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The Spectrum of Allene in the Photographic Infra-Red*

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The spectrum of allene between 7000 and 12,000A has been photographed under high dispersion, the observed bands being assigned as harmonics and combinations of fundamental frequencies of the molecule. Rotational analysis of the parallel band at 11,444A has given 97.0×10^{-40} g cm² as the large moment of inertia. The perpendicular band at 11,017A has been found to be unexpectedly complicated, but was too weak for detailed analysis. It has been concluded that the dimensions in ethylene and allene are:

$$C-H=1.087A, \quad C=C=1.330A, \quad H-C-H=116^\circ.$$

INTRODUCTION

ALTHOUGH the rotational structure of the parallel type rotation-vibration bands of symmetric rotators is simple and well understood, that of the perpendicular bands may be complicated by strong rotation-vibration interactions which, although adequately understood in most cases, appear capable of producing complexities which, as in the 4.5μ band of SiH_4 ,¹ remain at present unexplained. Consequently it has seemed of interest to investigate the rotational structure of the bands of allene in the photographic infra-red under dispersion sufficient to resolve the fine structure of both the perpendicular and parallel types, comparing that of the former with the structure predicted by the first order theory of Teller,² and with the use of that of the latter to determine the large moment of inertia of the molecule. Since this moment is insensitive to reasonable changes in the carbon-hydrogen bond distance and the carbon-hydrogen bond angle, a knowledge of its value would determine with considerable accuracy the carbon-carbon double bond distance, a quantity of great interest in the theory of molecular structure.

EXPERIMENTAL

The allene employed in these investigations was a portion of a very pure sample sent from Harvard University by Dr. W. E. Vaughan to Professor Linus Pauling and Dr. L. O. Brockway

for use in electron diffraction studies. A second sample for photographs at higher pressures was kindly sent by Dr. J. W. Linnett of Harvard University. A Pyrex absorption tube six meters in length and having a volume of one liter gave adequate absorption with relatively small gas samples. Exploration photographs taken at a pressure of one atmosphere on a Bausch and Lomb glass Littrow spectrograph revealed a rich spectrum in the region between 7000 and 12,000A, and all intense bands were then photographed in the first order of the 21-foot grating spectrograph of this laboratory, at pressures ranging from 40 mm to 1.5 atmospheres. Wavelength measurements on the prism spectrograms were made with respect to sodium, potassium, barium, and calcium lines, and on the grating spectrograms with respect to standard iron lines in the second and third orders. Eastman I-Z and 144-P plates, hypersensitized with ammonia, were used, and in every case visible radiation was removed with filters.

VIBRATIONAL STRUCTURE

In Fig. 1 are shown those three of the eleven allene symmetry coordinates which correspond to the modes of vibration most important in this region of the spectrum, namely those in which the motion consists chiefly of stretching of the C-H bonds, and also their distribution among the irreducible representations of the point group D_{2d} , which describes the symmetry of the molecule. The fundamental frequencies may, for clarity, be associated with these symmetry coordinates, which will in this case approximate the

* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 658.

¹ Steward and Nielsen, *Phys. Rev.* **47**, 828 (1935).

² E. Teller, *Hand- und Jahrbuch der Chemischen Physik* Vol. 9, No. 2 (1934), p. 125.

true normal coordinates with considerable accuracy. The symmetry selection rules are given in the usual fashion³ by the transformation properties of the electric moment and polarizability tensor components. The irreducible representations of these components and of the harmonic and combination states are given in Table I. Raman investigations of liquid allene by Kopper and Pongratz⁴ give values for two of the C-H frequencies, $\nu_1=2995$ and $\nu_3=3060$ cm⁻¹. Bonner and Hofstadter⁵ report 3086 cm⁻¹ as the position of the unresolved fundamentals ν_2 and ν_3 . With the aid of these approximate frequencies, the analogous frequencies in ethylene, and the symmetry selection rules, the strong bands between 7000 and 12,000Å may be assigned as harmonics and combinations of the three C-H stretching frequencies. In Table II are given the observed bands, their assignments, and the irreducible representations of the active components of the excited states, which are determinable from the observed band types. The unassigned bands, with the exception of the one at 8758Å which will be mentioned later, were extremely weak and were observable only on the low dispersion plates. The photographic data for allene, in conjunction with similar data for ethylene,⁶ whose fundamental frequencies are well known, lead one to the conclusion that the probable values of the C-H stretching frequencies in gaseous allene are:

$$\nu_1 = 3005, \quad \nu_2 = 2981, \quad \nu_3 = 3095.$$

 TABLE I. Selection rules for the group D_{2d} .

COMBINATIONS						HARMONICS	
	A_1	A_2	B_1	B_2	E	$[A_i^n] = \begin{cases} A_1, n \text{ even} \\ A_i, n \text{ odd} \end{cases}$	
A_1	A_1	A_2	B_1	B_2	E	$[B_i^n] = \begin{cases} A_1, n \text{ even} \\ B_i, n \text{ odd} \end{cases}$	
A_2		A_1	B_2	B_1	E	$[E^2] = A_1 + A_2 + B_2$	
B_1			A_1	A_2	E	$[E^3] = 2E$	
B_2				A_1	E	$[E^4] = 2A_1 + A_2 + B_1 + B_2$	
E				$A_1 + A_2$	E	$M_x \pm iM_y \sim E$	
				$+B_1 + B_2$	E	$M_x \pm iM_y \sim E$	
				$M_z \sim B_2$	E	$\alpha_{xx} + \alpha_{yy}, \alpha_{zz} \sim A_1, \alpha_{xz} - \alpha_{yy}, \alpha_{xy} \sim B_1, \alpha_{yz}, \alpha_{zx} \sim E$	

³ L. Tisza, Zeits. f. Physik **82**, 48 (1933).

⁴ Kopper and Pongratz, Weiner Berichte **B141**, 840 (1932).

⁵ Bonner and Hofstadter, Phys. Rev. **52**, 248 (1937).

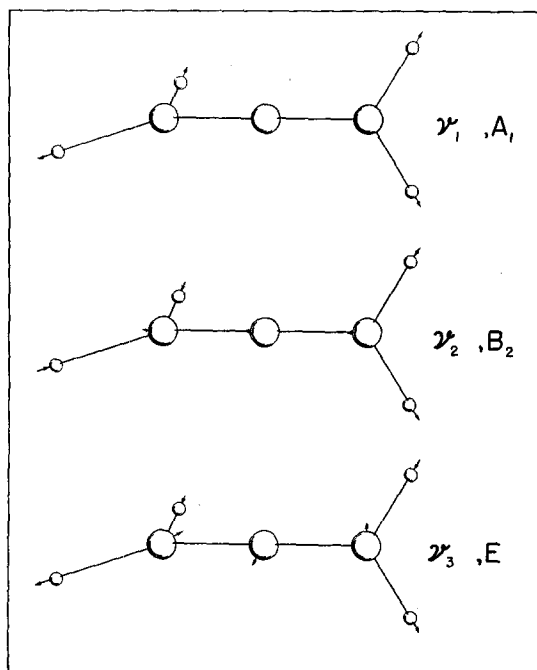
⁶ Bonner, J. Am. Chem. Soc. **58**, 34 (1936).


FIG. 1. C-H stretching symmetry coordinates for allene

ROTATIONAL STRUCTURE

Two of the bands, $3\nu_2$ and $2\nu_1 + \nu_2$, show rotational structure of the usual parallel type. The lines, however, are incompletely resolved even at a pressure of 40 mm, and cannot be detected on the microphotometer trace shown in Fig. 2, though on the original plates a number of them are distinctly visible. By reversing the plates on Velox No. 5 with contrast developer, about twenty lines in $3\nu_2$ could be measured directly under the comparator with respect to the iron comparison spectrum on the same print. The other band, however, was so badly overlapped by

TABLE II. Assignment of bands in the photographic infra-red.

WAVE-LENGTH (Å)	FREQUENCY (CM ⁻¹)	ASSIGNMENT	IRRED. REP.
11,444.32	8,738.96	$3\nu_2$	B_2
11,394.0	8,776.6	$2\nu_1 + \nu_2$	B_2
11,205	8,722		B_2
11,139	8,978	$2\nu_3 + \nu_2$	B_2
11,097	9,012	$2\nu_3 + \nu_1$	B_2
11,017.2	9,076.7	$3\nu_3$	E
10,920	9,718		
9,602	10,420		
9,338	11,710		
8,758	11,418		B_2
7,192	13,904	$5\nu_2$	B_2

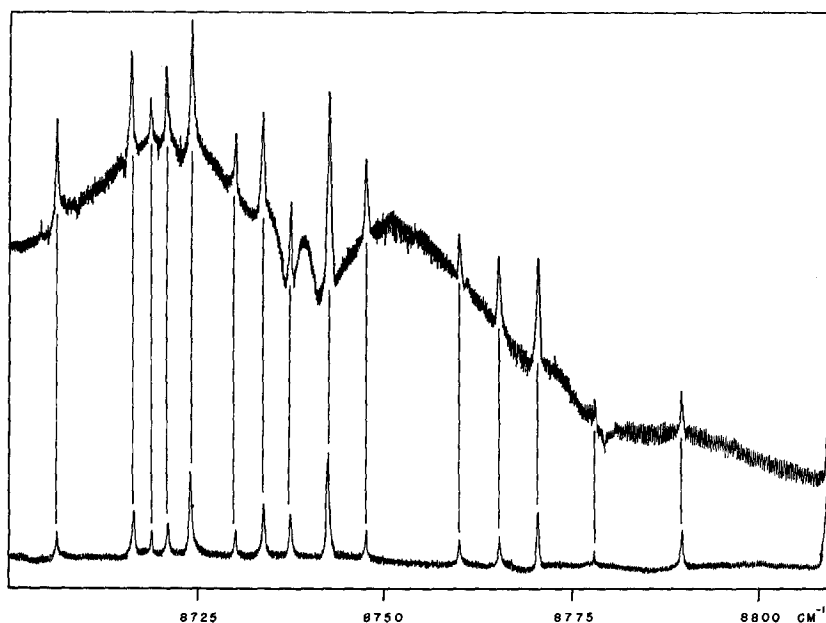


FIG. 2. Microphotometer trace of the 11,444 and 11,394 Å bands of allene; the lower trace shows the water lines in this region. The general trend in the background in the upper trace is not significant, and is absent in the lower trace only because the water plate was much more heavily exposed.

the much stronger $3\nu_2$ as to be quite useless for a determination of the rotational constant. Although it was impossible to measure the first few lines in either branch, the relative numbering of the lines in the P and R branches was easily made because the convergence was found to be extremely small. Furthermore, only one scheme of relative numbering produced a set of Δ''_2T 's which showed a reasonable dependence on J . The absolute numbering, determined by the position of the Q branch, may be in error by one unit because this branch is rather weak and wide, but the error thus induced in the value of the rotational constant will be insignificant owing to the small convergence. The broadness of the band lines, the presence of strong water lines, and the overlapping, with $2\nu_1 + \nu_2$ on the high frequency side made it impossible to obtain long branches or measurements of extreme accuracy. The usual combinations, shown in Table III, give a value of 97.0×10^{-40} g cm² for the large moment of inertia of the molecule.

The perpendicular band, $3\nu_3$ at 11,017.2 Å, was found to be extremely weak, and increasing the pressure above one atmosphere in the six meter tube served only to broaden the lines. A number

of broad, rather widely spaced band lines could be distinguished on the original plates, and were even more clearly evident in twofold enlargements made on Velox No. 5. A microphotometer trace made with the microphotometer slightly out of focus to eliminate the effects of the coarse grain of the Eastman type I plates, is shown in Fig. 3. Careful comparison with the enlarged prints has shown that the maxima in the trace do indeed correspond to the band features observable visually, but it must be remembered

TABLE III. Rotational lines and combinations in $3\nu_2$ at 11,444 Å.

J	$R(J)$	$P(J)$	$\Delta''_2T(J)$	$\Delta''_2T(J)/2(2J+1)$
5	8741.488			
6	42.046			
7	42.680			
8	43.330		9.574	0.2816
9	43.911	8733.106	—	—
10	44.507	—	11.934	0.2841
11	—	31.977	13.117	0.2852
12	45.731	31.390	—	—
13	46.274	30.841	15.484	0.2867
14	46.817	30.294	16.576	0.2858
15		29.698	17.637	0.2845
16		29.180		
17		28.677		
18		28.090		

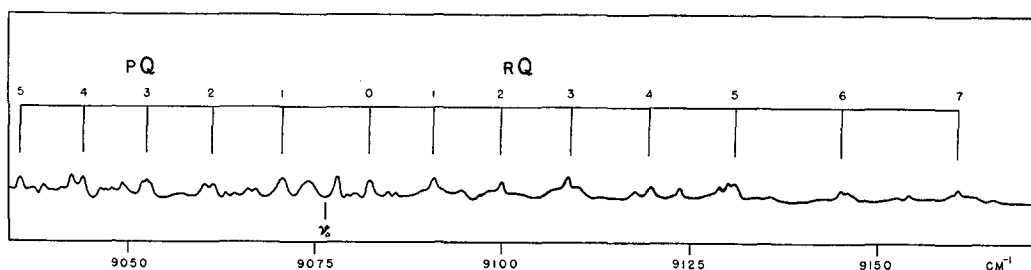


FIG. 3. Microphotometer trace of the perpendicular band of allene at 11,017Å, smoothed and corrected for the change in background. Suggested numberings of the Q branches are given. The pQ branch only extends to the fifth line because the band overlaps the 11,100Å bands beyond that point.

that many other weaker lines may have escaped detection. In spite of this fact, the rotational structure can be seen to deviate markedly from that predicted by Teller's theory, in that the spacings are not uniform, many of the Q branches are doubled or tripled, and a number of extra strong lines have made their appearance. It is, however, of interest to note that the small moment of inertia, calculated from the average spacing of the lines near the center of the band with the constant ζ in the Teller formula taken as zero, is 5.8×10^{-40} . One would expect the small moments of ethylene and allene to be very nearly equal, and this value does indeed agree very satisfactorily with the small moment 5.67×10^{-40} , determined by the fine structure of the 3.2μ and the 11.5μ bands of ethylene reported by Levin and Meyer.⁷ Hence one is led experimentally to the conclusion, which also follows from a consideration of symmetry coordinates in the representation E , that the value of ζ , which is a measure of the vibration-rotation interaction, is not large. A satisfactory explanation of the rotational structure of this band must quantitatively account for the difference between the rotational levels associated with this $3\nu_3$ level of allene and those associated with the analogous $3\nu_1$ levels of the methyl halides, which appear to be in complete agreement with the Teller theory. The data are at present far too meager to permit a quantitative consideration of the problem, but it seems appropriate to point out two alternative explanations of the complex rota-

tional structure of this band, and to suggest a possible method for distinguishing the correct one.

It is easy to show⁸ that whereas the $3\nu_3$ level of allene will be split into two degenerate E levels by the anharmonicity, the $3\nu_1$ level in the methyl halides will be split into three levels, only one of which is of the type E and capable of giving perpendicular bands in absorption from the ground state. The remaining twofold degeneracy of the E states will only be removed by terms in the Hamiltonian such as the vibration rotation interaction, which do not possess the symmetry of the molecule. Since the magnitudes of these two types of perturbations which remove the degeneracy of the quadruply degenerate third harmonic state cannot be estimated with any certainty, the possibility that the rotational structure of the perpendicular allene band may be due to either of the following causes must be considered.

1. In case the degeneracy of the E levels has not been removed, and if, moreover, they have not been widely separated by the anharmonicity, the 11,017Å band may be the result of transitions to the two E states, whose rotational levels have been so perturbed by interaction with the vibration that the resulting band cannot be simply decomposed into two ordinary perpendicular bands. In this case the difference between the allene and methyl halide third harmonics is easy to understand, and the fundamental perpendicular bands of the former might be expected to agree with the Teller theory.

2. Alternatively, it is possible that the two E levels of allene have been widely separated, and that the 11,017Å band is the result of a transition to only one of these states, whose degeneracy has been removed by a strong interaction with the

⁷ Levin and Meyer, J. Opt. Soc. Am. and Rev. Sci. Inst. **16**, 137 (1928).

⁸ In the notation of H. Sponer, *Molekülspektren* Vol. I (1935), p. 84.

rotation, not present in the methyl halides, and not described by the first order Teller theory. In this case the fundamental perpendicular bands should show a similar structure.

The writer proposes to investigate the fundamentals of the degenerate frequencies of allene in the near future, in the hope of determining the true cause of this unusually complicated perpendicular band structure.

The band at 11,100A, shown in Fig. 4, presents the appearance of a superposition of two parallel bands, and seems to be the result of the approximate coincidence of the levels $2\nu_3 + \nu_1$ and $2\nu_3 + \nu_2$, which have the symmetry properties characterized, respectively, by the irreducible representations $A_1 + A_2 + B_2$ and $A_1 + B_1 + B_2$. The only infra-red transitions to this composite state are to the two B_2 components, which will produce two parallel bands. Fine structure similar to that observed in the 11,444A band could be faintly distinguished on the original plates, but not even the Q branches, which are, of course, rather weak in a molecule of this extreme spindle type, can be located with certainty on the microphotometer traces.

The band at 8758A, shown in Fig. 5, is of special interest as the analog of the ethylene band at 8720A,⁹ whose anomalous intensity and

complicated rotational structure have never been satisfactorily understood. The allene band appears to consist of a superposition of two parallel bands of unequal intensity, and the components may be assigned as $3\nu_2 + 2\nu_4$ and $3\nu_3 + \nu_4 + \nu_5$, where the new fundamental frequencies are:

$$\nu_4 = 1381 (B_2), \quad \nu_5 = 1031 (E).$$

These frequencies, observed by Bonner and Hofstadter in the infra-red, are associated chiefly with the bending of C-H bonds. It is probable that the 8720A ethylene band is similarly a superposition of two or more combinations of C-H stretching and bending frequencies.

The remaining bands were too weak for high dispersion investigation, but the band at 7192A seems to be $5\nu_2$, and its doublet structure is clearly visible on the low dispersion plates.

STRUCTURES OF ALLENE AND ETHYLENE

Because of the importance of the carbon-carbon double bond distance in establishing the single-double bond resonance curve,¹⁰ it seems of considerable interest to attempt to interpret the moments of inertia of ethylene and allene in terms of bond distances and angles. The C-H

¹⁰ Pauling and Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

⁹ Badger and Binder, Phys. Rev. **38**, 1442 (1931).

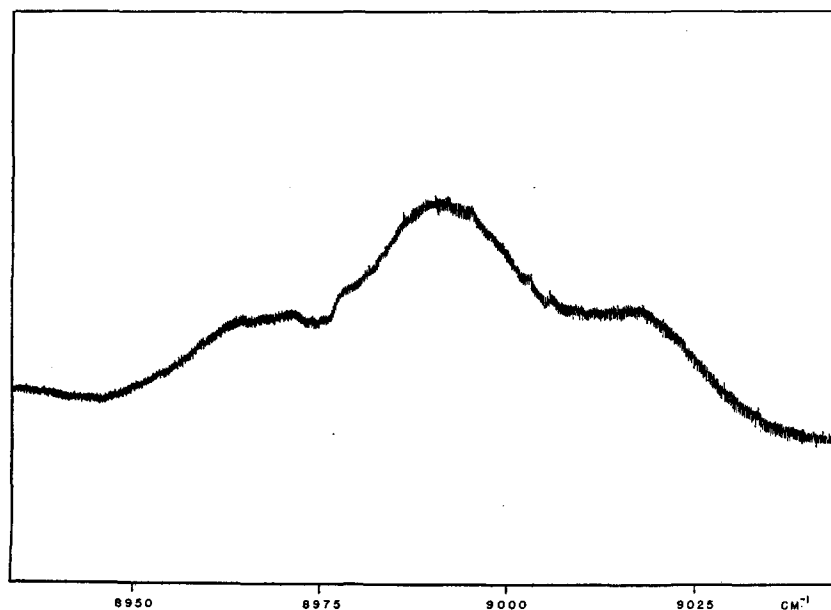


FIG. 4. Microphotometer trace of the 11,100A bands of allene.

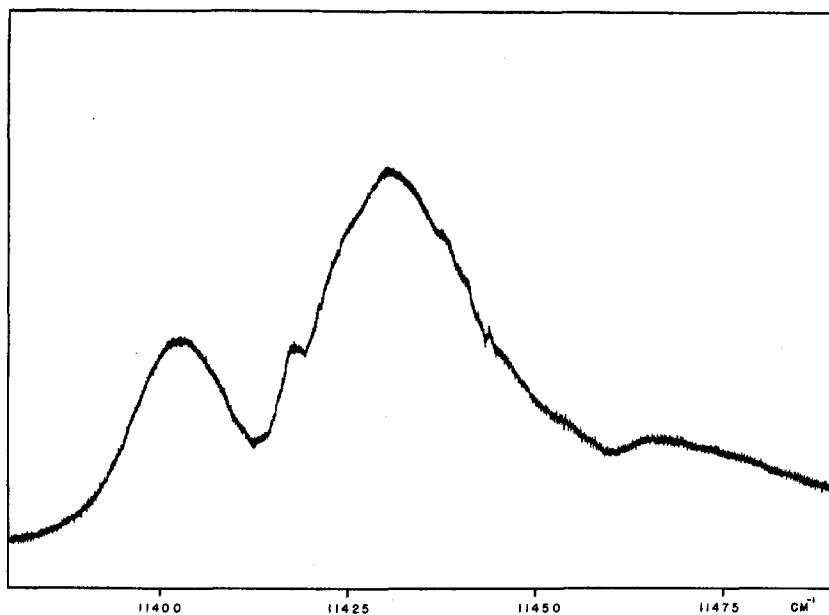


FIG. 5. Microphotometer trace of the 8758A bands of allene.

distance in these compounds can be obtained with some confidence by a consideration of the distances and force constants in a number of molecules containing the C—H group. When the C—H distances in C_2H_2 , HCN, CH_4 , and the ground state of CH are plotted against the inverse cube root of the C—H stretching force constant, following the procedure first suggested by Badger,¹¹ one obtains a very satisfactory straight line. The force constants of ethylene and allene may then be used to fix the C—H distance, which is thus found to be 1.087Å in both compounds. This information then makes it possible to calculate the C—H bond angle in ethylene from the small moment of inertia, giving the

angle H—C—H as 116° . Calculation of the C=C distance in ethylene and allene from their large moments of inertia, using the above parameters for both molecules, gives, respectively, 1.325 and 1.330Å. The difference is probably insignificant, since the large moment of inertia of ethylene, calculated by Badger¹² from the rotational Raman band of Lewis and Houston, is probably not so accurate as the others, and none of the moments of inertia have been corrected to the vibrationless state.

In conclusion, the writer is pleased to express his appreciation to Professor R. M. Badger for his valuable advice and assistance during the course of this investigation.

¹¹ Badger, J. Chem. Phys. **2**, 128 (1934).

¹² Badger, Phys. Rev. **45**, 642 (1934).