AIP The Journal of Chemical Physics

# The RotationVibration Spectra of Allene and Allened4

R. C. Lord and Putcha Venkateswarlu

Citation: J. Chem. Phys. **20**, 1237 (1952); doi: 10.1063/1.1700718 View online: http://dx.doi.org/10.1063/1.1700718 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v20/i8 Published by the American Institute of Physics.

# Additional information on J. Chem. Phys.

Journal Homepage: http://jcp.aip.org/ Journal Information: http://jcp.aip.org/about/about\_the\_journal Top downloads: http://jcp.aip.org/features/most\_downloaded Information for Authors: http://jcp.aip.org/authors



# The Rotation-Vibration Spectra of Allene and Allene- $d_4$

R. C. LORD AND PUTCHA VENKATESWARLU

Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge 39, Massachusetts

(Received February 25, 1952)

The infrared absorption spectra of allene and allene- $d_4$  vapor have been measured over the spectral range 250-5000 cm<sup>-1</sup> with a prism spectrometer. The infrared data, together with previously obtained Raman spectra, enable a complete vibrational analysis that satisfies the product rule well for all vibrational species. The torsional vibration is located at 865 cm<sup>-1</sup> in allene and 615 cm<sup>-1</sup> in allene- $d_4$ . Fine structure was resolved for all perpendicular fundamental bands except that of the lowest frequency in both compounds. With help of the zeta-sum rule, a modified equation of H. H. Nielsen and the statistical weights of the rotational levels, the fine structure is analyzed to yield a complete set of zeta-values for both molecules and a moderately accurate value for the moment of inertia about the figure axis. The latter gives for the HCH angle the figure 113°±1° if one assumes a C-H distance of 1.071A.

### INTRODUCTION

**F**OR many reasons the rotation-vibration spectra of the allene molecule  $-H_2C=C=CH_2$  – are of special interest. It is the smallest molecule with cumulative double bonds, and therefore knowledge of its structure is important. The frequency of its torsional mode of vibration and the size of the H-C-H bond angle are relevant data in the theory of its electronic structure and chemical binding. The unusual possibilities for rotation-vibration interaction in the  $D_{2d}$ structure of the molecule make it a nice example for spectroscopic study.

The infrared absorption spectrum of allene vapor has been investigated by Linnett and Avery,1 Thompson and Harris,<sup>2</sup> and Miller and Thompson.<sup>3</sup> The spectrum of allene in the photographic infrared region was also examined by Eyster.<sup>4</sup> Three of the perpendicular fundamentals were well resolved by Thompson and coworkers,<sup>2,3</sup> but the band centers were not definitely established. The low frequency perpendicular fundamental which was placed at 353 cm<sup>-1</sup> by earlier work in the Raman effect<sup>1</sup> lies outside the region investigated by previous infrared workers. No data have been published on the infrared spectrum of allene- $d_4$ . Investigation of the infrared and Raman spectra both of allene and allene- $d_4$  was thought to be desirable to establish the vibrational assignment and the structure without ambiguity. The Raman spectra of these molecules were studied by Lord and Ocampo in this Laboratory,<sup>5</sup> and in the present paper the infrared spectra of allene and allene- $d_4$  are reported. Together the infrared and Raman data lead to a complete vibrational analysis and a moderately accurate determination of the H-C-H angle.

# EXPERIMENTAL DETAILS

# Preparation of Allene and Allene- $d_4$

The preparation of allene was carried out as usual by the dehalogenation of 2,3-dibromopropene with zinc dust in alcoholic solution.<sup>6</sup> This method will produce allene contaminated with propene if the 2,3dibromopropene contains a slight amount of 2,3dibromopropane.<sup>2, 6</sup> In the sample of allene for which a Raman spectrum was reported earlier,<sup>5</sup> this contamination resulted in the presence of three weak lines at the points where propene has its most intense Raman lines (920, 1296, and 1646  $\text{cm}^{-1}$ ). In subsequent preparation of allene by this method, contamination by propene was absent, as shown by the absence from the infrared spectrum of the strong propene bands at 580, 920, and 1646 cm<sup>-1</sup>. Presumably this means that the 2,3dibromopropene used in the preparation of the allene on which the infrared studies were made was of higher purity than that from which the Raman sample was prepared.

Allene- $d_4$  was obtained as a by-product in the preparation of methyl acetylene- $d_4$ , with which it is isomeric. The latter was synthesized in large quantity from the tricarbide of magnesium (Mg<sub>2</sub>C<sub>3</sub>) by passing deuterium oxide vapor over the carbide at elevated temperatures (>150°C).<sup>7</sup> The presence of allene bands in the spec-

TABLE I. Equilibrium between methyl acetylene and allene.

Т°К	$-\Delta (F^{0} - E_{0}^{0}) / T$	$K_{eq}(calc)$	"K <sub>obs</sub> "
300	-0.78	0.040	
400	-0.86	0.078	< 0.01
523	-0.93	0.123	0.01
623	-0.97	0.157	0.05
800	-1.00	0.209	
1000	-1.00	0.258	

 $K_{eq} = p(\text{allene})/p(\text{methyl acetylene})$  $\Delta E_0^0 = +1689 \text{ cal (reference 10)}$ 

<sup>&</sup>lt;sup>1</sup> J. W. Linnett and W. H. Avery, J. Chem. Phys. **6**, 686 (1938). <sup>2</sup> H. W. Thompson and G. P. Harris, Trans. Faraday Soc. 40,

<sup>295 (1944).
&</sup>lt;sup>3</sup> C. H. Miller and H. W. Thompson, Proc. Roy. Soc. (London)
200, 1 (1949).

<sup>&</sup>lt;sup>4</sup> E. H. Eyster, J. Chem. Phys. 6, 580 (1938).

<sup>&</sup>lt;sup>5</sup> R. C. Lord and J. Ocampo, J. Chem. Phys. 19, 260 (1951).

<sup>&</sup>lt;sup>6</sup> See, for example, Kistiakowsky, Ruhoff, Smith, and Vaughn, J. Am. Chem. Soc. 58, 146 (1936).

<sup>&</sup>lt;sup>7</sup> See A. W. Baker, doctoral thesis, "The Preparation of Cyclopropane- $d_{6}$ , etc.," Massachusetts Institute of Technology, Sep-

trum of methyl acetylene prepared in this way was noted, as was an increase in the relative amount of allene when the preparation was carried out at higher temperature (ca 350°C). Investigation of the thermodynamics of the isomerization of methyl acetylene to allene shows that increased temperature does indeed favor the conversion.

In Table I are listed the equilibrium constants for the isomerization as calculated from the thermodynamic functions for methyl acetylene<sup>8</sup> and allene,<sup>1</sup> and the heats of hydrogenation of the two compounds.<sup>6,9</sup> It is

Obs. fre-						• .
quency					Rama	n data
(cm <sup>-1</sup>	Band	Inten-		Calc.	Freq.	Est'd.
in vac.)	typea	sityb	Assignment	freq.º	(cm <sup>-1</sup> )	int.
354	Not Res.	202	$\nu_{11}(e)$		356	3.
	_		2111		707	2 6
842	Res.	326	$\nu_{10}(e)$		848	50
			$\nu_4(b_1)$		865	_1
	_				(920)	Imp.
1015	Res.	64	$v_{\theta}(e)$		991	3
			$\nu_{3}(a_{1})$		1076	10 pol
			$\nu_4 + \nu_{11}(E)$	1221	1226	_1
					(1296)	Imp.
			$\nu_9 + \nu_{11}$	(1369)	1351	
1384 b	$P_{1}$					
1398 s	Q	85	$\nu_7(b_2)$		1421	2
1408 b	R					
			$\nu_2(a_1)$		1440	_9 pol
	-				(1646)	Imp.
1675 b	P	184	2 via ( B)		1694	
1698 6	R		ar 10(1/2/		10/1	
1942.2 b	P					
1950.2 s		1000	$\nu_6 + \nu_{11} - \nu_{11}$		1960	
1956.5 s	$Q_{i}$	1000	$\nu_6(b_2)$		1700	
1970 b	R)	-				
1996.7.7	<b>n</b> . n	7	a (B)			
2015	Part. Res.	95	$2\nu_{9}(B_{2})$	2030		~
		_	$2\nu_9(A_1)$	2030	2043	0
2428.5	Res.	1	V7 + V9(上)	2412		
	ע א		$\nu_2 + \nu_9(E)$	2455		
2814.5 0	P	10	1 (7)	0017		
2820.7 5	¥}	12	$\nu_2 + \nu_7(D_2)$	2837		
2840 0	K		2 (1)	2000	0041	
2809.5 \$	¥}	0	$2\nu_2(A_1)$	2880	2801	3
2884.7 0	R)		$\nu_4 + 2\nu_9(D_2)$	2895		
2920 0	r l	9	$\nu_3 + \nu_9 + \nu_{10}(B_2)$	2933		
2932.0 5	Q	12	(E)	2077		
2955		15	$\nu_6 + \nu_9(\mathbf{E})$	2973	2006	101
2005 4 5	ומ		$\nu_1(a_1)$		2990	TO DOI
2995.40	5	140	w. (h.)			
0000.45 00105h	¥{	149	P6(02)			
2025	Poo	50	n=(a)		2067	01
1065	P	50	V8(e)		3007	00
1086		10	$\nu_8 + \nu_9(B_2)$	4100		
1156	b i i i i i i i i i i i i i i i i i i i	1	$\mu_2 \pm \mu_0(E)$	4161		
1220 h	(P)		P3 ["P8(L)]	4101		•
1255 h	R	3	$2\nu_2 + \nu_7(B)_2$	4278		
1480 h	Part Ree	19	$\nu_7 + \nu_8(E)$	4483		
1766 b	1 311. 1005.	3	$u_{8} + 2u_{10}(E)$	4760		
		3	$(v_{\theta} + v_{\theta}(E))$	5043		
1988 b		5	$v_1 + v_2(B_2)$	4954		
5963 h		30	$\mu_1 + \mu_2(B_2)$	6000		
630		1	$\nu_1 + \nu_2(E)$	6080		
5141 b		17	$2\nu_8(B_2)$	6170		
				0110		

TABLE II. Infrared data for allene vapor (300-6100 cm<sup>-1</sup>).

\* Abbreviations: s = sharp, b = broad, n = no distinct maximum. P. Q. and R refer to peaks that are P. Q. and R branches, respectively. "Res" means the band is a perpendicular band whose constituent sub-bands have been resolved. The wave-number value given corresponds to the band P, Q, 'Res'' origin.

The intensity of the strongest band is assumed to be 1000 and the in-<sup>b</sup> The intensity of the strongest band is assumed to be 1000 and the intensities of the other bands are calculated with the assumption that the intensity is proportional to  $(1/pl)\log(I_0/I)$  where p and l are pressure and path lengths and where  $I_0$  and I are the incident and transmitted intensities, respectively. Since the width of the bands is not taken into consideration, and the dependence of peak height and slit width used and the effect of pressure broadening on peak heights are neglected, the relative intensities given are quite rough.

tember, 1950. The synthesis of methyl acetylene- $d_4$  will be de-

scribed in some detail as a part of the publication of this thesis. <sup>8</sup> B. L. Crawford, Jr., J. Chem. Phys. 8, 526 (1940); 9, 69 (1941). <sup>9</sup> Conn, Kistiakowsky, and Smith, J. Am. Chem. Soc. 61, 1868 (1939).

necessary to change the free energy values tabulated for allene in reference 1 because they were calculated with a symmetry number of 12. This value of the symmetry number is not explicitly mentioned anywhere in reference 1 but is apparent from the equation for the translational and rotational parts of the entropy as well as from the tabulated entropy values. The symmetry number for a  $D_{2d}$  structure is 4, and hence the entropy and  $-(F^0 - E_0^0)/T$  values need to be increased by  $R \ln 3$ , as was pointed out by Frank-Kamenetzki and Markovich.<sup>10</sup> These authors also computed the value of  $\Delta E_0^0$  from which the results of Table I were obtained.

TABLE III. Infrared data for allene- $d_4$  vapor (250-5000 cm<sup>-1</sup>).

Obs. fre-					Rama	in data
(cm <sup>-1</sup> in vac.)	Band type <sup>a</sup>	Inten- sity <sup>b</sup>	Assignment	Calc. freq.º	Freq. (cm <sup>-1</sup> )	Est'd. int.
306 b	Not Res.	413	v11(e)		315	2 b
498 s		59	; ;		450	Ū
667	Pea	650	$2\nu_{11}$		615	0
(830)	Part. Res.	128	$\nu_{10}(e)$ $\nu_{9}(e)$		847	2
			$3\nu_{11}$	920	8/4 933	10 poi 3
			<i>v</i> 4 + <i>v</i> 11∫ <i>v</i> 10 + <i>v</i> 11	982	987	3
1021.9 b 1034.2 s 1046.7 b	$\left. \begin{array}{c} P \\ Q \\ R \end{array} \right\}$	128	¥7(b2)		1053	2 b
1138 b		413	$\nu_9 + \nu_{11}$	1153	1151	
			$2\nu_4(A_1)$ $\nu_2(a_1)$	1230	1203 1228	1 8 pol
1325.3 b 1337.6 s	$\left. \begin{array}{c} P \\ Q \\ P \end{array} \right\}$	156	$2\nu_{10}(B_2)$	1332		
1360 n	N)	31	V7+V11(E)	1340		
1395 b	$\left. \begin{array}{c} r\\ R \end{array} \right\}$	54	$\nu_9 + 2\nu_{11}(B_2)$	1417		
1905.2 b	P)		$\nu_3 + \nu_7(B_2)$	1908	1587	3
1914.8 s	-		** + *** - ***			
1921.1 s	$\left. \begin{array}{c} Q \\ R \end{array} \right $	1000	$\nu_6(b_2)$			
2069 b	xc)	31	$\begin{cases} 2\nu_2 + \nu_{11}(E) \\ \nu_2 + \nu_9(E) \end{cases}$	2054 2058	2070	2 b
2130 b	Part. Res.	38	$2\nu_7(A_1)$ $\nu_9 + 2\nu_{10}(E)$	2106 2164	2120 2152	3 b 3
2204		67	$\nu_1(a_1)$ $\nu_6 + \nu_{11}(E)$	2227	2195	10 poi
2224 2229.6 2236.8	$\left. \begin{array}{c} P \\ Q \\ R \end{array} \right\}$	183	$\nu_{\delta}(b_2)$			
2267.4	<i>L</i> ()	15	$\nu_2 + \nu_7(B_2)$	2262		
2330 2603 77 h	Res.	57	v8(e)		2304	5 b
2614.3 s 2624.7 b	$\left. \begin{array}{c} Q \\ R \end{array} \right $	16	$\nu_8 + \nu_{11}(B_2)$	2636		
2780 b 2790.1 s	$\left. \begin{array}{c} \overline{P} \\ Q \end{array} \right\}$	42	$\nu_3 + \nu_6(B_2)$	2795		
2800.0 b 2870.2 b	R)	139	$\nu_5 + \nu_{10}(E)$	2890		
2947 b 2981.0	P)	31	$\nu_4 + \nu_8(E)$	2945		
2984.9 2989.6	$O \\ R $	131	$\nu_8 + \nu_{10}(B_2)$ $\nu_1 + \nu_9(E)$	2996 3000		
3129 b 3140	$\left. \begin{array}{c} P \\ Q \end{array} \right\}$	45	$\nu_8 + \nu_9(B_2)$	3135		
3151 b 3329 b	R)	11	$\nu_7 + \nu_8(E)$	3364		
4411 b	$\left  P \right\rangle$	5 28	$2\nu_7 + \nu_8(E)$ $\nu_1 + \nu_5(B_2)$	4398 4421		
4431 b 4489 b	K)	17	$\nu_1 + \nu_8(E)$	4499		
4010 b 4631.5 b	$\left. \begin{smallmatrix} P \\ R \end{smallmatrix} \right\}$	26	$2\nu_8(B_2)$	4660		

a, b, c See corresponding notes in Table II.

<sup>10</sup> D. A. Frank-Kamenetzki and V. G. Markovich, Acta Physicochim. U.R.S.S. 17, 308 (1942).



FIG. 1. Infrared absorption of allene vapor, 300-6100 cm<sup>-1</sup>.

In the formation of methyl acetylene and allene from  $Mg_2C_3$ , there is no assurance that the two are formed in equilibrium amounts, and the experimental evidence is indeed against this.<sup>11</sup> Although the calculated equilibrium at 150°C calls for roughly 10 percent allene, indications are that decidedly less than 1 percent allene is formed. As the temperature is increased, the percentage of allene goes up, the observed rate of increase being much larger than the calculated. However, it may simply be that the higher temperature facilitates isomerization and that the observed increase is attributable entirely to more rapid approach to equi-

librium. At the highest temperature where measurement was made, the observed allene concentration was still smaller than calculated by a factor three. Higher temperature studies were ruled out, so far as the purposes of the present investigation were concerned, by the considerable pyrolysis observed for the hydrocarbon products.

In Table I are also given values for the observed ratio " $K_{obs}$ " of allene to methyl acetylene produced by hydrolysis of Mg<sub>2</sub>C<sub>3</sub> at the indicated temperatures. The amount of allene was determined by difference in a gas-volumetric procedure in which the methyl acetylene was removed from a fixed volume of vapor mixture by precipitation as the silver complex, and then re-

<sup>&</sup>lt;sup>11</sup> See J. Ocampo, bachelor's thesis, Massachusetts Institute of Technology, September, 1950.



FIG. 2. Infrared absorption of allene- $d_4$  vapor, 250–5000 cm<sup>-1</sup>.

generated and measured volumetrically. It is impossible to reconcile the temperature dependence of " $K_{obs}$ " with that of the calculated  $K_{eq}$ . In view of the lack of evidence for equilibrium, the " $K_{obs}$ " values merely can be taken as qualitative indication of the preferential formation of methyl acetylene.

Allene- $d_4$  was separated from methyl acetylene- $d_4$  by slowly passing a mixture of the two gases formed at 350°C from heavy water and Mg<sub>2</sub>C<sub>3</sub> through an ammonical silver nitrate solution.<sup>11</sup> Ammonia was scrubbed from the allene- $d_4$  by dilute aqueous HCl and then water removed by passage through a drying train. From approximately 40 cc of liquid methyl acetylene- $d_4$ , 2 cc of liquid allene- $d_4$  were recovered. The Raman spectrum of this material was taken before the ammonia was removed,<sup>11</sup> but the amount of ammonia present was too small to detect in the Raman effect. The infrared studies here reported were carried out after the removal of ammonia and the fact that this removal was incomplete is indicated in Fig. 2.

In the course of the synthesis of cyclopropane- $d_6$ ,

propene- $d_6$  was prepared.<sup>7</sup> Comparison of the infrared spectrum of the latter with that of our sample of allene- $d_4$  showed no contamination of allene- $d_4$  by propene- $d_6$ . The infrared spectrum also showed that the removal of methyl acetylene- $d_4$  was complete.

# **Spectroscopic Procedures**

The infrared spectra of gaseous allene and allene- $d_4$ were recorded with a Perkin-Elmer 12B Spectrometer. This instrument was modified<sup>12</sup> to enable the elimination of water vapor absorption from the spectrum. Spectra were taken with prisms of LiF, CaF<sub>2</sub>, NaCl, KBr, and TlBr-TlI ("KRS-5"), each prism being used in its region of optimum dispersion. Achieved resolution is very close to 3 cm<sup>-1</sup> throughout the region 250– 3500 cm<sup>-1</sup>, and the frequency precision is seldom worse than 1 cm<sup>-1</sup> except possibly above 3200 cm<sup>-1</sup>. The absorption cell had a path length of 6 cm and windows of potassium iodide. Various gas pressures were used, as indicated in the figures. The spectra are shown in

<sup>12</sup> Lord, McDonald, and Miller, J. Opt. Soc. Am. 42, 149 (1952).

Figs. 1 and 2, and the frequencies in  $cm^{-1}$  tabulated in Tables II and III.

The Raman frequencies, also listed in Tables II and III, are essentially those reported earlier.<sup>5</sup> The low temperature Raman technique and the method of determining the state of depolarization of the Raman lines were those of Lord and Nielsen.<sup>13</sup> Apart from the previously mentioned identification of the Raman lines at 920, 1296, and 1646 cm<sup>-1</sup> as those of propene and not allene, no serious corrections are required by the results of the present paper in the data of reference 5. There are several lines reported there that have not been found earlier. These lie at 865, 991, 1351, 1421, and 2043 cm<sup>-1</sup>, and failure of Linnett and Avery<sup>1</sup> to report them is readily understandable from the published microphotometer record of their Raman spectrum. The line at 865 is quite weak and lies rather close to the somewhat broad line at 848, while the line at 1351 is weak and unresolved from the strong 3067 line excited by Hg-4047, which was not filtered out in their work. The 1421 line is not easy to separate from the intense line at 1440, and the 2043 line is extremely weak, though comparable to the 1959 line reported both in reference 1 and 5. The 991 line requires special comment. As excited by Hg-4358, it was obscured on their microphotometer trace by the 1076 line from Hg-4339. It is strong enough, however, to have been found as excited by Hg-4047, but at the precise position on the trace where it should occur, there is a clear-cut line contour labeled, unfortunately but no doubt correctly, "scratch." This point is brought out because the 991 line is later identified as a fundamental.

# **Discussion of Spectra**

The most probable structures for the allene molecule are of symmetry  $D_{2d}$  and  $D_{2h}$ . The former, which is favored by valence theory, is a symmetrical-top rotator and the latter, an asymmetrical-top rotator. A  $D_{2h}$ structure has a center of symmetry, while the  $D_{2d}$ structure does not. The infrared evidence is clear-cut that the allene molecule is a prolate symmetrical top, and the considerable number of coincidences between infrared and Raman frequencies rule out a symmetry center. On these general grounds, the  $D_{2h}$  structure is rejected, and, as will be shown below, the detailed features of both infrared and Raman spectra are in agreement with  $D_{2d}$  symmetry.

An allene molecule of  $D_{2d}$  symmetry has three totally symmetrical vibrations  $(A_1)$  which are Raman-active and polarized, one torsional vibration of species  $B_1$ , which is Raman-active and depolarized, three vibrations of species  $B_2$ , which is both infrared and Raman active (depolarized), and four doubly-degenerate vibrations of species E, also infrared and Raman-active (depolarized).<sup>14</sup> Thus all vibrations are Raman-active. The  $A_1$  species can be recognized by its polarized lines, the  $B_1$  species because it is inactive in the infrared, the  $B_2$  species by its parallel infrared bands, and the Especies by the perpendicular bands. There is thus a clear-cut means of assigning each observed Raman line and infrared band to its species. When this is done as indicated in Table IV, the resultant frequency values for allene and allene- $d_4$  satisfy the Teller-Redlich product rule<sup>15</sup> very well.

The fundamental assignment of Table IV is virtually identical with that of reference 1, but in view of the considerably firmer basis provided for it by improved spectroscopic techniques and the data for allene- $d_4$ , some comment is required.

#### Species $A_1$

The assignment is definite in view of the polarization measurements on both allene and allene- $d_4$ . The frequency values in allene- $d_4$ , however, indicate that qualitative descriptions such as those in column 3 of Table IV are only approximate. If the 1440 frequency in allene were a pure CH<sub>2</sub> bending, it should shift by  $1/\sqrt{2}$  in allene- $d_4$ , or to about 1020 cm<sup>-1</sup>. Actually the shift is only half this large. The symmetrical C=C=Cstretching frequency at 1076, which should be expected to change only slightly in allene- $d_4$ , moves a relatively larger amount. This means that both in allene and in allene- $d_4$ , especially the latter, the actual vibration forms are imprecisely described by the simple labels in column 3.

# Species $B_1$

In reference 1, the torsional frequency was placed in the neighborhood of  $820 \text{ cm}^{-1}$  from the results of heat capacity measurements, since it was not observed directly. This figure is still approximately valid in view of the unchanged frequency assignment, but receives additional support from the weak but quite definite

TABLE IV. Assignment of fundamental frequencies in allene and allene- $d_4$  ( $D_{2d}$  structure).

Vib'l.	Frea.		Frequenc	ies in cm⁻¹	Produ	ct rule
species	no.	Type of vibration	Allene	Allene-d4	$\tau_{\rm obs}$	$\tau_{calc}$
<i>A</i> <sub>1</sub>	1 2 3	C-H stretching CH <sub>2</sub> bending C=C=C stretching	2996 1440 1076	2195 1288 874	1.97	2.000
$B_1$	4	CH <sub>2</sub> torsion	865	615	1.407	1.414
$B_2$	5 6 7	C-H stretching C=C=C stretching CH <sub>2</sub> bending	3005 1957 1398	2230 1921 1034	1,86	1.907
Ε	8 9 10 11	C-H stretching CH <sub>2</sub> rocking C=C=C bending	${ \begin{array}{c} 3085 \\ 1015 \\ 842 \\ 354 \end{array} }$	2330 830 667 306	2.43	2.391

<sup>14</sup> See G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 339; see also reference 1 and R. C. Herman and W. H. Shaffer, J. Chem. Phys. 17, 30 (1949).

17, 30 (1949). <sup>15</sup> See Herzberg, reference 14, p. 231 *ff*; also F. Halverson, Revs. Modern Phys. 19, 87 (1947).

<sup>&</sup>lt;sup>13</sup> R. C. Lord and E. Nielsen, J. Opt. Soc. Am. 40, 655 (1950); J. Chem. Phys. 19, 1 (1951).

line at 865 cm<sup>-1</sup> observed by Lord and Ocampo<sup>5</sup> in the Raman effect. The corresponding line in allene- $d_4$ should lie at 615 cm<sup>-1</sup>, and should be weaker by  $\sqrt{2}$ . A very weak line is observed at this point but unfortunately can be interpreted also as the first overtone of the fundamental at 306 cm<sup>-1</sup>. In any event, the combined evidence of thermal and spectroscopic data is entirely consistent with the identification of the 865  $cm^{-1}$  line in allene with the torsional vibration.

# Species $B_2$

The values for the  $B_2$  frequencies in Table IV are those observed in the infrared. Corresponding lines have been observed in the Raman effect for  $\nu_6$  and  $\nu_7$ at 1960 and 1421 in allene and for  $\nu_7$  in allene- $d_4$ . The  $v_5$  fundamentals are obscured in the Raman effect by  $\nu_1$ , and  $\nu_6$  for all ne- $d_4$  was not observed. The vaporliquid shift for  $\nu_7$  is rather considerable, but the ratio of the allene: allene- $d_4$  values is the same in both phases. Hence the product rule agreement shown in Table IV would be unaffected by the shift. The product rule is useful in deciding between the assignment of the infrared band at 1034 and that at 1138 to  $v_7$  in allene- $d_4$ .

#### Species E

The degenerate vibrations are readily located in the infrared by their perpendicular bands. Analysis of these bands, by means of which the vibrational frequencies are obtained, is described below. It leads to the satisfactory location shown in Table IV for the centers of all except the band of  $\nu_9$  in allene- $d_4$ . The product rule is reasonably well satisfied for both the infrared and the Raman assignments. However, the sign and magnitude of the discrepancy observed for the Ramaneffect values indicate that probably 315 cm<sup>-1</sup> for  $\nu_{11}$ in allene- $d_4$  is in error and should agree more closely with the infrared value of 306. The location of the band origin of  $\nu_9$  in allene- $d_4$  is difficult because of the proximity of the broad band due to  $\nu_{10}$ . The trace of ammonia previously mentioned also gives some interference. However, the 830 estimate agrees reasonably well with the Raman value of 847.

# 100 p=630mm PERCENT ABSORPTION l=6cm `م 50 3300 3200 3100 3000 СМ

FIG. 3. Rotational structure of perpendicular band  $\nu_8$ and parallel band  $\nu_5$  in allene.

# Analysis of the Rotational Structure

The infrared bands of allene and allene- $d_4$  are of three kinds: (1) those that show fine structure with alternation of intensity "strong, weak, strong, weak ...." for the successive sub-bands. This feature is expected for the perpendicular bands of the symmetrical-top structure, and all such bands are therefore assigned as perpendicular bands; (2) those that show a weak but sharp Q branch with more intense, broad P and Rbranches. Such bands are of the parallel type, and under lower dispersion show only P and R branches, the weaker Q branch being usually unobservable; (3) those that show an unresolved broad envelope with maximum intensity at the center. These bands are of the perpendicular type, but their constituent subbands are too closely spaced for resolution with our instrumental setup.

#### Parallel Bands

The fine structure of the parallel bands is determined by the large (double) moment of inertia and cannot be resolved with our instrument. However, from a study of the structure of the parallel band  $3\nu_5$  in the photographic infrared, Eyster<sup>4</sup> obtained a set of values for the quantities<sup>16</sup>  $\Delta_2 F''(J)/2(2J+1)$  that had an average value 0.2847 cm<sup>-1</sup>, which is therefore the value of the rotational constant B'' for allene. From this,  $I_B = 98.3$  $\times 10^{-40}$  g cm<sup>2</sup>. If one uses an estimated value of  $120^{\circ}$ for the HCH angle and 1.071A for the C-H distance (the value in ethylene), one finds the C = C distance as 1.344A. From these approximate values, rough working values of  $I_B$  and B for allene- $d_4$  of  $125 \times 10^{-40}$  g cm<sup>2</sup> and 0.22 cm<sup>-1</sup>, respectively, are obtained. It will be seen later that these estimates agree closely with the values obtained using a bond angle of 113° determined from the perpendicular-band analysis.

The moment of inertia about the figure axis is similarly estimated to be roughly  $5.7 \times 10^{-40}$  g cm<sup>2</sup>, with the result that  $I_A/I_B$  is 0.06. So small a ratio means that the integrated intensity of the Q branch is of the order of one-fifth that of the P or R branch.<sup>17</sup> Hence rather good resolution on the part of the prism spectrometer is required to separate the weak Q branch from the P and R components of the parallel bands.

### Perpendicular Bands

As was first shown by Teller,<sup>17</sup> the rotational structure of degenerate (i.e., perpendicular) vibrational bands in the infrared is complicated by the existence of angular momentum of vibration. Interaction of this angular momentum with that of molecular rotation about the figure axis introduces a linear term into the rotational energy which contains the interaction constant  $\zeta$ , the rotational quantum number K, and the

<sup>&</sup>lt;sup>16</sup> See Herzberg, reference 14, p. 434. <sup>17</sup> E. Teller, Hand- und Jahrbuch der chem. Physik, **9II**, 28 (1934). See also reference 14, p. 421.

Assign- ment	v <sub>vac</sub> in cm <sup>-1</sup>	1	$^{R}Q_{K}-^{P}Q_{K}$	Δν	$\frac{{}^{R}Q_{K}-{}^{P}Q_{K}}{2K}$	Assign- ment	vvae in cm⁻1	1	$R_{QK} - P_{QK}$	Δυ	$\frac{{}^{R}Q_{K}-{}^{P}O_{K}}{2K}$
RQ11 RQ10 RQ9 RQ8 RQ7 RQ6 RQ5 RQ4 RQ3	3194.2 3184.0 3174.7 3164.2 3152.0 3142.5 3133.6 3124.6 3115.7	s w s w	105.9 89.8 71.8 53.5	10.2 9.3 10.5 12.2 9.5 8.9 9.0 8.9	8.83 8.98 8.98 8.98 8.92	$\begin{array}{c} \hline R Q_2 \\ R Q_1 \\ R Q_0 \\ P Q_1 \\ P Q_2 \\ P Q_3 \\ P Q_4 \\ P Q_5 \\ P Q_6 \end{array}$	3107.0 3098.5 3089.5 3080.3 3070.5 3062.2 3052.8 3043.8 3036.6	s w s w s w s w	36.5 18.2	8.7 8.5 9.0 9.2 9.8 8.3 9.4 9.0 7.2	9.13 9.10

TABLE V. Wave numbers of the sub-bands in  $\nu_8(e)$  of allene at 3085 cm<sup>-1</sup>.

rotational constant A.  $\zeta$  can lie between -1 and +1for the first vibrational state. A zero value for  $\zeta$ means that there is no vibrational angular momentum, and hence that the vibrating electric dipole moment rotates about the symmetry axis at the same rate as the molecule itself. The minus sign corresponds to a speeding-up of the rotation of the vibrating moment about the symmetry axis, and hence to an increase in the rotational spacing in the spectrum. A plus sign gives a retardation of the rotation of the vibrating moment, and a decrease in the rotational spacing.

As a result of this interaction, the equation for the Q branches of the constituent sub-bands of a perpendicular band  $(\Delta J=0, \Delta K=\pm 1)$  takes the form:<sup>18</sup>

$$\nu = \nu_0 + [A_{\nu'}(1 - 2\zeta_i) - B_{\nu'}] \pm 2[A_{\nu'}(1 - \zeta_i) - B_{\nu'}]K + [(A_{\nu'} - B_{\nu'}) - (A_{\nu''} - B_{\nu''})]K^2, \quad (1)$$

where as usual A and B are the rotational constants for  $I_A$  and  $I_B$ , ' and " refer to the upper and lower vibrational states of the band, and v is the vibrational quantum number for each state. The subscript *i* designates which doubly-degenerate vibration is concerned, since of course the  $\zeta$ -values differ for different vibrations. In Eq. (1), the  $\pm$  sign indicates the two branches of sub-bands, the + sign giving the R branch ( $\Delta K = +1$ ) and the minus sign the P branch ( $\Delta K = -1$ ).

The form of a perpendicular band given by Eq. (1) and the appropriate Boltzmann factors is that of a broad spread of Q branches with no clear-cut maximum to the band as a whole (see Fig. 4). Hence the numbering of the different Q branches [i.e., assignment of the correct K values of Eq. (1)] and the corresponding location of  $\nu_0$  are not immediately obvious. Considerable assistance is offered, however, if there is an alternation of intensity in the Q branches.

Alternation of intensity results from alternation in the statistical weights of the rotational energy levels, which in turn results from molecular symmetry and nuclear spin. Wilson<sup>19</sup> has discussed the group-theoretical procedures for evaluation of statistical weights, and has applied the procedure to various molecules, none, however, of  $D_{2d}$  symmetry. By straightforward application of his methods to the  $D_{2d}$  model of allene<sup>20</sup> and allene- $d_4$ , for both of which the rotational subgroup is  $D_2$ , it can be shown that, apart from the Boltzmann factor, the intensity alternation 10:6 should be observed for sub-bands of even:odd K in allene and 45:36 in allene- $d_4$ .

This alternation is of great help in assigning numbers to the constituent sub-bands and the determination of the band centers. The sub-band with the strongest Qbranch is the first in the R branch side (i.e.,  ${}^{R}Q_{0}$ ), and the first weak Q branch on the low frequency side of  ${}^{R}Q_{0}$  is the first in the P branch ( ${}^{P}Q_{1}$ ). The band center lies between  ${}^{R}Q_{0}$  and  ${}^{P}Q_{1}$ , and the frequencies listed on Tables II-IV for infrared-active vibrations have been determined in this way for all resolved perpendicular bands. As indicated above, the bands at 354 in allene and 306 cm<sup>-1</sup> in allene- $d_{4}$  are not resolved, and hence their centers have been determined from the band maxima, which are to be taken to be the band centers.

The best way to obtain the coefficient of K in Eq. (1) is to plot  ${}^{R}Q_{K} - {}^{P}Q_{K}$  against K. This plot is a straight line of slope  $4[A_{v}'(1-\zeta_{i})-B_{v}']$ . Another method is to average the quantity  $({}^{R}Q_{K}-{}^{P}Q_{K})/2K$ . The practical way to obtain the coefficient of  $K^{2}$  is to plot  ${}^{R}Q_{K}+{}^{P}Q_{K}$  against  $K^{2}$ . This plot should be a



FIG. 4. Rotational structure of perpendicular bands  $\nu_9$  and  $\nu_{10}$  in allene.

<sup>20</sup> After the present work was completed, the authors learned that Dr. J. de Heer [J. Chem. Phys. **20**, 637 (1952)] had also worked out the statistical weights as well as an equation corresponding to Eq. (5) below. As de Heer points out, there is a difference in appearance of Eq. (5) if one uses the convention K = K' rather than the convention of Herzberg, K = K'', as is done here. After correction for this, the two equations are in agreement. However, there are differences in the exact locations of the band centers and in the  $\zeta$  values. The additional information provided by the allene- $d_4$  spectrum and the  $\zeta$  sum rule accounts for these differences. The authors are much indebted to Dr. de Heer for the privilege of seeing his manuscript before it appeared in print.

<sup>&</sup>lt;sup>18</sup> See reference 14, p. 429 and Eq. IV, 60.

<sup>&</sup>lt;sup>19</sup> E. B. Wilson, Jr., J. Chem. Phys. 3, 276 (1935).

TABLE VI. Wave numbers of the sub-bands of  $\nu_{\theta}(e)$  in allene at 1015 cm<sup>-1</sup>.

Assign- ment	vac in cm <sup>-1</sup>	I	$R_{QK}$ $-P_{QK}$	Δν	As- sign- ment	$\nu_{\rm vac} in cm^{-1}$	I	$-{}^{R}_{POK}$	Δν
$R_{Q_{13}}$ $R_{Q_{12}}$ $R_{Q_{11}}$ $R_{Q_{10}}$ $R_{Q_{9}}$ $R_{Q_{8}}$	1161.7 1149.6 1136.9 1124.2 1112.6 1101.2	W S W S W S	140.2	12.1 12.7 12.7 11.6 11.4	$\begin{array}{c} {}^{R}Q_{2} \\ {}^{R}Q_{1} \\ {}^{R}Q_{0} \\ {}^{P}Q_{1} \\ {}^{P}Q_{2} \\ {}^{P}Q_{3} \end{array}$	1037.8 1028.3 1019.2 1010.7 1002.7 994.7	s w s w s w	35.1 17.6	10.3 9.5 9.1 8.5 8.0 8.0
$R\tilde{Q}_7$ $R\tilde{Q}_6$ $R\tilde{Q}_6$ $R\tilde{Q}_4$ $R\tilde{Q}_3$	1090.4 1079.9 1069.5 1059.2 1048.1	พ ร พ ร พ	122.7 105.4 88.5 71.6 53.4	10.8 10.5 10.4 10.3 11.1	PQ4 PQ5 PQ6 PQ7 PQ8	987.6 981.0 974.5 967.7 961.0	s w s		7.1 6.6 6.5 6.8 6.7

straight line whose slope is  $2[(A_v' - B_v') - (A_v'' - B_v'')]$ .

The wave numbers and the assignment of the subbands of the perpendicular band  $\nu_8$  at 3085 cm<sup>-1</sup> are given in Table V and the band is shown in Fig. 3. It will be seen that the spacing is somewhat irregular, for reasons not clear at present. This feature was also pointed out by Miller and Thompson.<sup>3</sup> Nevertheless, the sub-bands can be presented approximately by the formula

$$\nu = 3089.0 \pm 9.0K + 0.03K^2. \tag{2}$$

It follows from Eqs. (1) and (2) that

$$2[A_{v}'(1-\zeta_{8})-B_{v}']=9.0.$$
 (3)

The case of the bands for  $\nu_9$  and  $\nu_{10}$  at 1015 and 842 cm<sup>-1</sup>, shown in Fig. 4, is more complicated. Here there is a Coriolis interaction, first described by Nielsen,<sup>21</sup> between the two fundamentals, in addition to that interaction between the degenerate components of each vibration which leads to Eq. (1). If the individual degeneracy of  $\nu_9$  and  $\nu_{10}$  is neglected, the sub-bands of  $\nu_9$  and  $\nu_{10}$  can be represented by

$$\nu = (\nu_{9} + \nu_{10})/2 + (A - B) \pm 2(A - B)K$$
  
 
$$\pm \frac{1}{2} \{ (\nu_{9} - \nu_{10})^{2} + 4(K \pm 1)^{2} \zeta^{2}_{9, 10} A^{2} [(\nu_{9}/\nu_{10})^{\frac{1}{2}} + (\nu_{10}/\nu_{9})^{\frac{1}{2}}]^{\frac{3}{2}} \}^{\frac{1}{2}}.$$
(4)

TABLE VII. Wave numbers of the sub-bands of  $\nu_{10}(e)$  in allene at 842.2 cm<sup>-1</sup>.

Assign- ment	v <sub>vac</sub> in cm <sup>-1</sup>	I	$R_{QK}$ $-P_{QK}$	Δν	Assign- ment	vac in cm <sup>-1</sup>	I	Δν
<sup>R</sup> O <sub>10</sub>	913.0	s	167.0		PQ4	809.5	s	9.9
$R \check{O}_9$	908.0	w	151.2	5.0	${}^{P}\tilde{O}_{5}$	799.7	w	9.8
RŎ8	902.3	5	134.2	5.7	$P\check{Q}_6$	789.3		10.5
$RO_{7}$	896.4	w	117.1	5.9	$P \tilde{O}_7$	779.3		10.0
$RO_6$	889.8	5	100.5	6.6	$P\breve{O}_8$	768.1		11.2
$RO_{5}$	883.4	w	83.7	6.4	$PO_9$	756.8		11.3
$R O_4$	876.9	5	67.4	6.5	$P\check{O}_{10}$	745.9		10.9
$RO_3$	869.5	w	50.1	7.4	$P \check{O}_{11}$	734.3		11.6
$PO_2$	862.1	S	33.9	7.4	$P\breve{Q}_{12}$	722.2		12.1
$R\check{O}_1$	854.7	w	16.9	7.4	$P \check{Q}_{13}$	710.8		11.4
$R\check{O}_0$	846.5	5		8.2	$P \tilde{Q}_{14}$	699.3		11.5
$PO_1$	837.8	w		8.7	$P \check{Q}_{15}$			
$P\breve{O}_2$	828.3	s		9.5	$P\check{Q}_{16}$			
$P\breve{Q}_3$	819.4	w		8.9	010			

<sup>21</sup> H. H. Nielsen, J. Opt. Soc. Am. 34, 521 (1944).

Here  $\zeta_{9,10}$  is the constant for the interaction of  $\nu_9$  and  $\nu_{10}$ . The positive sign before the coefficient of the term corresponds to the R branches and the negative sign to the P branches. The positive sign before the final term corresponds to the sub-bands for  $\nu_9$ , and the negative, to those for  $\nu_{10}$ . The factor  $(K+1)^2$  in the final term goes with the R branches and  $(K-1)^2$  with the P branches. As it was in Eq. (1), the parameter K is K'', that is, the value of K in the lower vibrational state. If K is set equal to K', its value in the upper vibrational state, Eq. (4) is changed by replacement of the first positive sign with a negative one, and the  $(K \pm 1)^2$  term by  $K^2$ . It then is identical, apart from symbolism, with Eq. (11) of reference 21. The subscripts and superscripts on A and B have disappeared because the effect of the vibrational state on A and Bhas been assumed negligibly small.

Nielsen<sup>21</sup> first suggested that the unusual fine structure observed for the 842 and 1015 cm<sup>-1</sup> bands in allene by Thompson and Harris<sup>2</sup> could be accounted for on the basis of Eq. (4), and Miller and Thompson<sup>3</sup> applied the suggestion to their later and much improved spectra of these bands. However, Eq. (4) does not apply as it stands because each of the vibrations concerned is doubly degenerate. If one takes the Coriolis interaction due to the degeneracy into account, one obtains, instead of Eq. (4),

$$\nu = (\nu_{9} + \nu_{10})/2 + (A - B) - A(\zeta_{9} + \zeta_{10}) \\ \pm 2[(1 - \{\zeta_{9} + \zeta_{10}\}/2)A - B]K \pm 1/2[\{\nu_{9} - \nu_{10} \\ \mp 2A(K \pm 1)(\zeta_{9} - \zeta_{10})\}^{2} + 4\xi^{2}_{9,10}(K \pm 1)^{2}A^{2} \\ \times \{(\nu_{9}/\nu_{10})^{\frac{1}{2}} + (\nu_{10}/\nu_{9})^{\frac{1}{2}}\}^{2}]^{\frac{1}{2}}.$$
 (5)

Here  $\zeta_9$  and  $\zeta_{10}$  are the interaction constants for  $\nu_9$  and  $\nu_{10}$ , the first  $\pm$  sign gives the *P* branches (-) and *R* branches (+), the second  $\pm$  sign gives the bands for  $\nu_9$  (+) and  $\nu_{10}$  (-), and the  $\pm$  and  $\mp$  signs within the square brackets enclosing the last term go with the *P* branches (lower sign) and *R* branches (upper sign).<sup>22</sup>

$$\begin{split} E(\pm)/hc &= \frac{1}{2} \{ \begin{bmatrix} E_{1,0}/hc + E_{0,1}/hc \end{bmatrix} \pm (\begin{bmatrix} E_{1,0}/hc - E_{0,1}/hc \end{bmatrix}^2 \\ &+ 4\zeta^2_{9,10} K'^2 A^2 \begin{bmatrix} (\nu_9/\nu_{10})^{\frac{1}{2}} + (\nu_{10}/\nu_{9})^{\frac{1}{2}} \end{bmatrix}^2 \}, \end{split}$$
(a)

where  $E_{1,0}/hc$  and  $E_{0,1}/hc$  are the unperturbed energy terms for the first excited vibrational levels of  $\nu_0$  and  $\nu_{10}$ , K' is the rotational quantum number, and zero-point energy is omitted. If the double degeneracy of  $\nu_0$  and  $\nu_{10}$  is taken into consideration, the unperturbed energy terms can be represented by

$$E_{1,0}/hc = \nu_9 + BJ(J+1) + (A-B)K'^2 - 2AK'\zeta_9 l$$
 (b)

and

$$E_{0,1}/hc = \nu_{10} + BJ(J+1) + (A-B)K'^2 - 2AK'\zeta_{10}l.$$
 (c)

The quantum number l has only the values  $\pm 1$ , depending on whether the vibrational angular momentum  $jh/2\pi$  is parallel or antiparallel to the rotational angular momentum. Teller<sup>1</sup> has shown that in perpendicular transitions where the upper level is degenerate, only +l levels combine with the lower (ground) levels for  $\Delta K = +1$ , and only -l levels for  $\Delta K = -1$ . The levels

<sup>&</sup>lt;sup>22</sup> The derivation of Eq. (5) is as follows: Eq. (9) of reference 21, corrected for obvious typographical errors and translated into the notation of the present paper, gives, for  $E(\pm)/hc$ , the interacting rotational-vibrational levels of  $\nu_9$  and  $\nu_{10}$  in cm<sup>-1</sup>, the expression

From Eq. (5) it can be seen that for the band due to  $\nu_9$ , the  $\Delta\nu$  between the individual sub-bands of the *R* branch increases as *K* increases, but decreases as *K* increases for the sub-bands of the *P* branch. The reverse is true of  $\nu_{10}$ . The constant in Eq. (5)

$$\left[ (\nu_{9} + \nu_{10})/2 + (A - B) - A(\zeta_{9} + \zeta_{10}) \right]$$

(denoted C below) is given by the average value of the combinations

$$\left[{}^{R}Q_{K}(\nu_{9}) + {}^{R}Q_{K}(\nu_{10}) + {}^{P}Q_{K}(\nu_{9}) + {}^{P}Q_{K}(\nu_{10})\right]/4$$

for different K's. This value is  $933.2 \text{ cm}^{-1}$ . The following relations also can be seen to hold:

$$\begin{bmatrix} {}^{R}Q_{K}(\nu_{9}) + {}^{R}Q_{K}(\nu_{10}) \end{bmatrix} = 2C + 4 \begin{bmatrix} A(1 - \{\zeta_{9} + \zeta_{10}\}/2) - B \end{bmatrix}, \quad (6a)$$

and

$$\begin{bmatrix} {}^{P}Q_{K}(\nu_{9}) + {}^{P}Q_{K}(\nu_{10}) \end{bmatrix} = 2C - 4[A(1 - \{\zeta_{9} + \zeta_{10}\}/2) - B]. \quad (6b)$$

The slope of the straight lines which we get by plotting the left-hand sides of Eqs. (6) versus K will thus give

TABLE VIII. Wave numbers of the sub-bands in  $\nu_8(e)$  of allene- $d_4$  at 2330 cm<sup>-1</sup>.

Assign- ment	vac in cm <sup>-1</sup>	I	Δν -	$\frac{2Q_{K}-P_{QK}}{2K}$	Assign- ment	<sup>v</sup> vac in cm <sup>-1</sup>	I	Δν
RO <sub>8</sub>	2365.7	5	3.6	4.31	PO3	2319.5	w	4.2
$RO_7$	2362.1	w	3.6	4.37	₽Ŏ₄	2314.8	S	4.7
$R \check{O}_{6}$	2358.1	S	4.0	4.37	$PO_5$	2310.2	w	4.6
$R \breve{O}_5$	2353.9	w	4.2	4.37	$PO_6$	2305.6	s	4.6
₽Ŏ₄	2349.4	5	4.5	4.33	PŎ,	2300.9	w	4.6
$R \breve{O}_3$	2345.0	w	4.4	4.25	$P\check{O}_8$	2296.7	5	4.2
$R \breve{O}_2$	2340.9	S	4.1	4.3	$PO_{9}$	2292.2	w	4.5
$R\breve{O}_1$	2336.3	w	4.6	4.15	$PO_{10}$	2288.0	s	4.2
$R \tilde{O}_0$	2332.1	S	4.2		$P \tilde{O}_{11}$	2283.5	w	4.5
$P\breve{O}_1$	2328.0	w	4.1		Ç.,			
₽Ŭ2	2323.7	5	4.3					

the coefficient of K in Eq. (5), apart from a factor two. From the lines given in Tables VI and VII, this procedure gives

$$2[A(1 - \{\zeta_9 + \zeta_{10}\}/2) - B] = 8.55.$$
(7)

Finally, from analogous combination relations and the above results, there follows the numerical formula

$$\nu = 933.2 \pm 8.55K \pm \frac{1}{2} [\{172.8 \mp 0.4(K \pm 1)\}^{2} + 135(K \pm 1)^{2}]^{\frac{1}{2}}.$$
 (8)

Equation (8) represents well the sub-bands of  $\nu_9$  and

of the ground term  $E_{0,0}$  are given by

$$E_{0,0}/hc = BJ(J+1) + (A-B)K''^{2}.$$
 (d)

When Eqs. (b) and (c) are substituted in Eq. (a) the correct set of levels for the interacting degenerate vibrations is obtained. The frequencies for allowed transitions from the ground levels (d) to this set of levels are then given by Eq. (5).



FIG. 5. Rotational structure of bands in allene- $d_4$ . Upper: Perpendicular  $\nu_8$  and parallel  $\nu_5$ . Lower: Perpendicular  $\nu_{10}$ .

 $\nu_{10}$ . A comparison of Eqs. (5) and (8) shows

$$2A(\zeta_9 - \zeta_{10}) = 0.4 \tag{9}$$

$$4A^{2}\zeta_{9,10}^{2}\left[(\nu_{9}/\nu_{10})^{\frac{1}{2}}+(\nu_{10}/\nu_{9})^{\frac{1}{2}}\right]^{2}=135, \qquad (10)$$

$$2A\zeta_{9,10} = 5.78.$$
 (11)

It can also be seen from Eqs. (5) and (8) that when K is very large (i.e., when  $\{172.8 \pm 0.4(K \pm 1)\}^2 \ll 135(K \pm 1)^2$ ),  $\Delta \nu$  approaches limiting values in both the P and R branches of  $\nu_9$  and  $\nu_{10}$ . The limiting value for the R branch of  $\nu_9$  and the P branch of  $\nu_{10}$  is  $2[A(1-\{\zeta_9+\zeta_{10}\}/2)-B]+2A\zeta_{9,10}$ . The same expression with the

TABLE IX. Wave numbers of the sub-bands in  $\nu_{10}(e)$  of allene- $d_4$  at 667 cm<sup>-1</sup>

Assign- ment	vac in cm <sup>-1</sup>	I	Δν	Assign- ment	vac in cm <sup>-1</sup>	I	$\Delta \nu$
$RQ_{14}$	726.8			$^{P}O_{1}$	664.1	w	4.9
$RO_{13}$	723.3		3.5	$PO_2^-$	659.4	S	4.7
$R \check{O}_{12}$	719.8		3.5	$P\breve{O}_3$	654.9	w	4.5
$R \tilde{O}_{11}$	716.3		3.5	PŎ₄	650.7	s	4.2
$RO_{10}$	712.7		3.6	PŎ5	645.5	w	5.2
RŎa	709.0		3.7	$P\breve{O}_6$	640.7	5	4.8
$R \check{O}_8$	705.3		3.7	PŎ7	635.8	w	4.9
RŎ	701.1		4.2	$P\breve{O}_8$	630.6	5	5.2
$R \tilde{O}_8$	697.0	5	4.1	₽Ŏ <sub>9</sub>	625.6	w	5.0
$R\check{O}_{5}$	692.6	w	4.4	${}^{P}\breve{O}_{10}$	620.4	5	5.2
$R \tilde{O}_4$	688.1	5	4.5	$P \check{O}_{11}$	615.1		5.3
RŎ3	683.3	w	4.8	$P \tilde{O}_{12}$	609.6		5.5
$R\tilde{O}_2$	678.4	S	4.9	$P \tilde{O}_{13}$	604.0		5.6
$R O_1$	673.7	w	4.7	$PO_{14}$	597.5		6.5
$R \check{O}_0$	669.0	s	4.7	$PO_{15}$	592.2		5.3
2.				$PO_{16}$	586.6		5.6

1246

last sign negative holds for the P branch of  $\nu_9$  and the R branch of  $\nu_{10}$ . From Eqs. (8) and (11) these values of  $\Delta \nu$  are, respectively, 14.3 and 2.77 cm<sup>-1</sup>. However, they would only be approached experimentally if subbands were observed for K values beyond about 35.

The band due to  $v_{11}$  at 354 cm<sup>-1</sup> is not resolved. Since the achieved resolution of the instrument is 3.5 cm<sup>-1</sup> or better in this region, we may write

$$2[A(1-\zeta_{11})-B] = \Delta \nu_{11} \quad (0 < \Delta \nu_{11} < 3.5).$$
 (12)

The wave numbers and the assignment of the subbands of the perpendicular band  $\nu_8$  of allene- $d_4$  are given in Table VIII (see Fig. 5). For this band

$$2[A^*(1-\zeta_8^*)-B^*]=4.35,$$
 (13)

and the sub-bands can be represented by the equation

$$\nu = 2332.1 \pm 4.35K.$$
 (14)

The asterisks denote the deuterium compound.

The wave numbers and the assignment of the subbands of  $\nu_{10}^*$  at 667 cm<sup>-1</sup> in allene- $d_4$  are given in Table IX (see Fig. 5). One can expect a mutual interaction between  $\nu_9^*$  and  $\nu_{10}^*$  in allene- $d_4$  similar to that of allene. The band  $\nu_9^*$  at 830 cm<sup>-1</sup> in allene- $d_4$  is weak and only partially resolved. Further, it is overlapped to some extent by the spectrum of ammonia which is present as a minor impurity. However, as for  $\nu_{10}$  in allene, the  $\Delta \nu$  of the sub-bands of  $\nu_{10}^*$  in allene- $d_4$ appears to be approaching "asymptotic" values in both the *P* branch and *R* branch at sufficiently large *K* values. If this is taken as evidence of interaction between  $\nu_9^*$  and  $\nu_{10}^*$  in allene- $d_4$ , then Eq. (5) can be applied to the sub-bands of  $\nu_{10}^*$ .

As the sub-bands of  $\nu_9^*$  could not be measured well, the constants in Eq. (5) cannot be obtained very accurately. However, the sub-bands of  $\nu_{10}^*$  (Table IX) can be fairly well represented by the equation

$$\nu_{10}^* = 750.7 \pm 4.6 \pm \frac{1}{2} [\{163.0 \mp 0.2(K \pm 1)\}^2 + 20(K \pm 1)^2]^{\frac{1}{2}}.$$
 (15)

Equation (15) implies that  $\nu_9^* = 830 \text{ cm}^{-1}$ ,  $\nu_{10}^* = 667 \text{ cm}^{-1}$ , and

$$2[A^*(1 - \{\zeta_9^* + \zeta_{10}^*\}/2) - B^*] = 4 \mathfrak{H}, \qquad (16)$$

$$2A^*(\zeta_9^* - \zeta_{10}^*) = 0.2, \tag{17}$$

TABLE X. Rotational constants and related quantities for allene and allene- $d_4$ .

Quantity	Allene	Allene- $d_4$		
A	5.28 cm <sup>-1</sup>	2.64 cm <sup>-1</sup>		
В	0.285 cm <sup>-1</sup>	0.224 cm <sup>-1</sup>		
ζ8	0.09	0.09		
<u>ک</u>	0.16	0.07		
ζ10	0.12	0.03		
(11	0.66	0.86		
ζ9, 10	0.55	0.42		
∕ HCH	113°	(Assuming $r(C-H)$		
r(C=C)	1.335A	= 1.071A		

and

$$\{2\zeta_{9,10}^{*}A^{*}[(\nu_{9}/\nu_{10})^{\frac{1}{2}}+(\nu_{10}/\nu_{9})^{\frac{1}{2}}]\}^{2}=20.$$
 (18)

The band for  $\nu_{11}^*$  at 306 cm<sup>-1</sup> was not resolved. Therefore, as before,

$$2[A^{*}(1-\zeta_{11}^{*})-B^{*}] = \Delta \nu_{11}^{*} \quad (0 < \Delta \nu_{11}^{*} < 3.5). \quad (19)$$

# Determination of A and the $\zeta$ -Values

Use of the foregoing numerical relations among the rotational spacings to determine the constant A and the  $\zeta$ -values can be made with the help of the  $\zeta$ -sum rule of Teller.<sup>17</sup> As Teller and also Dennison<sup>23</sup> have pointed out, the  $\zeta$ -sum for the vibrations of a given symmetry species in a molecule is independent of the nature of the molecular potential system provided it is harmonic. Hence the  $\zeta$ -sum can be determined by assuming special force fields for the molecule (Dennison's "limiting force fields," for example) that yield individual  $\zeta$ -values easily, and then summing.

By application of the limiting-force-field type of reasoning to the  $D_{2d}$  model for allene,<sup>24</sup> it can be shown that

$$\sum_{i} \zeta_{i} = 1 + B/2A, \qquad (20)$$

where the sum is taken over the four vibrations of species *E*. From Eq. (20) and the various equations relating the  $\zeta$ -values and the rotational constants *A* and *B* to the fine-structure spacings  $\Delta \nu_i$ , simple addition leads to the results

$$6A - 9B = 26.1 + \Delta \nu_{11}, \qquad (21a)$$

$$6A^* - 9B^* = 13.55 + \Delta \nu_{11}^*$$
. (21b)

The asterisk denotes allene- $d_4$ , and the symbols  $\Delta \nu_{11}$ and  $\Delta \nu_{11}^*$  appear on the right-hand side because, as was stated above, these quantities could not be measured experimentally with the prism instrument. Since  $A = 2A^*$ , B has been evaluated<sup>4</sup> as 0.285 cm<sup>-1</sup>, and B<sup>\*</sup> can be reasonably estimated as 0.22 cm<sup>-1</sup>, it follows that

$$\Delta \nu_{11} - 2\Delta \nu_{11}^* = 2.4 \text{ cm}^{-1}.$$
 (22)

The error in Eq. (22) is hard to estimate, but is probably not larger than 0.5 cm<sup>-1</sup>. From the achieved resolution of the prism instrument on the water-vapor bands near 350 cm<sup>-1</sup> it can safely be concluded that  $\Delta \nu_{11}$  experimentally is smaller than 3.5 cm<sup>-1</sup>. Therefore, from Eq. (22),  $\Delta \nu_{11}=3.0\pm0.6$  and  $\Delta \nu_{11}*=0.3$  $\pm0.3$  cm<sup>-1</sup>. From this value of  $\Delta \nu_{11}$  and the value of *B*,

<sup>&</sup>lt;sup>23</sup> See, for example D. M. Dennison and M. Johnston, Phys. Rev. 47, 93 (1935); 48, 868 (1935).

<sup>&</sup>lt;sup>24</sup> It has not been plainly stated heretofore, so far as the writers can find, that the z-sums need not be computed on an *ad hoc* basis for each molecule by the limiting-force-field method, but can be determined as readily on general grounds as can the number of vibrations of a given symmetry species. Tables for determination of the latter quantities (such as Tables 34-36 of reference 14) have been in the literature for some time. The preparation of analogous tables for the z-sums of axially symmetrical molecules is entirely feasible.

Assign- ment	vac in cm <sup>-1</sup>	Int.	$\Delta \nu$	$^{R}Q_{K}-^{P}Q_{K}$	$\frac{(^{R}Q_{K}-^{P}Q_{K})}{2K}$	Assign- ment	$v_{\rm vac} in cm^{-1}$	Int.	$\Delta \nu$
<sup>R</sup> Q <sub>8</sub>	(2495.0)			120.4	7.5	$PO_2$	2410.9	s	6.5
₽Ŏ7	(2484.4)		10.6	104.8	7.5	$PO_3$	2404.8	w	6.1
$^{R}\breve{O}_{6}$	2474.9	5	9.6	88.9	7.4	$PO_4$	2398.2	5	6.6
$R\tilde{O}_5$	2465.6	าย	9.3			<b>C</b> .			
$R\tilde{O}_{4}$	2456.1	s	9.5	57.9	7.4	$PO_6$	2386.0ª	s	$2 \times 6.1$
$R \tilde{O}_3$	2447.0	w	9.1	42.2	7.0	$PO_{7}$	2379.6ª		6.4
кŎ2	2439.3	s	7.7	28.4	7.1	${}^{P}O_{8}$	2375.3ª		4.3
<sup>R</sup> Ŏ1	2431.3	w	8.0	13.9	7.0	e.			
$^{R}O_{n}$	2424.3	S	7.0						
$PO_1$	2417.4	710	6.9						

TABLE XI. Wave numbers of resolved sub-bands of the combination band in allene at 2420.9 cm<sup>-1</sup>.

• Beginning with  ${}^{P}Q_{\epsilon}$ , the sub-bands are overlapped by CO<sub>2</sub>-absorption (present in the sample). There appear to be several more sub-bands below 2375 cm<sup>-1</sup>.

A is found to be  $5.28\pm0.1$  cm<sup>-1</sup>, whence  $A^*=2.64\pm0.05$ . If these values of A and  $A^*$  are now substituted back into Eqs. (7)-(13), (16)-(19) for the  $\Delta \nu_i$ , along with B and B<sup>\*</sup>, the  $\zeta$ -values listed in Table X are obtained.

Most of the overtone and combination bands can be satisfactorily assigned, as shown in Tables II and III. Some of these have been resolved and, in conjunction with the constants A and B, can also yield information about the  $\zeta$ -values. In Table XI are listed the wave numbers of the sub-bands of the perpendicular band at 2420.9 cm<sup>-1</sup>, which is well resolved. They can be represented by the formula

$$\nu = 2424.3 \pm 7.3K \pm 0.17K^2. \tag{23}$$

This band could be  $\nu_7 + \nu_9(E)$  or  $\nu_2 + \nu_9(E)$ . In either event,  $\Delta \nu$  and  $\zeta$  would be the same as for the fundamental band of  $\nu_9$  apart from anharmonicity and the dependence of A and B on the vibrational state. Equation (23) gives  $\zeta_9 = 0.26$ , whereas from the fundamental it is 0.16. Most of the discrepancy has to be ascribed to a combination of experimental error and anharmonicity, because the difference between A' and A'', as shown by the coefficient of  $K^2$  in Eq. (23), is too small and in the wrong direction to explain it. Another possibility is that the band is  $3\nu_{10}(E)$ . In this case the  $\zeta$ -value is not necessarily the same as that of the fundamental ( $\zeta_{10}$ =0.12), but the anharmonicity would have to be rather large.  $2\nu_{10}(B_2)$  is found with considerable intensity in both allene and allene- $d_4$ , and  $3\nu_{10}$  in the latter would probably be obscured by  $\nu_6$ .

The combination band  $2\nu_{10} + \nu_{11}(E)$  at 2015 cm<sup>-1</sup> in allene is partially resolved. The spacing is irregular and the average  $\Delta \nu$  is 3.4 cm<sup>-1</sup>. This value is consistent with that estimated from the sum rule and other relations to be  $3.0\pm0.6$  cm<sup>-1</sup> for  $\Delta \nu_{11}$ .

The equilibrium value of A in allene depends on two parameters, the C-H distance and the HCH angle, and since neither of these changes in allene- $d_4$ , of course  $A^*$ , as indicated above, is the same as A except for the factor two from the D:H mass ratio. Hence to find either parameter from A, the other must be known. The safest procedure appears to be to assume the value of the C-H distance to be the same as that in ethylene, since small changes in the C-H distance are accompanied by large changes in the C-H stretching frequency, and in ethylene and allene the C-H frequencies are very nearly the same. If r(C-H) is assumed equal to 1.071A, the HCH angle is found to be  $113^{\circ} \pm 1^{\circ}$ from  $A = 5.28 \pm 0.1$  cm<sup>-1</sup>. From this angle and the B value, r(C=C) is 1.335A. Finally  $I_B$  and B for allene- $d_4$ turn out to be  $124.9 \times 10^{-40}$  g cm<sup>2</sup> and 0.224 cm<sup>-1</sup>, respectively, in good consistency with the rough working values used for these constants.

It is perhaps worth noting that the large number of  $\zeta$ -values (six independent values, in principle) and vibrational frequencies of the *E* species would be more than enough for a calculation of the complete set of potential constants, ten in all, for this species. The  $\zeta$ 's are not too accurately known, however, from the present work, and hence the constants would perhaps suffer somewhat in accuracy also. A similar calculation for ethane using the frequencies and  $\zeta$ -values from ethane and ethane- $d_6$  has recently been made by Hansen and Dennison.<sup>24</sup>

### ACKNOWLEDGMENT

The authors wish to acknowledge the support of the Office of Ordnance Research (Contract DA-19-020-ORD-896, Project TB5-0002 (5)), under whose auspices the present work was completed. Heavy water was obtained by allocation from the AEC, whose cooperation is gratefully acknowledged.

<sup>24</sup> G. E. Hansen and D. M. Dennison, J. Chem. Phys. 20, 313 (1952).