InfraRed and Raman Spectra of Polyatomic Molecules. IV. Allene

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The infra-red absorption spectrum and the Raman spectrum of allene were examined. In the infra-red nine bands were observed at 4200, 2960, 2420, 1980, 1700, 1389, 1165, 1031 and 852 cm^{-1} and in the Raman effect there were ten individual shifts of 3062, 2992, 2858, 1956, 1684, 1430, 1069, 838, 705 and 353 cm^{-1}. With the aid of heat capacity data it was possible to assign values to the frequencies of all the eleven fundamental modes of vibration of allene. The assignment accounted for all the features of the Raman and infra-red spectra. Calculations were made of the free energy, the entropy and the heat capacity and expressions for the first two, as functions of temperature, derived.

BECAUSE of the simple atomic arrangement in the allene molecule and of its close relation structurally to ethylene the determination of the vibration frequencies of this molecule is of some interest. The Raman spectrum of allene has been studied by Bourguel and Piaux[1] and by Kopper and Pongratz.[2] The frequencies found by the former authors were 1073, 1438, 3000 and 3072 and by the latter 1074, 1435, 2995 and 3060 cm^{-1}. Both describe the 1073 and 3000 cm^{-1} lines as intense and the other two as of medium intensity. The infra-red spectrum has been studied by Bonner and Hofstadter.[*] The results summarized by them seem to agree well with those described here particularly as regards the bands with frequencies below 3000 cm^{-1}.

Raman Spectrum

The Raman spectrum of allene was investigated using the apparatus which has been described in Part II.[3] The sample of allene used in these experiments was kindly supplied to us by Professor G. B. Kistiakowsky, it being a part of that which had been employed in the determination of the heat of hydrogenation.[4] The allene, in the liquid state, was contained in a cylindrical tube, the volume of which was *ca.* 50 cc, closed at one end by a plane Pyrex window. The allene was illuminated through the sides of the tube by four mercury vapor lamps. The light filter solutions were those previously described. The Raman tube was kept at temperatures from −40°C to −50°C by means of a current of air which had been cooled by passage through a copper spiral immersed in a mixture of alcohol and dry ice.

The results are summarized in Table I. In the first column are listed the frequencies (in vacuum) of the lines observed. The second column gives the suggested interpretation of these lines, the accompanying letter indicating the exciting mercury line. Measurements were made on four plates. The line at 24011 cm^{-1} was observed on one plate only and on this was so faint as to be measurable only with difficulty. Microphotometer records were made of each plate and all lines were identified on these in addition to being observed directly on the plates. A microphotometer record of one of the plates is shown in Fig. 1.

There appear, therefore, to be ten individual Raman frequencies. These are summarized in

Table I. *Observed frequencies (cm^{-1} in vacuum) with displacements from mercury lines: 22938 (e), 22995 (f), 23039 (g), 24516 (i) and 24705 cm^{-1} (k).*

ν in cm^{-1}	$\Delta\nu$ in cm^{-1}	ν in cm^{-1}	$\Delta\nu$ in cm^{-1}
(24011)	694 (k)	21868	1070 (e)
23865	840 (k)	21713	2992 (k)
23636	1069 (k)	21643	3062 (k)
23447	1069 (i)	21508	1430 (e)
23274	1431 (k)	21254	1684 (e)
22585	353 (e)	20982	1956 (e)
22233	705 (e)	20080	2858 (e)
22102	836 (e)	19946	2992 (e)
21970	1069 (g)	19876	3062 (e)
21927	1068 (f)		

[1] Bourguel and Piaux, Bull. Soc. Chim. **51**, 1041 (1932).
[2] Kopper and Pongratz, Wien Ber. **141** IIb, 840 (1932).
[*] Bonner and Hofstadter, Phys. Rev. **52**, 249 (1937).
[3] Gershinowitz and Wilson, J. Chem. Phys. **6**, 247 (1938).
[4] Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **58**, 146 (1936).
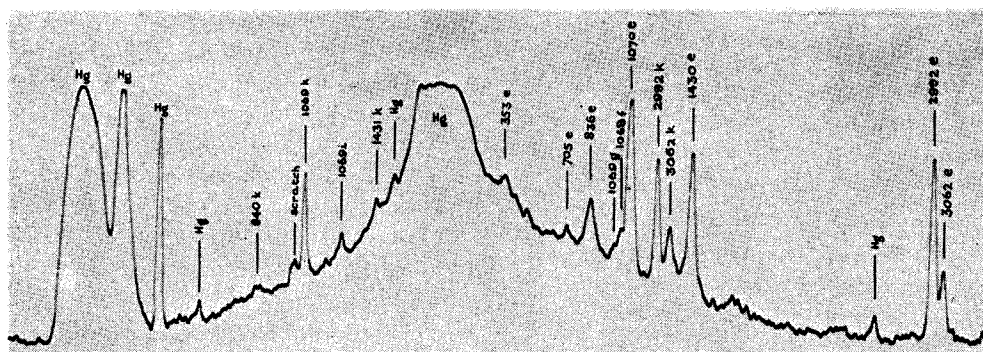
FIG. 1. A microphotometer record of the Raman spectrum of allene.

Table II together with the estimated relative intensities with which these appear.

THE INFRA-RED SPECTRUM

The apparatus used to measure the infra-red absorption of this compound was that described in Part I.[5] The gaseous allene was contained in cylindrical cells closed by windows of rocksalt or KBr, the material of the windows depending on the region of the spectrum that was under investigation. The cells were 20 cm long and pressures of allene ranging from 30 mm to 760 mm were used.

Figure 2 shows the transmission curve that was obtained experimentally. It will be seen that there are six relatively intense absorption bands, the centers of which were situated at the wave-

TABLE II. *Observed frequencies in infra-red and Raman spectra together with the relative intensities.*

INFRA-RED	RAMAN
4200 (1)	
	3062 (10)
2960 (4)	2992 (20)
	2858 (2)
2420 (2)	
1980 (10)	1956 (1)
1700 (8)	1684 (2)
	1430 (12)
1389 (12)	
[1165 (1)]	
	1069 (20)
1031 (8)	
852 (30)	838 (5)
	705 (2)
	353 (4)

[5] Gershinowitz and Wilson, J. Chem. Phys. **6**, 197 (1938).

lengths: 3.38; 5.05; 5.88; 7.2; 9.7; and 11.73μ. The corresponding frequencies (in cm^{-1}) together with the relative intensities of the bands are 2960 (4); 1980 (10); 1700 (8); 1389 (12); 1031 (10) and 852 (30). In addition to these there were faint bands at 2.4 and 4.13μ, and the band at 9.7μ which appeared unsymmetrical at higher pressures showed a "shoulder" at lower pressures (see Fig. 2). The frequencies and intensities of the 2.4 and 4.13μ bands are 4200 (1) and 2420 cm^{-1} (2). It was difficult to estimate the position of the band which gave rise to the "shoulder" on the absorption curve of the 9.7μ band since the much greater intensity of the latter meant that under no conditions could a definite maximum of absorption be observed for the fainter nearby absorption band. Examination of the curves indicated that the maximum must be near 8.6μ. The frequencies and relative intensities of the infra-red bands are included in Table II with the Raman frequencies, the correspondence between the two sets being indicated.

SYMMETRY PROPERTIES

The allene molecule belongs to the symmetry point group V_d. It has seven nondegenerate and four doubly degenerate fundamental modes of vibration. These are divided among the four symmetry classes given in the first column of Table III in the manner shown in the second column. The third and fourth columns indicate the selection rules for the vibrations of these classes for the Raman and infra-red spectra. The last three columns list the symmetry of the vibrations in the various classes with respect to
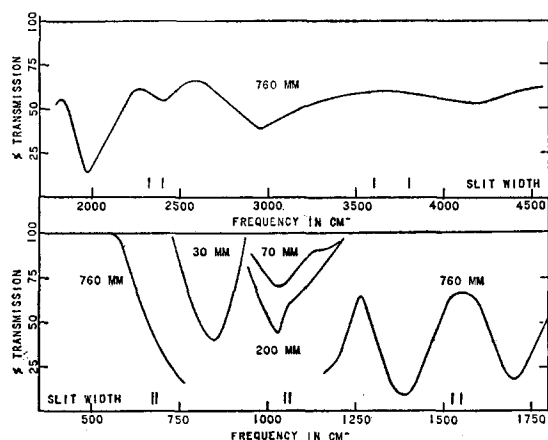
FIG. 2. Infra-red transmission of gaseous allene. Path length 20 cm.

the two planes, σ_1 and σ_2, and the alternating axis of symmetry S_4, S and A indicating symmetrical and anti-symmetrical, respectively. The symmetry of the degenerate vibrations cannot be given since the symmetry of the vibrations of the two complementary sets separately will depend on how the sets are chosen.

DISCUSSION OF THE OBSERVED FREQUENCIES

The observed vibration frequencies may be summarized from Table II as follows: 4200 (I.R.), 3062 (Ram. I.R. ?), 2992 (Ram. I.R. ?), 2859 (Ram.), 2420 (I.R.), 1968 (Ram. I.R.), 1692 (Ram. I.R.), 1430 (Ram.), 1389 (I.R.), 1165 (I.R.), 1069 (Ram.), 1031 (I.R.), 845 (Ram. I.R.), 705 (Ram.), 353 (Ram.). It is possible at once to make a partial assignment. It is often, though not always, found that the most symmetrical vibrations appear most intensely in the Raman effect. On these grounds we may assign to the three vibrations of class A_1 the values 2992, 1430 and 1069 cm^{-1}. In agreement with this selection these frequencies do not appear in the infra-red spectrum. The vibrations of the symmetry classes B_2 and E are active in both spectra. Each class will include one carbon-hydrogen valency vibration. That in B_2 may be expected to have a frequency similar to that of the carbon-hydrogen valency vibration in A_1 since both are symmetrical to the two symmetry planes of the molecule. It will therefore be *ca.* 3000 cm^{-1}. The carbon-hydrogen valency vibra-

tion in E then presumably has the frequency 3062 cm^{-1} giving rise to the Raman lines with this shift. The frequencies below 3000 cm^{-1} appearing in the infra-red spectrum are 1968, 1692, 1389, 1165, 1031 and 845 cm^{-1}. Of these 845 cm^{-1} is the most intense and must correspond to a fundamental. 1692 cm^{-1} is then probably the first overtone of this fundamental. Since the first overtone of a B_2 fundamental is inactive in the infra-red spectrum this indicates that 845 cm^{-1} is a fundamental of the symmetry class E. Of the remaining five bands that at 1165 cm^{-1} is quite faint and probably corresponds to an overtone or combination level. There are left, therefore, four infra-red bands with frequencies 1968, 1389, 1031 and 845 cm^{-1} for fundamentals in the classes B_2 and E. This still leaves one of the fundamentals in these two classes unaccounted for. There remains the 353 cm^{-1} Raman shift which may or may not appear also in the infra-red spectrum since our measurements could not be extended into this region. This might therefore be the seventh fundamental of the two classes B_2 and E or it might be the B_1 fundamental.

FREQUENCY CALCULATIONS

It has been pointed out by Thompson and Linnett[6] that if the values of the force constants found in ethylene are carried over for use in allene with a similar potential function the calculated frequencies agree remarkably well with those observed. For the totally symmetrical vibrations they calculated by this means the frequencies 3003, 1459 and 1069 cm^{-1}. This indicates that the values assumed above for the A_1 fundamentals were correct since the calculated frequencies differ by only 0.3, 2.0 and 0.0 percent, respectively, from the observed figures.

TABLE III.

SYM-METRY CLASS	NUMBER OF FUNDAMENTAL VIBRATIONS IN CLASS	PERMITTED TO APPEAR IN		SYMMETRY WITH RESPECT TO		
		RAMAN	INFRA-RED	σ_1	σ_2	S_4
A_1	3	Yes	No	S	S	S
B_1	1	Yes	No	A	A	A
B_2	3	Yes	Yes	S	S	A
E	4	Yes	Yes	Degenerate		

[6] Thompson and Linnett, J. Chem. Soc. 1384 (1937).

Such agreement is as good as can be expected when the force constants employed for one molecule are transferred unaltered for use in another. The constants given by Thompson and Linnett[7] can be used also to calculate the frequencies of the B_2 fundamentals. The values obtained are 2998, 1415 and 2001 cm^{-1}. For these calculations the dimensions assumed for the allene molecule were: for the carbon-hydrogen bond length 1.08A, for the carbon-carbon bond length 1.33A and for the HCH angle 118°. These are the values suggested by Penney[8] for ethylene and are in agreement with the electron diffraction data of Wierl[9] who gave 1.31±0.05A and of Pauling and Brockway[10] who gave 1.34±0.02A. The above calculated frequencies indicate that the B_2 fundamentals below 3000 are in reality 1389 and 1968 cm^{-1}. The agreement in both cases is within 2 percent. It seems, therefore, that we may definitely make the assignments A_1: 2992, 1430, 1069; B_2: ca. 3000, 1968, 1389; E: 3062, 1031 and 845 cm^{-1}.

THE VIBRATION FREQUENCIES

From the above considerations, therefore, nine of the eleven frequencies have been determined and moreover, the magnitude of one of the remaining two is 353 cm^{-1}. Preliminary measurements on the heat capacity of gaseous allene

TABLE IV.

SYMMETRY CLASS	FREQUENCY	RAMAN EFFECT	INFRA-RED SPECTRUM
A_1	2992	2992	forbidden
	1430	1430	forbidden
	1069	1069	forbidden
B_1	820	(838)	forbidden
B_2	ca. 3000	(2993)	broad band over this region
	1968	1956	1980
	1389	not observed	1389
E	3062	3062	broad band over this region
	1031	not observed	1031
	852	(838)	852
	353	353	unobservable

[7] Thompson and Linnett, J. Chem. Soc. 1376 (1937).
[8] Penney, Proc. Roy. Soc. **158A**, 306 (1937).
[9] Wierl, Ann. d. Physik **13**, 453 (1932).
[10] Pauling and Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

TABLE V.

OBSERVED FREQUENCY	SPECTRUM	SUGGESTED COMBINATION	SYMMETRY OF LEVEL
705	Raman	$2 \times 353 = 706$	$A_1 + E$
1165	I.R.	$353 + 820 = 1173$	E
1684	Raman }	$2 \times 852 = 1704$	$A_1 + E$
1700	I.R. }		
2420	I.R.	$1389 + 1031 = 2420$	E
2858	Raman	$2 \times 1430 = 2860$	A_1
4200	I.R.	$3062 + 1069 = 4131$	E
		$3062 + 820 + 353 = 4235$	$A_1 + A_2 + B_1 + B_2$
		$3062 + 852 + 353 = 4267$	$4E$
		$2992 + 852 + 353 = 4197$	$A_1 + A_2 + B_1 + B_2$
		$3000 + 852 + 353 = 4205$	$A_1 + A_2 + B_1 + B_2$
		$3 \times 1389 = 4167$	B_2
		$1389 + 2 \times 1430 = 4249$	B_2

have been made in this laboratory and we wish to thank Professor Kistiakowsky, Dr. Lacher and Mr. Rice for kindly giving us permission to make use of their results before publication. A study of the observed heat capacity between 150 and 330°K indicates that the 353 cm^{-1} frequency is to be assigned to the doubly degenerate class and that the B_1 fundamental has a frequency of about 820 cm^{-1}.* The knowledge of the heat capacity was invaluable in determining whether the low 353 cm^{-1} fundamental was doubly degenerate or not and after this in fixing the approximate value of the eleventh fundamental. The final assignment which accounts for all the features of the Raman and infra-red spectra and also for the heat capacity over a considerable temperature range is shown in Table IV. This table also summarizes the manner in which the fundamentals appear in the spectra. It will be seen that in no case is an infra-red active fundamental above 400 cm^{-1} not observed and in only two cases are Raman active fundamentals definitely absent. It seems likely that the 3000 cm^{-1} frequency in the class B_2 which should appear in the Raman spectrum is obscured by the intense line arising from the A_1 fundamental. The 838 cm^{-1} Raman line is probably caused by a superposition of lines from the 820 cm^{-1} B_1 vibration and the vibration in the degenerate class. For this reason the value for the degenerate frequency has been revised to 852 cm^{-1} which is the position of the infra-red band.

* The relation of this to the spectroscopic data will be discussed later.

OVERTONE AND COMBINATION LEVELS

The interpretation of the observed overtones in terms of the fundamental vibration frequencies listed in Table IV is summarized in Table V. The first column gives the observed frequency, the second where it is observed, the third the suggested combination together with the calculated frequency and the last the symmetry class to which the overtone or combination belongs. It will be observed that in the last column a fifth symmetry class A_2 is mentioned. This was not included in Table III since there are no fundamental vibrations of the allene molecule which fall into this class. Overtone levels in A_2 would appear in the Raman effect but not in the infrared spectrum. It will be observed in Table V that the value of 820 cm^{-1} for the B_1 fundamental is required to account for the faint infra-red band of frequency 1165 cm^{-1}. Without this the best means of accounting for this band would be 353 $+852 = 1205$ cm^{-1} which is highly unsatisfactory. This therefore provides evidence for the value of 820 cm^{-1} in addition to that derived from the heat capacity. Further spectroscopic evidence is obtained from the fact that the infra-red frequency at 852 cm^{-1} does not correspond sufficiently closely with the Raman frequency at 838 cm^{-1}, this also being accounted for by the B_1 fundamental at 820 cm^{-1}.

All the levels below 3000 cm^{-1} are accounted for as fundamentals or as binary combinations. Only for the faint infra-red band at 4200 cm^{-1} are ternary combinations postulated and then it would appear that absorption is observed because there are so many superimposed bands. It is interesting that in ethylene the Raman frequency at 2880 cm^{-1} is ascribed to the first overtone of the fundamental frequency 1444 cm^{-1} in just the same manner that the 2858 cm^{-1} Raman shift in this instance is ascribed to the first overtone of the 1430 cm^{-1} fundamental.

THE TWISTING FREQUENCY

The vibration in the class B_1 which is antisymmetrical to the two symmetry planes may best be described as a twisting vibration. The magnitude of the frequency of this vibration is of particular interest since the analogous vibration in ethylene is completely inactive and its frequency can only be obtained by indirect means. *A priori* it might be expected that the twisting frequency in ethylene would be higher than in allene since the two methylene groups are joined by one double bond in the former and by two through a central carbon atom in the latter. Since the distortion has two double bonds in which to dissipate itself in allene compared with one in ethylene it might be expected that the force constant for allene would be about half as great as that for ethylene. This means that the ratio of the frequencies would be 1 : $\sqrt{2}$ and on the basis of a value of 820 cm^{-1} for allene that the ethylene twisting frequency would be about 1150 cm^{-1}. This frequency has been given various values by different investigators. Bonner[11] gave 830 cm^{-1}; Eucken and Parts,[12] 747; and Teller and Topley,[13] 1110. The evidence here is extremely indirect but at least it indicates that such twisting frequencies may not be as low as has been supposed.

CALCULATION OF THERMODYNAMIC QUANTITIES

Since all the fundamental frequencies of the allene molecule have been determined it is possible to calculate the free energy, entropy and heat capacity for the substance in the gaseous state. To compute the translational and rotational components of the free energy F and entropy S it is necessary to know the moments of inertia of the molecule. These have been calculated assuming that the molecular dimensions are as listed earlier in this paper. In Table VI the results of the calculation of the thermodynamic quantities are summarized. In the second and third columns are given the translational and rotational components of $-(F-E_0^0)/T$ and S at the temperatures, T, listed in the first column. The fourth and fifth columns give the vibrational parts of $-(F-E_0^0)/T$ and S and the sixth and seventh the total values. The last column gives the value of the heat capacity, C_p^0. The necessary constants were obtained from the *International Critical Tables* and the assumption made that the vibrations were harmonic.

[11] Bonner, J. Am. Chem. Soc. **58**, 34 (1936).
[12] Eucken and Parts, Zeits. f. physik. Chemie **B20**, 184 (1933).
[13] Teller and Topley, J. Chem. Soc. 885 (1935).

TABLE VI.*

T °K	Translational and Rotational		Vibrational		Total		
	$-\dfrac{(F-E_0^0)}{T}$	S	$-\dfrac{(F-E_0^0)}{T}$	S	$-\dfrac{(F-E_0^0)}{T}$	S	C_p^0
100	36.27	44.22	0.03	0.16	36.30	44.38	8.61
150	39.49	47.44	0.14	0.64	39.63	48.08	9.77
200	41.78	49.73	0.35	1.34	42.13	51.07	11.08
250	43.55	51.50	0.63	2.20	44.18	53.70	12.55
300	45.00	52.95	0.97	3.18	45.97	56.13	14.16
350	46.23	54.17	1.36	4.25	47.59	58.42	15.73
400	47.29	55.23	1.80	5.39	49.09	60.62	17.22
500	49.06	57.01	2.75	7.75	51.81	64.76	19.84
600	50.51	58.46	3.78	10.11	54.29	68.57	22.02
700	51.73	59.68	4.85	12.43	56.58	72.11	23.86
800	52.80	60.74	5.94	14.66	58.74	75.40	25.44
900	53.73	61.68	7.02	16.81	60.75	78.49	26.48
1000	54.57	62.52	8.10	18.85	62.67	81.37	28.02

* The units used in this table are calories per mole and degrees Absolute.

Murphy[14] has given analytical expressions for describing the free energy, entropy and heat capacity as functions of the temperature. He considered however only very simple molecules in which the contribution from the vibrational degrees of freedom was not as great as in the present case. It was found possible to extend Murphy's equation for $-(F-E_0^0)/T$ and S by introducing an extra term so that a good fit for the values listed in Table VI could be obtained. The expression derived for C_p^0 from this was not satisfactory. This presumably arose from two causes. Firstly because C_p^0 is related to S as a temperature derivative and hence errors in the expression for S are multiplied on passing to C_p^0 and secondly because the vibrational component of C_p^0 forms a much larger part of the whole than does the vibrational component of S. The equations for the translational and rotational parts of $-(F-E_0^0)/T$ and S are:

$$-(F-E_0^0)/T = 18.300 \log T - 0.332$$

and
$$S = 18.300 \log T + 7.616$$

and for the vibrational parts:

14 Murphy, J. Chem. Phys. 5, 637 (1938).

$$-\frac{(F-E_0^0)}{T} = 44.920 - \frac{9.936 \times 10^2 \log T}{T}$$
$$-18.608 \log T + 2.482 \times 10^{-2}T$$
$$-0.379 \times 10^{-5}T^2 + \frac{9.749 \times 10^2}{T},$$

$$S = 36.838 - 18.608 \log T + 4.964 \times 10^{-2}T$$
$$-1.138 \times 10^{-5}T^2 - \frac{4.315 \times 10^2}{T}.$$

The equations for the total values of $-F/T$ and S are then:

$$-\frac{(F-E_0^0)}{T} = 44.588 - \frac{9.936 \times 10^2 \log T}{T}$$
$$-0.308 \log T + 2.482 \times 10^{-2}T$$
$$-0.379 \times 10^{-5}T^2 + \frac{9.749 \times 10^2}{T},$$

$$S = 44.454 - 0.308 \log T + 4.964 \times 10^{-2}T$$
$$-1.138 \times 10^{-5}T^2 - \frac{4.315 \times 10^2}{T}.$$

The equations for the vibrational components of $-(F-E_0^0)/T$ and S give values within 0.02 and 0.04 units, respectively, over the range from 100° to 1000°K. The two analytical expressions for the full values of $-(F-E_0^0)/T$ and S give figures within 0.1 percent of those in Table VI.*

* There are several effects which will lead to uncertainty in the calculated values of the thermodynamic quantities. The most important of these are: (a) uncertainties in the knowledge of the absolute frequencies arising both from errors in measurement and also because the Raman spectra was observed with the liquid, and (b) neglect of the anharmonicities of the various vibrations.