpha_i^{(c)}$ for ν_1 and ν_2 states. When the perturbation method is used, the value of A can be obtained from the deviation of the observed lines from the symmetric-top pattern through the value of $(B-C)^2/(A-(B+C)/2)$. The values of A_0, $\alpha_1^{(a)}$, and $\alpha_2^{(a)}$ thus obtained are listed also in Table 3.

TABLE 3. DERIVED MOLECULAR CONSTANTS (in MHz)

	CH_2CHCCH	CH_2CHCCD
A_0	49 900 ± 750	48 900 ± 1600
B_0	4 744.66 ± 0.03	4 403.82 ± 0.08
C_0	4 329.68 ± 0.03	4 037.58 ± 0.08
$\alpha_1^{(a)}$	1 370 ± 50	2 010 ± 70
$\alpha_1^{(b)}$	−18.32 ± 0.03	−16.66 ± 0.05
$\alpha_1^{(c)}$	− 7.73 ± 0.03	− 7.05 ± 0.05
$\alpha_2^{(a)}$	−907 ± 50	−1 640 ± 50
$\alpha_2^{(b)}$	− 2.78 ± 0.03	− 2.18 ± 0.03
$\alpha_2^{(c)}$	− 8.97 ± 0.03	− 7.84 ± 0.03

Assignment of the rotational transitions in ν_3, ν_4, and ν_5 states was unsuccessful, because the Coriolis coupling between the states disturbs the spectra strongly in both CH_2CHCCH and CH_2CHCCD, and the $\nu_1+\nu_2$ state of the latter interacts with ν_4 and ν_5 through Fermi resonance. Further analysis and discussion on the problem will be given in a separate paper.

The Stark effects of the transitions $J=1\leftarrow0$ and $J=2\leftarrow1$ in the ground vibrational state were measured. From the results (Table 4), the electric dipole moments μ_a of the molecule were derived to be 0.223±0.020 and 0.206±0.008 Debye for normal and monodeutero-vinylacetylene, respectively. Analysis of the Stark effect revealed that μ_b is very small. Its value can not be determined accurately in spite of the fact that some of the transitions such as $3_{1,3}\leftarrow2_{1,2}$ $(M=0)$ have an appreciable dependence on μ_b^2.

As suggested by Morgan and Goldstein,[4] who observed five lines of the transitions $J=3\leftarrow2$ in the ground vibrational state of CH_2CHCCH, the effect of the centrifugal distortion is not negligible, and centrifugal distortion shifts of a few MHz is observed even in $J=3\leftarrow2$ transitions. However, because of the smallness of the molecular asymmetry and the failure to observe b-type transitions, it was not possible to determine the centrifugal distortion constants.

Discussion

Molecular Structure. The rotational constants observed in the present study were used by Fukuyama *et al.*[1] in combination with their electron-differaction data to determine the structure of the molecule.

Vibration-Rotation Constants. The rotational energy levels in an excited vibrational state are known to approximate a rigid rotor model when no vibrational state perturb the state,[5] and the rotational constants in the state v are expressed as B_v, which can be written in terms of α_v constants as

$$B_v^{(x)} = B_0^{(x)} - \alpha_v^{(x)} \qquad (1)$$

The $\alpha_v^{(x)}$ constants are the sum of two terms, one determined by the harmonic terms in the internal

TABLE 4. STARK EFFECTS OF ABSORPTION LINES (in 10^{-5} MHz(V/cm)^2) AND ELECTRIC DIPOLE MOMENT OF THE MOLECULE (in Debye)

Transition		CH_2CHCCH Obsd	Calcd	CH_2CHCCD Obsd	Calcd
$0_{0,0}\rightarrow1_{0,1}$	$M=0$	0.290 ±0.003	0.293	0.256 ±0.006	0.269
$1_{0,1}\rightarrow2_{0,2}$	$M=0$	−0.0887±0.0005	−0.0836	−0.0772±0.0006	−0.0771
	$M=1$	0.0730±0.0008	0.680	0.0619±0.0006	0.0620
$1_{1,1}\rightarrow2_{1,2}$	$M=0$	0.0745±0.0006	0.0696	0.0658±0.0008	0.0635
	$M=1$	2.873 ±0.07	2.930		
$1_{1,0}\rightarrow2_{1,1}$	$M=0$	0.0617±0.0007	0.0665	0.0614±0.0008	0.0608
	$M=1$	−2.554 ±0.06	−2.840		
μ_a		0.223 ±0.020		0.206 ±0.008	
μ_b		0.02		0.02	

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[4] H. W. Morgan and J. H. Goldstein, *J. Chem. Phys.*, **20**, 1981 (1952).

[5] H. H. Nielsen, *Phys. Rev.*, **75**, 1961 (1949); T. Oka and Y. Morino, *J. Mol. Spectry.*, **6**, 472 (1961); T. Oka, *J. Chem. Phys.*, **47**, 5410 (1967).

[6] Y. Morino and C. Hirose, *J. Mol. Spectry.*, **22**, 99 (1967).

[7] Y. Morino and C. Hirose, *ibid.*, **24**, 204 (1967).

TABLE 5. THE VALUES OF $\alpha v^{(x)}/(B_0{}^{(x)})^2$

	$\alpha_1{}^{(b)}/B_0{}^2$	$\alpha_1{}^{(c)}/C_0{}^2$	$\alpha_2{}^{(b)}/B_0{}^2$	$\alpha_2{}^{(c)}/C_0{}^2$	
C_4H_4	−8.14	−4.12	−1.23	−4.76	10^{-7}MHz^{-1}
C_4H_3D	−8.59	−4.32	−1.12	−4.81	

potential field and the other which depends on the anharmonic potential field; both are proportional to the square of the rotational constants.5) The values of $\alpha_v{}^{(x)}/B_0{}^{(x)2}$ derived from the constants given in Table 3 are listed in Table 5. The values for C_4H_4 and C_4H_3D show a good correspondence with each other.

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