PHOTOGRAPHIC INVESTIGATIONS IN MOLECULAR SPECTROSCOPY

Thesis

by

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INTRODUCTION

The determination of the energy levels and the probabilities of transition between them, by the formal analysis of observed electronic, vibrational, and rotational band structures, forms the direct goal of all investigations of molecular spectra, but the significance of such data lies in the possibility of relating them theoretically to more concrete properties of molecules and the radiation field. From the well developed electronic spectra of diatomic molecules, it has been possible, with the aid of the non-relativistic quantum mechanics, to obtain accurate moments of inertia, molecular potential functions, electronic structures, and detailed information concerning the coupling of spin and orbital angular momenta with the angular momentum of nuclear rotation. The silicon fluoride molecule has been investigated in this laboratory, and is found to emit bands whose vibrational and rotational structures can be analyzed in this detailed fashion.

Like silicon fluoride, however, the great majority of diatomic molecules are formed only under the unusual conditions of electrical discharge, or in high temperature furnaces, so that although their spectra are of great theoretical interest, the chemist is eager to proceed to a study of polyatomic molecules, in the hope that their more practically interesting structures might also be determined with the accuracy and assurance which characterize the spectroscopic determinations of the constants of diatomic molecules. Some progress has been made in the determination of molecule potential functions from the vibrational term values deduced from Raman and infrared spectra, but in no case can the calculations be carried out with great generality, since the number of known term values is always small compared with the total number of potential constants in even so restricted a potential function as the simple quadratic type. For the determination of nuclear configurations and bond distances, however, a knowledge of the rotational terms is required. The spectra of about twelve of the simpler polyatomic molecules have been subjected to rotational analyses, and a number of bond distances are known with considerable accuracy, yet the number of molecules whose rotational fine structure has been resolved even with the most powerful instruments is small. Consequently, it was felt desirable to investigate the spectra of a number of other promising polyatomic molecules, with the purpose of carrying out complete rotational analyses of all resolvable bands, and ascertaining the value of the unresolved band envelopes in determining the structures of such molecules, in the cases in which resolution is no longer possible. Although many of the compounds investigated absorbed too feebly to be photographed under high dispersion with the present infrared sensitizations, the location and relative intensities of their bands, determined by low dispersion measurements, will be reported in the hope that these compounds may be reinvestigated in the future with improved techniques.

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The Structure of the α and β Band Systems of SiF

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A new vibrational analysis of the α system of SiF is presented. The rotational structure of the (0, 0) band of this system is analyzed, giving $B_0''=0.5795$ and $B_0'=0.5743$, and confirming the nature of the transition to be $^2\Pi_{\text{reg.}}\rightarrow{}^2\Pi_{\text{reg.}}$, with the upper state extremely near to case *b* and the lower state near case *a*. The doublet separation in the lower state is determined, but the spin doubling in the upper state is found too small to be accurately evaluated. The Λ type doubling is discussed. The rotational structure of the (0, 0) band of the β system is also analyzed, and the transition confirmed to be of the type $^2\Sigma\rightarrow{}^2\Pi_{\text{reg.}}$, the $^2\Pi$ state being the lower state in the α system. For the $^2\Sigma$ state $B_0=0.622$ is obtained, being less accurate than the values for the other two states because of experimental difficulties encountered in photographing this band. The spin doubling in the $^2\Sigma$ state is discussed, and the constants of the known electronic states of SiF are summarized.

INTRODUCTION

THE spectrum of a discharge through silicon tetrafluoride gas was carefully photographed several years ago by Johnson and Jenkins,[1] who discovered a large number of strong bands in the region between 2100 and 7000A, in addition to the blue system observed by Porlezza[2] in 1911. They were able to divide this entire spectrum into five band systems, to which they assigned the designations α, β, γ, δ, and ε. Vibrational

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[1] Johnson and Jenkins, Proc. Roy. Soc. **A116**, 327 (1927).

[2] Porlezza, Rend. Acad. Linc. **20**, 488 (1911); also **33**, 283 (1924).

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analyses of the α and β systems were proposed, and a rotational analysis of the strong band at 4368A, called the (0, 0) band of the former, attempted. Their results led them, however, to rather improbable conclusions concerning the emitter of the spectrum. It was subsequently shown in this laboratory, by Badger and Blair,[3] that the band at 4368A was of a more complex nature than had been supposed from the apparently simple structure at its origin. A new interpretation of the original band head data was recently given by Asundi and Samuel,[4] who proposed vibrational analyses for the α, β, and γ systems, attributing the first to a $^2\Pi \rightarrow {}^2\Pi$, and each of the latter to a $^2\Sigma \rightarrow {}^2\Pi$ transition. While their analyses of the β and γ systems are satisfactory, that of the α system not only appears incompatible with the observed band intensities, but also gives as the ratio A/B for the upper state, which must be very near to case b because of the strong satellite branches, the value 48, which is certainly many times too large.

In the following report is presented a new interpretation of these data which removes the two above objections, and also rotational analyses of the (0, 0) bands of both the α and β systems.

EXPERIMENTAL

For all of the photographs employed in this investigation, the spectrum was excited by a discharge through silicon tetrafluoride gas, in essentially the manner described by Johnson and Jenkins. The excellent set of high dispersion plates of the α system obtained in this laboratory by Dr. C. M. Blair, who has kindly placed them at my disposal, were taken in the third order of a 21-foot concave grating, where the dispersion was 0.78 A/mm. The bands appeared with such great intensity that a small air-cooled Pyrex discharge tube with aluminum electrodes provided an adequate source. Exposures were of the order of one to two hours. The lines were relatively sharp, and all could be easily measured directly under the comparator with respect to standard iron lines in the third order.

The β system was photographed by the author in the fourth order of the same grating, obtaining a dispersion of 0.58 A/mm. A filter consisting of a saturated solution of very pure nickel sulfate was found effective in separating this order from the third, which contained some of the bands of the much stronger α system. A 5 mm layer completely removed the region of the spectrum between 3600 and 4300A, but was very transparent in the ultraviolet. The low intensity of the β system, the high dispersion, and the poor reflecting power of the grating in this region of the spectrum made adequate exposures difficult to obtain. A large Pyrex discharge tube with a quartz window and massive aluminum electrodes was used. It was completely water cooled, and run on the secondary of a 5 kva General Electric transformer. The silicon tetrafluoride was pumped continuously through the tube at about 1 mm pressure, and the voltage in the primary adjusted to give maximum intensity. The most satisfactory plates were exposed for fifty hours, but even then much of the structure was difficult or impossible to measure directly under the comparator. Consequently most of the lines were measured on enlarged microphotometer curves, using as references the strong lines of the Q branches, which were directly measurable on the plates with respect to iron lines in the third order. Test measurements of a number of standard iron lines photographed in the second and third orders have disclosed no systematic error arising from the use of the method of coincidences with this grating.

THE STRUCTURE OF THE α SYSTEM

Vibrational analysis

Careful consideration of the high dispersion plates of the α system reveals that all strong heads may be grouped in pairs of approximately equal intensity, separated by an interval very nearly equal to the doublet separation in the β system. Each strong head is, in addition, accompanied by an apparently weaker head on the high frequency side, so that a complete band consists of four heads. The strongest of these bands, which includes the head at 4368A, appears to be the (0, 0) band of the system. The principal sequence can be traced to the (8, 8) band, and the first four bands of the (1, 0) sequence are clearly visible, though many times weaker than the

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[3] Badger and Blair, Phys. Rev. **47**, 881 (1935).

[4] Asundi and Samuel, Proc. Ind. Acad. Sci. **3**, 346 (1936).

former. The (0, 1) and (5, 5) bands are both rather weak and seem to be in almost perfect coincidence, but some of the higher members of the (0, 1) sequence are observed, separated from the overlapping bands of the principal sequence. A few bands of the (0, 2) sequence are also present, but too weak to have been accurately measured. This analysis of the data of Johnson and Jenkins is presented in Table I.

Comparison of the $\Delta G''(v)$ values obtained from the strong heads with those obtained by Asundi and Samuel from the Q heads of the β system shows satisfactory agreement, and indicates that these two systems do indeed possess a common lower state. Since band heads, instead of origins, have been used, differences are to be expected, but these should decrease for higher values of v, since the heads appear to draw in toward the origins in ascending each sequence, approaching rather rapidly some nearly constant separation. Such is seen to be the case. From the $\Delta G'(v)$ values the vibrational constants of the upper state may be determined, and when most weight is given those differences for which v is

TABLE I. *Vibrational analysis of the α system of SiF.*

v' \ v''	0	1	2	3	4	5	6	7	8	
0	22958.4 22886.2 22780.1 22718.3	— 22040.1 — 21878.2	— — — 21037							687.7
1	23613 23573.9 23448.4 23411.6	22789.4 22729.9 22613.4 22565.9	— 21900 — —	— — — 20911						676.5
2		23440.1 23404.3 23772.4 23242.4	22610.7 22568.1 22442.8 22405.4	— — — 21577	— 20930 — 20761					659.0
3			23256.1 23226.7 23090.1 23065.0	22434.2 22399.1 22267.4 22236.9	21622 21577 21456 21413	— 20733 — 20611				642
4				23066.3 23041.7 22901.3 —	22252.8 22222.9 22086.4 22061.0	— 21413 — 21252	— 20611 — 20448			627
5						— 22040.1 — 21878.2	— — — —	— — — 20421		
6							— 21851.5 — 21689	— — — —	— — — 20112	
7								— 21655 — 21497	— — — —	
8									— 21456 — —	↑
	845.3 847.3	836.0 838.2	827.9 828.0	817.4 817.7	809.5 811.5	803 800.8	(α system) (β system)	←	Means of first differences	

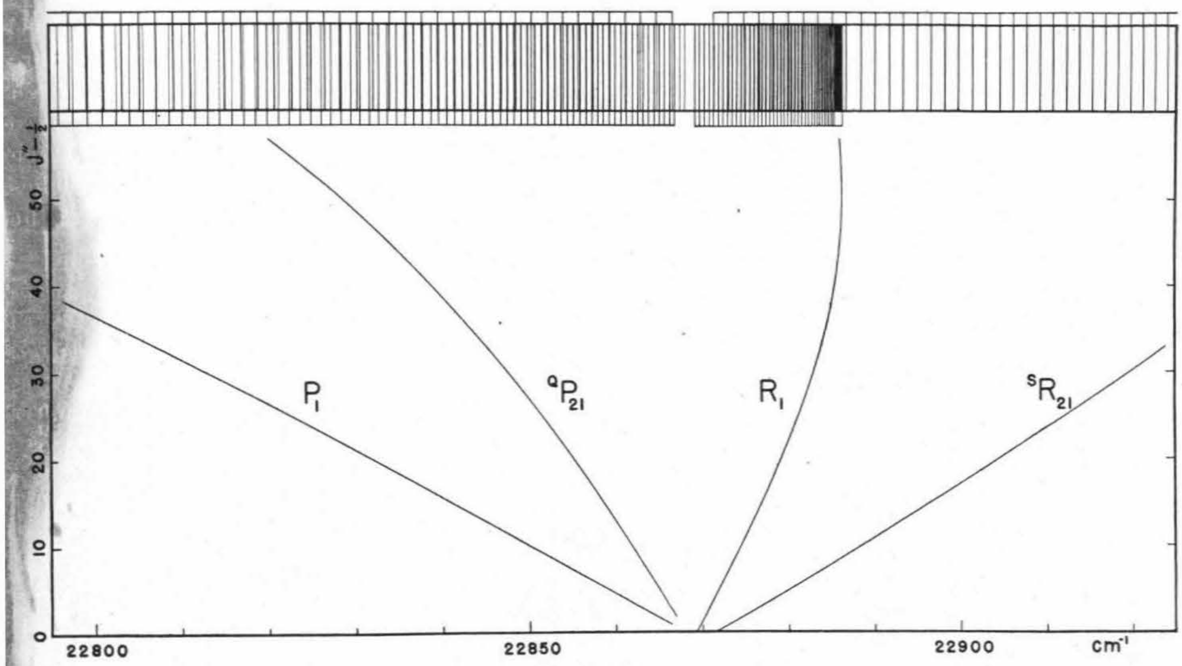

FIG. 1. The lines, disposition of branches, and Fortrat diagram of the high frequency sub-band of the (0, 0) band of the α system. The two unmarked lines near the origin are the first two lines of the weak Q_1 branch.

large, the results should be rather reliable. The best values obtained by this method are:

$$\omega_e = 710.9\ \text{cm}^{-1}, \qquad x_e\omega_e = 8.6\ \text{cm}^{-1}.$$

These results at once imply certain conclusions concerning the electronic states involved in the α system. Since the lower state seems certainly to be $^2\Pi$, the absence of strong Q branches at the origin of the (0, 0) band means that the upper state must also be $^2\Pi$. But the approximate equality of the doublet separations in the α and β systems suggests that this $^2\Pi$ state is very near to case b, under which circumstances branches violating the Σ selection rule, as observed in the ultraviolet spectrum of O_2^+ by Stevens,[5] are to be expected. Each band would then include four head forming branches, as observed in the α system. Since $\omega_e'' - \omega_e'$ is nearly equal to the doublet separation in the lower $^2\Pi$ state, overlapping of bands is so complete that the rotational analysis has been of necessity limited to the (0, 0) band.

Rotational analysis

The analysis of the (0,0) band of the α system, whose four heads occur at 4354, 4368, 4388, and 4400A, was begun on the assumption that it arose from a transition between states of the type described above. In the most general case, such a band is divided into two twelve-branch sub-bands, separated by a frequency equal approximately to the magnetic coupling constant, A''. The high frequency sub-band includes the $^SR_{21}$, R_1, $^RQ_{21}$, Q_1, $^QP_{21}$, and P_1 branches, and the low frequency component the R_2, $^QR_{12}$, Q_2, $^PQ_{12}$, P_2, and $^OP_{12}$ branches, each of which is itself a double branch because of the Λ type doubling of the rotational levels. Actually, however, the latter is small, and the resulting four Q branches are not only weak, but also coalesce with their P and R branch neighbors when the spin doubling in the upper state is small, which proves to be the case in this system. Hence each sub-band consists essentially of four branches, whose arrangement is shown in Fig. 1 for the high frequency component of the (0, 0) band. The appearance of the other sub-band is very similar to that shown, with the positions of regular and satellite branches interchanged.

The lines of the $^SR_{21}$ and R_2 branches, which occupy analogous positions in the two sub-bands, were completely free from overlapping beyond

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[5] Stevens, Phys. Rev. **32**, 1292 (1931).

their first ten lines, which were hence easily located by extrapolation. The R_1 and $^QR_{12}$ branches were observable from their first lines to their heads, but in neither case could the returning branch be detected. The $^QP_{21}$ and P_2 branches were followed from their first lines to beyond $J=60\frac{1}{2}$, but the P_1 and $^OP_{12}$ branches, whose spacings are about twice those of the former, coincided with them at around $J=19\frac{1}{2}$, and were impossible to follow below $J=15\frac{1}{2}$. In the high frequency sub-band, these coincidences were so good that the P_{21} and R_1 branches were mistaken by Johnson and Jenkins for the P and R branches of a simple $\Sigma\rightarrow\Sigma$ band. Since the first lines of the

TABLE II. *The (0, 0) band of the α system of SiF.*

$J-\frac{1}{2}$	$^SR_{21}$	R_1	$^QP_{21}$	P_1	R_2	$^QR_{12}$	P_2	$^OP_{12}$
0	22871.33	22869.24						
1	73.08	69.77		22866.64	22712.38	22709.13		22705.96
2	74.82	70.36	22866.89	64.80	14.07	09.64	22706.32	04.09
3	76.55	70.89	66.30	62.97	15.75	10.14	05.48	02.22
4	78.27	71.44	65.70	61.15	17.41	10.63	04.77	00.36
5	79.98	71.97	65.11	59.33	19.05	11.11	04.13	698.47
6	81.68	72.49	64.50	57.57	20.68	11.57	03.46	96.65
7	83.37	72.99	63.88	55.77	22.30	12.02	02.82	94.80
8	85.05	73.54	63.25	54.06	23.90	12.48	02.10	93.00
9	86.70	74.05	62.62	52.25	25.48	12.97	01.38	91.16
10	88.40	74.57	62.00	50.47	27.05	13.33	00.64	89.23
11	90.05	75.04	61.33	48.63	28.60	13.73	699.94	87.32
12	91.70	75.55	60.70	46.89	30.13	14.13	99.17	85.47
13	93.30	76.02	60.03	45.06	31.65	14.54	98.39	83.58
14	94.95	76.50	59.38	43.24	33.13	14.91	97.58	81.65
15	96.54	76.97	58.69	41.39	34.63	15.25	96.78	79.67
16	98.16	77.43	58.03	39.58	36.09	15.55	95.95	77.70
17	99.76	77.91	57.35	37.77	37.54	15.82	95.10	75.68
18	901.32	78.34	56.65	35.90	38.96	16.13	94.24	73.69
19	02.89	78.77	55.93	34.01	40.35	16.40	93.37	71.66
20	04.49	79.21	55.22	32.19	41.77	16.67	92.49	69.66
21	06.05	79.59	54.53	30.34	43.15	16.94	91.63	67.60
22	07.59	80.02	53.80	28.38	44.51	17.13	90.70	65.55
23	09.12	80.43	53.06	26.59	45.87	17.38	89.76	63.44
24	10.66	80.80	52.29	24.66	47.17	17.57	88.80	61.40
25	12.19	81.18	51.54	22.78	48.48		87.81	59.27
26	13.68	81.61	50.77	20.86	49.75		86.83	57.10
27	15.17	81.96	49.97	18.94	51.01		85.86	54.96
28	16.65	82.33	49.18	17.02	52.27		84.84	52.83
29	18.12	82.69	48.39	15.10	53.49		83.80	50.63
30	19.59	83.03	47.57	13.07	54.68		82.73	48.47
31	21.02	83.33	46.77	11.18	55.88		81.63	46.25
32	22.43	83.65	45.93	09.22	57.06		80.54	44.03
33	23.86	83.91	45.09	07.25	58.17	head	79.44	41.76
34	25.25	84.18	44.22	05.25	59.27	18.38	78.31	39.48
35	26.64	84.39	43.34	03.26	60.38		77.15	37.21
36	28.00	84.62	42.47	01.11	61.43		75.96	34.93
37	29.35	84.90	41.60	799.18	62.47		74.76	32.57
38	30.69	85.06	40.68	97.16	63.49		73.52	30.21
39	31.97	85.27	39.75	95.11	64.50		72.30	27.86
40	33.31		38.82	93.05	65.44		71.06	25.49
41	34.54		37.86	90.98	66.41		69.75	23.11
42	35.81		36.87	88.87	67.34		68.45	20.63
43	37.13		35.91	86.78	68.18		67.12	18.18
44	38.30		34.91	84.63	69.10		65.81	15.70
45	39.47		33.85	82.51	69.91		64.40	13.27
46	40.66	head	32.82	80.36	70.74		62.97	10.74
47	41.78	86.22	31.79	78.15	71.51		61.54	08.11
48	42.97		30.70	76.02	72.32		60.09	05.33
49	44.05		29.63	73.83	72.97		58.63	
50	45.12		28.51	71.55	73.65		57.15	
51	46.15		27.33	69.34	74.35		55.58	
52	47.23		26.21	67.08	74.96		53.99	
53	48.22		25.00	64.76	75.59		52.42	
54	49.17		23.77	62.29	76.19		50.81	

Also the lines $Q_1(\frac{1}{2})=22867.47$ and $Q_1(1\frac{1}{2})=22868.04$. $^PQ_{12}(1\frac{1}{2})$ was too confused to be measured.

R_1, ${}^QR_{12}$, ${}^QP_{21}$, and P_2 branches were visible, their numberings were determined at once. The first lines, and hence the numberings, of the extrapolated ${}^SR_{21}$ and R_2 branches were then chosen to provide the correct number of missing lines. The numbering and the frequency of the lower lines of the two remaining branches were determined by means of the term differences in the upper state. The ${}^RQ_{21}$ and Q_1 branches were found to have coalesced with the R_1 and ${}^QP_{21}$ branches, but since the Q_1 branch begins with $J=\frac{1}{2}$ and the ${}^QP_{21}$ with $J=2\frac{1}{2}$, the first two lines of the former were observed, and proved to be of the expected low intensity. In the other sub-band an analogous situation occurs, the first line of the ${}^PQ_{12}$ branch being observable, since it begins with $J=1\frac{1}{2}$, while the P_2 branch begins with $J=2\frac{1}{2}$. All of the lines below $J=55\frac{1}{2}$ are listed in Table II, the measurements being made in all cases to the center of the Λ doublets.

The rotational terms of the upper and lower states may be expressed by the following equations, which follow immediately from the application to the ${}^2\Pi$ state of the general expressions for case *a* and case *b* molecular multiplets,[6] assuming the Λ doubling negligible in the upper state, and including all functions independent of J, K, and Σ as the quantity T_0, which will hence be constant for any one band:

$$\begin{aligned} T_1'(K)&=T_0'+f(K,+\tfrac{1}{2})+B_v'K(K+1)\\ &\qquad+D_v'K^2(K+1)^2+\cdots,\\ T_2'(K)&=T_0'+f(K,-\tfrac{1}{2})+B_v'K(K+1)\\ &\qquad+D_v'K^2(K+1)^2+\cdots,\\ T_1''(J)&=T_0''-A''/2-B_{v1}''^*/4+\phi_i(-\tfrac{1}{2},J)\\ &\qquad+B_{v1}''^*J(J+1)+D_{v1}''^*J^2(J+1)^2+\cdots,\\ T_2''(J)&=T_0''+A''/2-9B_{v2}''^*/4+\phi_i(+\tfrac{1}{2},J)\\ &\qquad+B_{v2}''^*J(J+1)+D_{v2}''^*J^2(J+1)^2+\cdots. \end{aligned}\tag{1}$$

The constants of the lower state marked with asterisks are introduced to allow for a tendency toward case *b*. They are given, according to the theory of Hill and Van Vleck,[6] by the following expression, for a ${}^2\Pi$ state:

$$B_v^*=B_v(1\pm B_v/A).\tag{2}$$

The value of B_{v2}^* is given by the upper, and of B_{v1}^* by the lower sign.

Aside from the Λ doubling, the term differences are given by the relations:

$$\begin{aligned} \Delta_2T_1'(J)&=R_1(J)-P_1(J)\\ &={}^QR_{12}(J)-{}^OP_{12}(J),\\ \Delta_2T_2'(J)&=R_2(J)-P_2(J)\\ &={}^SR_{21}(J)-{}^QP_{21}(J),\\ \Delta_2T_1''(J)&=R_1(J-1)-P_1(J+1)\\ &={}^SR_{21}(J-1)-{}^QP_{21}(J+1),\\ \Delta_2T_2''(J)&=R_2(J-1)-P_2(J+1)\\ &={}^QR_{12}(J-1)-{}^OP_{12}(J+1). \end{aligned}\tag{3}$$

Eqs. (1) show that, if the small quantities $\Delta_2f(K, J-K)$ be neglected:

$$\begin{aligned} \Delta_2T_1'/2(2K+1)&=\Delta_2T_2'/2(2K+1)\\ &=B_v'+2D_v'(K^2+K+1)+\cdots. \end{aligned}\tag{4}$$

Hence when the left side of (4) is plotted against $(K+\frac{1}{2})^2$, a straight line of slope $2D_v'$ and intercept $B_v'+\frac{3}{2}D_v'$ should be obtained. Such a graphical treatment of the term differences obtained from the ${}^SR_{21}$, ${}^QP_{21}$, R_2, and P_2 branches enabled B_0' to be evaluated within an uncertainty of ± 0.0001 cm^{-1}, and D_0' within limits of about ± 1.5 percent. Exactly analogous expressions in terms of J apply to the lower state, and the constants were found in the same manner, with comparable results. The values so determined are as follows:

$$\begin{aligned} B_0''&=0.5795\ \text{cm}^{-1}, & D_0''&=-1.12\times10^{-6}\ \text{cm}^{-1},\\ B_0'&=0.5743\ \text{cm}^{-1}, & D_0'&=-1.59\times10^{-6}\ \text{cm}^{-1}. \end{aligned}$$

The value of A'' was determined by the following relation, obtained from Eqs. (1) by neglecting the term $\phi_i(\Sigma, J)$:

$$\begin{aligned} A''+(B_{01}''^*-9B_{02}''^*)/4&={}^QP_{21}(J)\\ &\quad-P_2(J)-J(J+1)(B_{02}''^*-B_{01}''^*)+\cdots. \end{aligned}\tag{5}$$

The right-hand expression was found to be constant within the experimental error, when evaluated for the first twelve lines of the two branches, and gave the average value of 160.83 cm^{-1}. Hence, with Eq. (5), the value of A'' may be obtained, and is found to be $+161.99$ cm^{-1}, making A''/B_0'' equal to $+279.53$. The latter indicates that the lower ${}^2\Pi$ state is, as was assumed, intermediate between case *a* and case *b*, but much closer to the former.

The intensity of the satellites, the doublet separation in the α system, and the coalescence of branches already remarked indicate that the

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[6] Mulliken, Rev. Mod. Phys. **2**, 105, 114 (1930).

upper ${}^2\Pi$ state is very near to case b. It would hence be anticipated[7] that the spin doublet separation be given by the expression:

$$\Delta f(K)=[A'/K(K+1)+\gamma_i](K+\tfrac{1}{2}), \qquad (6)$$

where the value of γ_i is different for the c and d sub-levels.[8] Since γ_i is almost negligibly small in this case, and since, moreover, the Λ doublets are unresolved at low values of J, it may be replaced by an average value $\gamma_{\text{av.}}$, in the calculation of A'. With this assumption, Eq. (6), combined with Eqs. (1), gives the expression:

$$[{}^QR_{12}(J)-P_2(J+1)]/(J+1)-2B_{02}''^{*}-4J^2D_{02}''^{*}=A'/(J+\tfrac{1}{2})(J+\tfrac{3}{2})+\gamma_{\text{av.}} \qquad (7)$$

An analogous equation applies in the other sub-band. The left-hand expression in (7) plotted against $1/(J+\frac{1}{2})(J+\frac{3}{2})$ should give a straight line of slope A' and intercept $\gamma_{\text{av.}}$. When actually attempted, it was found that these quantities were of the order of magnitude of the experimental errors, so that no unique line was determined. It can only be stated that A' is surely positive, and probably less than 0.10 cm^{-1}. This means that A'/B_0' is about 0.17, and that the upper state is as close to case b as the ${}^2\Pi$ state of BeH.[9]

The origins of the two sub-bands cannot be precisely determined without exact values of A' and γ_i, but the following values, obtained from the R_1 and P_2 branches are probably quite accurate:

$$\nu_{01}=T_0'-T_0''+A''/2+B_{01}''^{*}/4=22868.50\text{ cm}^{-1},$$
$$\nu_{02}=T_0'-T_0''-A''/2+9B_{02}''^{*}/4=22707.70\text{ cm}^{-1}.$$

The P_2 and ${}^QP_{21}$ branches can be followed out to very high values of J, where the Λ doublets are well resolved. Between $J=35\frac{1}{2}$ and $70\frac{1}{2}$, the doubling in the ${}^2\Pi_{\frac{1}{2}}$ state is well represented by the expected relation:[10]

$$\phi_c(J)-\phi_d(J)=a(J+1/2). \qquad (8)$$

The constant a is found to be 0.0067 cm^{-1}. The doubling in the ${}^2\Pi_{1\frac{1}{2}}$ state is less accurately observable because of the overlapping (1, 1) band, but beyond $J=40\frac{1}{2}$ it is of about the same order of magnitude, but increasing more rapidly and nonlinearly with $J+1/2$. This behavior of the Λ doublets indicates that they arise almost entirely from doubling of the rotational levels of the case a ${}^2\Pi$ state.

THE STRUCTURE OF THE β SYSTEM

Vibrational structure

Asundi and Samuel's analysis of the band head data attributes the β system to a ${}^2\Sigma\rightarrow{}^2\Pi$ transition, but the constants of Johnson and Jenkins have been but slightly altered, since the doublet separation was found to be very nearly equal to $\omega_e'-\omega_e''$. The resulting superposition is remarkably accurate in the bands near the origin of the system, measurable separations commencing only in the weaker (2, 0), (0, 2), and (0, 3) sequences, where the extra heads were supposed by Johnson and Jenkins to arise from a vibrational isotope effect. Of course the isotopic displacement coefficient failed to agree with any calculated from masses of silicon isotopes. Careful investigation of heavily exposed photographs of this system taken on a quartz Littrow spectrograph giving a dispersion of 3.7A/mm in the vicinity of 2900A showed no evidence of true isotopic heads.

Because of the coincidence remarked above, only the low frequency sub-band of the first band of each sequence would be expected to be free from complete overlapping. Fortunately, however, the Franck-Condon diagram for the system is a narrow parabola, the only member of the principal sequence appearing with appreciable intensity being the (0, 0) band itself. Beside being confused by this superposition, the (0, 1) and (1, 0) bands were too weak after 50 hours exposure to permit analysis, which consequently was limited to the (0, 0) band.

Rotational analysis

The (0, 0) band, whose heads occur at 2880, 2881, 2893, and 2894A, would be expected to consist of six regular and two satellite branches, if the spin doubling in the ${}^2\Sigma$ state were small. Such is found to be the case, though measurable spin doublets are observed in the higher members of the Q_1 branch. Of the six regular branches, three are head forming, while the fourth head of the complete band is formed by one of the satellites. All six main branches are observed, but only the head forming ${}^OP_{12}$ satellite is found, and its individual lines, despite their favorable

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[7] Mulliken and Christy, Phys. Rev. **38**, 87 (1931).

[8] Mulliken, Rev. Mod. Phys. **2**, 108, 110 (1930).

[9] Watson and Parker, Phys. Rev. **37**, 167 (1931).

[10] Mulliken, Rev. Mod. Phys. **3**, 113 (1931).

location, were not measurable. The $^{S}R_{21}$ branch is presumably hidden by the stronger regular branches. The observed intensity relations among these branches confirm Asundi and Samuel's conclusion that the β system arises from a $^{2}\Sigma \rightarrow {}^{2}\Pi$ transition.

Because of the low total intensity, of which, moreover, less than half is divided among the P and R branches, the latter were hidden at low values of J by the strong Q branches, while all of the branches of the low frequency sub-band were lost when they overlapped the P_1 head of the second sub-band. The latter branch, moreover, could not be followed through the strong Q_1 head. It was therefore necessary to number the lines in an indirect manner. Only one method of numbering gave both the same term differences in the upper state, given by Eqs. (3), and also a reasonable value of D_0'. The term differences in the lower state were then found in agreement with those obtained from the α system. The Q branches were numbered by the approximate relation

$$R(J)-Q(J)=Q(J+1)-P(J-1). \qquad (9)$$

TABLE III. *The (0, 0) band of the β system of SiF.*

$J-\frac{1}{2}$	P_1	Q_1	R_1	$^{0}P_{12}$	P_2	Q_2	R_2
0							
1						34559.91	
2	head	head		head	head	60.78	
3	34702.43	34717.39		34559.98	34556.47	61.76	
4						62.76	
5						63.81	
6						64.99	
7						66.22	
8		18.04				67.54	
9		18.47				69.61	
10		18.94				70.51	
11		19.54				72.18	
12		20.23				73.85	
13		——				75.69	
14		——				77.62	
15		——	34740.86			79.63	
16		22.85	43.15		61.16	81.63	
17		23.83	45.65		62.15	83.79	
18		24.97	48.12		63.04	85.98	
19		26.26	50.61		64.10	88.32	
20		27.57	53.18		65.41	90.83	34618.71
21		29.05	55.88		66.62	93.39	22.51
22		30.60	58.71		68.04	95.98	26.37
23		32.23	61.22		69.41	98.60	30.46
24	03.35	33.94	64.07		70.93	601.37	34.46
25	03.92	35.82	67.24		72.68	04.28	38.41
26	04.52	37.70	70.17		74.34	07.31	42.54
27	05.18	39.71	73.32		76.04	10.33	46.78
28	05.96	41.84	76.68		77.90	13.71	51.10
29	06.90	44.11	80.04		79.94	17.56	55.49
30	07.82	46.38	83.54		82.09	20.14	60.11
31	08.84	48.76	86.95		84.16	23.57	64.80
32	09.97	51.18	90.50		86.40	27.10	69.53
33	11.16	53.95	94.10		88.83	30.67	74.56
34	12.63	56.56	98.13		91.17	34.30	79.12
35	14.17	59.39	802.00		93.76	38.09	
36	15.78	62.24	05.78		96.36	41.93	
37		65.16	09.80		98.99	45.87	
38		68.33	14.09		601.77	49.86	
39		71.50	18.36		04.63	53.96	
40		74.88	22.68		07.65	58.07	
41		78.04	27.23		11.04	62.46	
42		81.39	32.31		14.26	66.78	
43		85.02	37.03		17.51	70.07	
44		88.57	41.95		20.72	75.75	
45		92.36	47.06		24.34		
46		96.11	52.12				
47		800.12	57.25				
48		04.21	62.45				
49		08.25	67.42				
50		12.47	72.77				

TABLE IV. *Constants of the SiF molecule.*

STATE	$T_e+G(0)$ (cm^{-1})	$T_e+G(0)$ (volts)	ω_e (cm^{-1})	$x_e\omega_e$ (cm^{-1})	B_0 (cm^{-1})	r_0 (A)
$C^2\Sigma$	39531.5[1]	4.877[1]	891.7[1]	6.2[1]		
$B^2\Sigma$	34717.39	4.283	1011.2[1]	4.8[1]	0.662	1.54
$A^2\Pi_{\text{reg.}}$	22868.50	2.821	710.9	8.6	0.5743	1.606
	160.83	0.020				
$X^2\Pi_{\text{reg.}}$	0	0	856.7[1]	4.7[1]	0.5795	1.599

[1] Asundi and Samuel, Proc. Ind. Acad. Sci. **3**, 346 (1936).

An independent numbering was also possible, since when the first differences are plotted against J, they extrapolate to $-B_{01}''^*$ at $J=-1/2$, for the Q_1, and to $+B_{02}''^*$ at $J=-3/2$, for the Q_2 branch. The two numberings were found identical, though it seems impossible to obtain the Λ doubling in the $^2\Pi$ state by the usual combinations with the Q branches. This is probably to be expected from the small magnitude of the doubling, and the extreme difficulties and certain errors involved in the measurements of the lines. The frequencies and numbering of the lines are shown in Table III.

B_0' was determined by the graphical method already described, but since so few combinations were available, the slope of the line was determined independently by Kratzer's relation

$$D_e=-4B_e^3/\omega_e^2. \tag{10}$$

From the slope so obtained, B_0' was found to be equal to 0.622 cm^{-1}.

From the separations of the Q_1 and $^RP_{21}$ branches, which are measurable beyond $J=50\frac{1}{2}$, the value of the spin doubling coefficient γ was found to be approximately 0.011 cm^{-1}.

CONCLUSION

It is felt that the present analysis establishes with reasonable certainty the nature of three of the electronic states of the SiF molecule, while Asundi and Samuel's vibrational analysis of the γ system suggests the nature of a fourth state to be $^2\Sigma$, though it could scarcely be distinguished with certainty from a close $^2\Delta$ without further investigation. The known constants of these four states are collected in Table IV, where the upper state of the γ system is designated $C^2\Sigma$, in accordance with the conclusions of Asundi and Samuel.

The $A^2\Pi$ state of this molecule has proved to be a most unusual and interesting one. The occurrence of nearly pure case b coupling in the $^2\Pi$ state of so heavy a molecule is itself unique, and the (0, 0) band of the α system, with its visible origin and strong satellite branches, provides an excellent example of the rotational structure of a $^2\Pi$ (case b)$\rightarrow$$^2\Pi$ (case a) band. In addition, this state appears to constitute a genuine exception to such empirical relations as Badger's rule[11] between r_e and ω_e, for while r_e is very nearly the same in the two states, ω_e differs by 145.8 cm^{-1}. Of course, such empirical rules mean only that a fairly consistent relationship has been found to exist between the position of the minimum in the potential functions of ordinary molecules and the value of the second derivative at that point, while their failure in any particular case signifies a deviation of its potential function from the usual type. The $^1\Pi$ state of AlH, for example, is obviously unusual in possessing a dissociation energy of only 0.26 ev, and ω_e is observed to be about 600 cm^{-1} lower than calculated from r_e. Though the extreme case b coupling in the $A^2\Pi$ state of SiF is extraordinary, there exists no obvious correlation between it and the low value of ω_e, for the latter shows no trend away from the normal in the $^2\Pi_u$ state of O_2^+, which approaches case b, nor in the nearly pure case $b^2\Pi$ states of CH or BeH. Since there exist no extended vibrational progressions in the α system, little can be definitely stated concerning the magnitude of the dissociation energy for the $A^2\Pi$ state, and the nature of the potential function at points far from the equilibrium position. It does, however, appear that the two $^2\Pi$ states are derived from the same electronic states of the silicon and fluorine atoms, and should be analogous to the $^2\Pi$ states of O_2^+.

The author is pleased to express his appreciation to Professor R. M. Badger, at whose suggestion this investigation was undertaken, for his encouragement and assistance in its completion, as well as to Dr. C. M. Blair, to whom he is especially indebted for the photographs of the α system, and measurements of several of the branches of its (0, 0) band.

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[11] R.M. Badger, J. Chem. Phys. **3**, 710 (1935).

12.

NOTE ON THE INTERPRETATION OF UNIDENTIFIED INTERSTELLAR LINES

ABSTRACT

Spectroscopic objections to recent assignments of Merrill's unidentified stationary lines to molecular absorption bands are outlined.

Since the suggestion of the possible molecular origin[1] of Merrill's four interstellar lines,[2] attempts to correlate them with absorption bands of known molecules have been made.[3,4] The resulting identifications are, unfortunately, open to purely spectroscopic criticism, and indeed it seems highly improbable that these lines can be interpreted as molecular bands.

Molecular absorption in the visible spectrum might be formally attributed either to rotation-vibration bands or to electronic bands. In considering the absorption due to the small number of molecules which could conceivably exist in interstellar space, however, bands of the first type must surely be excluded, for the intensities of the high harmonics and combinations which lie in the visible are so extremely small that one could hope to observe such bands only in the relatively dense, cool planetary atmospheres. For this reason alone Swings's[3] identification of the interstellar lines λ 6283.91 and

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[1] Russell, *M. N.*, **95**, 635, 1935.

[2] *Pub.*, *A.S.P.*, **46**, 206, 1934; *Ap. J.*, **83**, 826, 1936.

[3] Swings, *M.N.*, **97**, 212, 1937.

[4] Saha, *Nature*, **139**, 840, 1937.

13.

λ 6613.9 with $7\nu_3$ and $\nu_1 + 4\nu_2 + 5\nu_3$, respectively, of carbon dioxide seems very doubtful. The absence of the very much stronger Venus bands in interstellar absorption[5] confirms this conclusion.

On the other hand, it would appear reasonable to investigate the intense electronic absorption bands arising from molecular ground states. To identify satisfactorily an interstellar line with a given absorption band, however, it must be possible to show that (1) the shape of the line is compatible with the predicted envelope of the band at some reasonable temperature; (2) the wave-length of the line is equal to the wave-length of the intensity maximum in the band; and (3) the identification is compatible with the intensity distribution in the band system. These three requirements can best be illustrated by a brief outline of the extent to which each is satisfied in Saha's assignment of the interstellar line λ 6283.91 to the (11, 0)[6] band of the sodium molecule.[4]

1. *Shape.*—The *R* branch of the (11, 0) band has formed a head at its third line, so that even at 3.2° absolute the band would be strongly asymmetric, with a sharp, intense head on the short wave-length side. The interstellar line is observed to be approximately symmetric, although a definite statement as to its symmetry is impossible because of the proximity of an atmospheric oxygen band.

2. *Wave-length.*—The best absorption and magnetic rotation data[7] show that the center of the interstellar line is at a wave-length 3.60 A shorter than that of the (11, 0) band head. So large a discrepancy is surely real, and is obviously independent of assumptions concerning the effective temperature of the absorbing molecules.

3. *Intensity distribution.*—Absorption measurements in sodium vapor[8] lead one to expect the red system of the sodium molecule in interstellar absorption to consist solely of those bands originating in the lowest vibrational state—i.e., of the v' progression ($v'' = 0$)—which includes at least seven bands of greater intensity than (11, 0), none of which is observed as an interstellar line.

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[5] Private communication from Dr. Merrill.

[6] The vibrational analysis of this system has been revised so that the band called (8, 0) by Saha is now recognized to be (11, 0).

[7] Fredrickson and Stannard, *Phys. Rev.*, **44**, 632, 1933.

[8] Fredrickson and Watson, *ibid.*, **30**, 431, 1927.

14.

Saha's tentative identification of the λ 5780.55 interstellar line with the (5, 0) band of *NaK* is subject to essentially the same criticism. The wave-length discrepancy[9] in this case is 3.38 A.

Because of extremely low pressures in interstellar space, and the relatively high probability of the dissociation of molecules either by collisions with "high temperature" atoms and electrons or by photodissociation, it seems very reasonable to consider the probability of the existence of an appreciable concentration of polyatomic molecules as negligible and to rule out, as well, all diatomic molecules of low dissociation energy. Furthermore, since there is no experimental evidence for v' progressions ($v'' = 0$) of more than one member, only those electronic transitions which would produce such spectra—i.e., transitions involving only small changes of the moment of inertia—need be considered. A careful survey of the spectra of all known diatomic molecules which satisfy these conditions has revealed no possible identification of the strong interstellar lines, and it seems highly probable that their explanation will be found elsewhere.

It is a pleasure to thank Dr. Paul W. Merrill both for the privilege of inspecting his microphotometer tracings of the interstellar lines and for a number of helpful discussions during the preparation of this note.

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August 14, 1937

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[9] Loomis and Arvin, *ibid.*, **46**, 286, 1934.

THE SPECTRUM OF ALLENE IN THE PHOTOGRAPHIC INFRARED

INTRODUCTION

Although the rotational structure of the nondegenerate rotation-vibration bands of symmetric rotators is simple and well understood, that of the degenerate bands may be complicated by a strong rotation-vibration interaction which, though adequately explained in most cases, appears to produce unpredictable complexities in others[1]. Consequently it seemed of interest to investigate the rotational structure of the bands of allene in the photographic infrared under dispersion sufficient to resolve the rotational fine structure of both the degenerate and nondegenerate types, comparing that observed for the former with the structure predicted by the first order theory of Teller[2], and using 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 hydrogen-carbon-hydrogen bond angle, a knowledge of its value would determine the carbon-carbon distance with considerable accuracy. In addition, since the existing Raman and near infrared data for this molecule have never been systematized, it was found useful to first assign frequencies and carry out a normal coordinate treatment for those belonging to the nondegenerate representations. The frequencies in the degenerate representation still remain rather uncertain.

EXPERIMENTAL

The allene sample used in this investigation was part of a sample used by Pauling and Brockway for electron diffraction investigation of this molecule, furnished by Dr. W. E. Vaughan of Harvard University. A second sample for the high pressure photographs was kindly sent by Dr. J. W. Linnet, also of Harvard University. The gas was confined in a six meter pyrex absorption tube, having a volume of approximately one liter. 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 12000 A., and all intense bands were then photographed in the first order of the 21 foot grating spectrograph of this laboratory; at pressures varying from 40 mm. to 1.5 atmospheres. Wave length measurements on the prism spectrograms were made with respect to sodium, potassium, and barium 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 were used, and in every case visible radiation was removed with filters.

FUNDAMENTAL FREQUENCIES AND FORCE CONSTANTS

In Figure 1 are shown a set of eleven symmetry coordinates and their distribution among the irreducible representations of the point group V_d, under whose operations the equilibrium configuration of the molecule is invariant. Fundamental frequencies may, for clarity, be assigned to these symmetry coordinates, which will approximate the true normal coordinates rather closely except in the representation E, where the frequencies are so close together that there will be strong mixing.

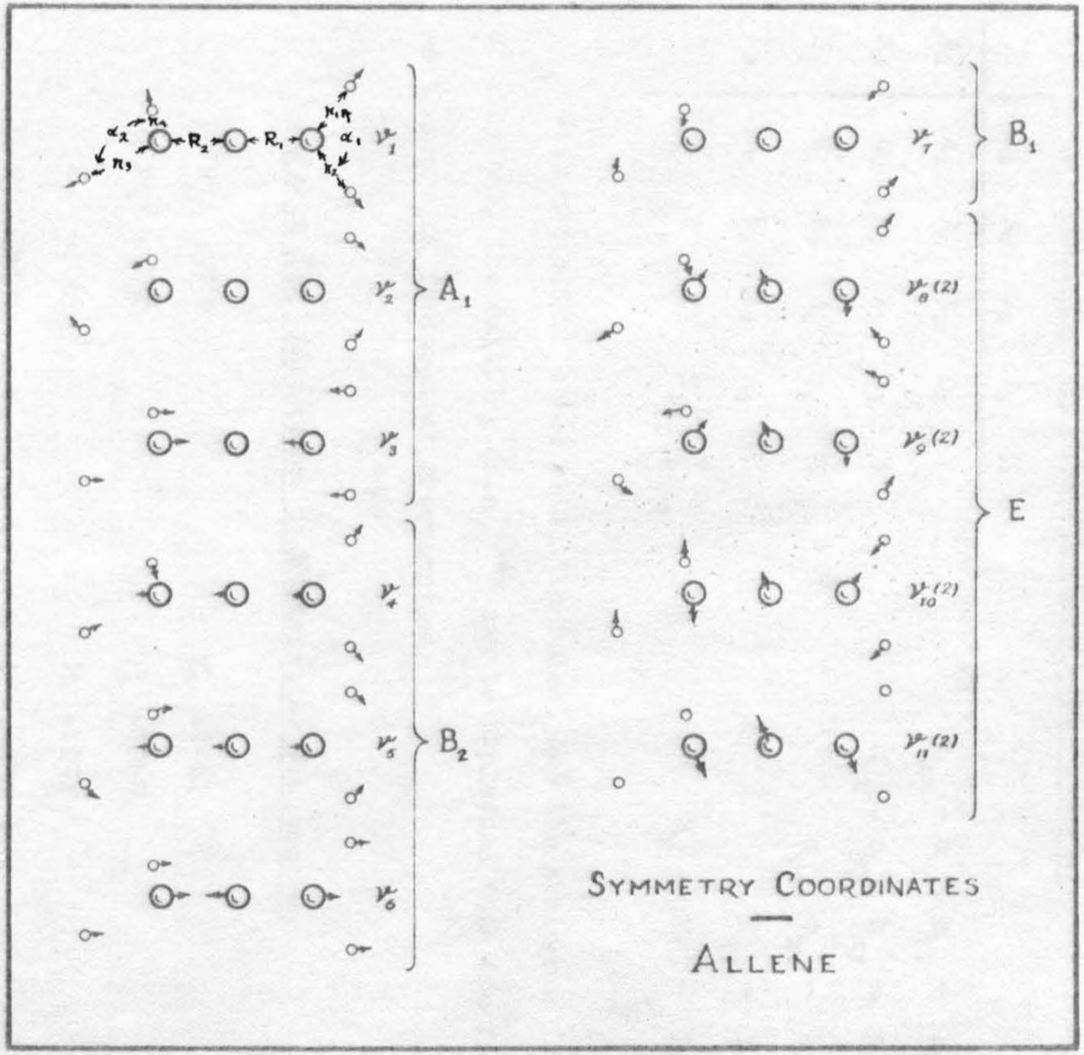

r_4
α_2
r_3
R_2
R_1
r_1
r_2
α_1
ν_1
ν_2
A_1
ν_3
ν_4
ν_5
B_2
ν_6
ν_7
B_1
$\nu_8^{(2)}$
$\nu_9^{(2)}$
E
$\nu_{10}^{(2)}$
$\nu_{11}^{(2)}$
SYMMETRY COORDINATES
ALLENE

Fig. 1

The selection rules for the infrared and Raman spectra are determined by the transformation properties of the electric moment and polarizability tensor components, and the multiplication table for the irreducible representations of V_d,[3] both of which are shown in Table I.

Table I. Selection Rules for the Group V_d.

	A_1	A_2	B_1	B_2	E
A_1	A_1	A_2	B_1	B_2	E
A_2	A_2	A_1	B_2	B_1	E
B_1	B_1	B_2	A_1	A_2	E
B_2	B_2	B_1	A_2	A_1	E
E	E	E	E	E	$A_1 + A_2 + B_1 + B_2$

$\alpha_{xx} + \alpha_{yy}, \alpha_{zz} \sim A_1$

$\alpha_{xx} - \alpha_{yy}, \alpha_{xy} \sim B_1$

$\alpha_{yz}, \alpha_{xz} \sim E$

$M_z \sim B_2$

$M_x \pm iM_y \sim E$

With the aid of these selection rules, and the analogous frequencies of ethylene, the existing data[4,5,6] can be explained with the following assignments of fundamental frequencies:

Table II. Assignment of Fundamental Frequencies

$\nu_1 = 2992$

$\nu_2 = 1430$

$\nu_3 = 1069$

$\nu_4 = 2981$

$\nu_5 = 1381$

$\nu_6 = 1961$

$\nu_8 = 3060$

$\nu_9 = 1031$

$\nu_{10} = 838$

$\nu_{11} = 353$

The other infrared bands of Bonner and Hofstadter may then be assigned as follows:

Table III. Assignment of Combinations and Harmonics

$1143 = \nu_{10} + \nu_{11}$

$1678 = 2\nu_{10}$

$2392 = \nu_5 + \nu_9$

$4525 = \nu_2 + \nu_8$

$6289 = 2\nu_8$

It should be pointed out that other assignments are formally possible in the degenerate representation; in particular, 353 might be ν_7, 1678 ν_9, 1031 ν_{10}, and 838 ν_{11}, but this seems to place the C=C=C bending frequency improbably high, and does not provide so satisfactory a correlation between the C-H bending frequencies of allene and those of ethylene. A search for 353 in the infrared would settle the question.

A normal coordinate treatment has also been made for the six frequencies in the representations A_1 and B_2, using the following potential function:

$$\begin{aligned} 2V = {} & K(\delta R_1^2 + \delta R_2^2) + L(\delta r_1^2 + \delta r_2^2 + \delta r_3^2 + \delta r_4^2) + Mr^2(\delta \alpha_1^2 + \delta \alpha_2^2) \\ & + 2A(\delta r_1 \delta r_2 + \delta r_3 \delta r_4) + 2B(\delta r_1 \delta R_1 + \delta r_2 \delta R_1 + \delta r_3 \delta R_2 + \delta r_4 \delta R_2) \\ & + 2C(\delta R_1 \delta R_2) , \end{aligned}$$

where the significance of the symbols is given in Fig. 1. In a function of this type, the six frequencies will determine only five independent constants, whose values, expressed in megadynes / cm., are found to be:

$L+A = 0.5048$

$B = 0.02532$

$M = 0.06096$

$C = 0.02302$

$K = 0.8828$

PHOTOGRAPHIC INVESTIGATIONS

The allene spectrum was first photographed under low dispersion to determine the positions of bands suitable for high dispersion study. In Fig. 2 is shown a microphotometer trace, twice enlarged, of such a spectrogram, corrected for the change in plate sensitivity with wavelength and for the effects of plate grain. The stronger bands were then photographed under high dispersion, and with the aid of the assigned fundamentals, the selection rules, and the observed rotational structures, the ten bands in the region between 7000 and 12000 A. may be assigned as in Table IV.

Table IV. Assignment of Bands in the Photographic Infrared

Wavelength(A.)	Frequency(cm.$^{-1}$)	Assignment	Irr. Rep.
11444.32	8738.96	$3\nu_4$	B_2
11394.0	8776.6	$2\nu_1 + \nu_4$	B_2
11139	8978	$2\nu_8 + \nu_4$	B_2
11097	9012	$2\nu_8 + \nu_1$	B_2
11017.2	9076.7	$3\nu_8$	E
10920	9718	$3\nu_4 + \nu_9$	E
9602	10420	$3\nu_8 + \nu_5$	E
9338	11710	$3\nu_4 + \nu_1$	B_2
8758	11418	$\begin{cases} 3\nu_4 + 2\nu_5 \\ 3\nu_8 + \nu_5 + \nu_9 \end{cases}$	B_2
7192	13904	$5\nu_4$	B_2

Two of the bands, $3\nu_4$ and $2\nu_1 + \nu_4$, show a well resolved rotational structure of the usual parallel type, yet the lines are not

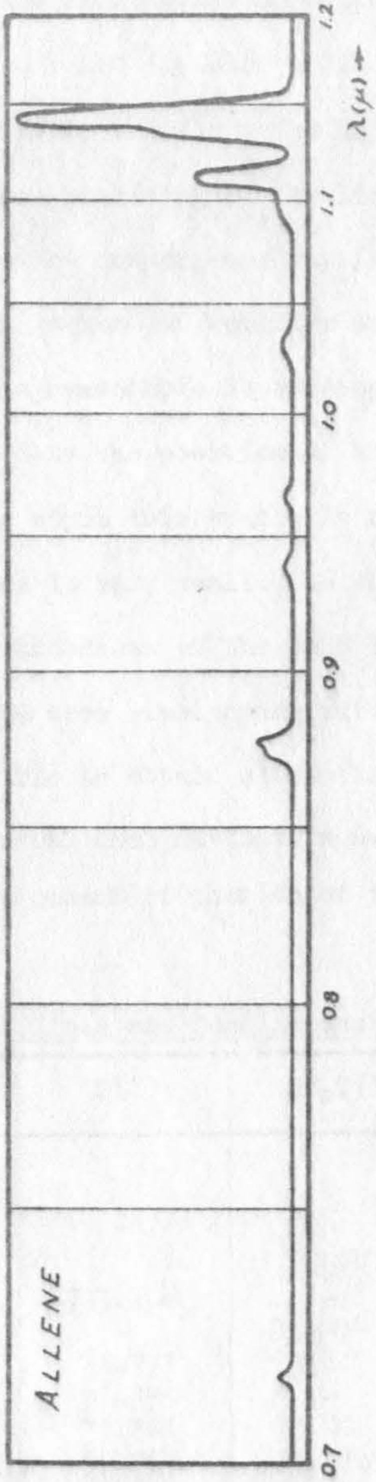


Fig. 2

sharp even at a pressure of 40 mm. (Fig. 3a). By reversing the plates on Velox number five with contrast developer, about twenty lines in $3\nu_4$ could be measured directly under the comparator. Although it was impossible to measure the first few lines in either the P or R branches, the relative numbering of the lines in the two 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, might conceivably be in error since this branch is relatively weak and wide, but since the convergence is very small, the error so induced would be insignificant. The broadness of the band lines, the presence of strong water absorption, and some overlapping with $2\nu_1 + \nu_4$ on the high frequency side made it impossible to obtain either long branches or extremely accurate measurements. The usual combinations, shown in Table V, give 97.0×10^{-40} g. cm.^{2} as the large moment of inertia of the molecule in the ground state.

Table V. Rotational Lines and Combinations in $3\nu_4$ at λ11444.32

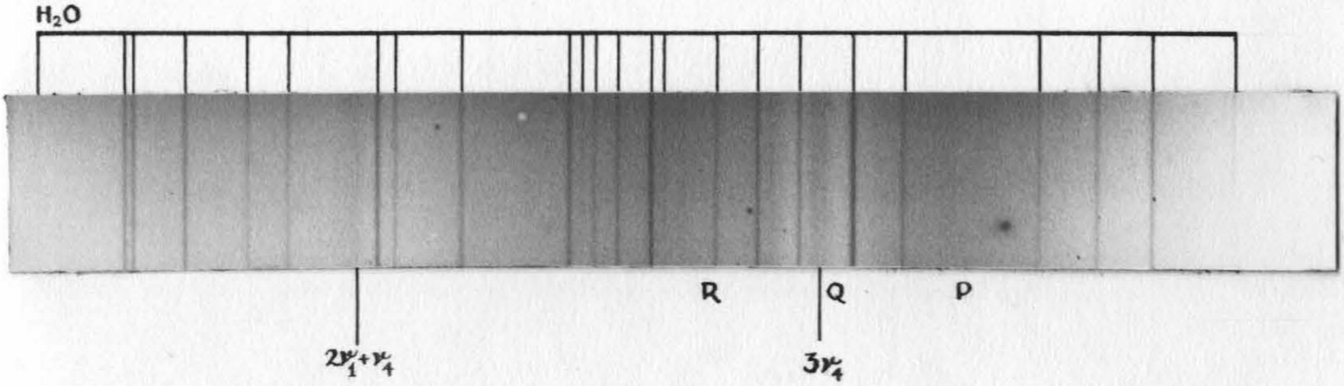
J	R(J)	P(J)	$\Delta''_2T(J)$	$\frac{\Delta''_2T(J)}{2(2J+1)}$
5	8741.488			
6	42.046			
7	42.680			
8	43.330		9.574	0.2816
9	43.911	8733.106	-	-
10	44.507	-	11.934	0.2841
11	-	31.977	13.117	0.2852
12	45.731	31.390	-	-
13	46.274	30.841	15.484	0.2867
14	46.817	30.294	16.576	0.2858
15		29.698	17.637	0.2845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

Since the convergence of the lines is so small, no attempt was made to correct for terms in the energy expression proportional to $J^2(J + 1)^2$. The band $2\nu_1 + \nu_4$, at λ11394, is clearly of the same type (Fig. 3a), but individual lines could not be measured because of overlapping with the much stronger $3\nu_4$.

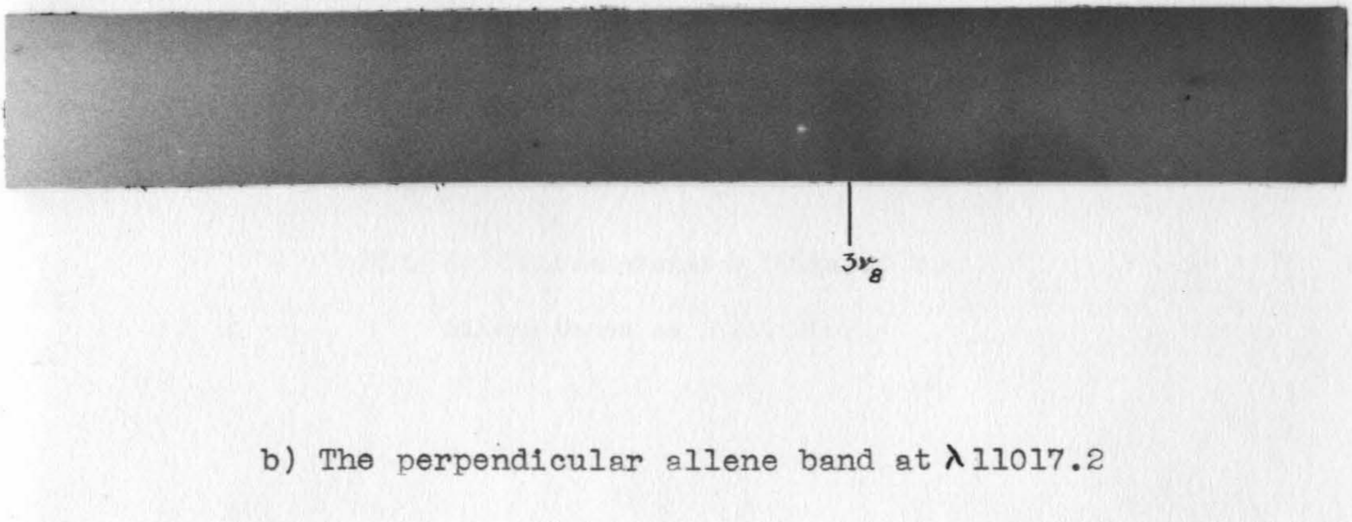
The band at λ11000 (Fig. 4) presents the appearance of a superposition of two similar parallel type bands, and seems to be the result of resonance between the nearly degenerate vibrational levels $2\nu_8 + \nu_1$ and $2\nu_8 + \nu_4$, which both contain components belonging to the active representation B_2. Fine structure of the parallel type can 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 trace.

The band at λ8758 (Fig. 5), of special interest as the analog of the famous ethylene band at λ8720,[7] whose complex rotational structure has never been satisfactorily analyzed, appears to constitute another such resonance doublet. The Q branch of the stronger component is clearly visible in this case. The levels $3\nu_4 + 2\nu_5$ and $3\nu_8 + \nu_5 + \nu_9$ again have components in B_2.

The only perpendicular band photographed under high dispersion was $3\nu_8$ at λ11017.2, and its rotational structure, though too weak to be analyzed in detail, can be seen to deviate markedly from that predicted by Teller's theory, in a way which clearly cannot be attributed to resonance doubling, since the band is quite symmetric, apart from the effects of rotational stretching, about the position indicated as its center in Fig. 3a. It can only be suggested that here, as in SiH_4,



a) The allene bands at λ11444.32 and λ11394.0



b) The perpendicular allene band at λ 11017.2

Fig. 3

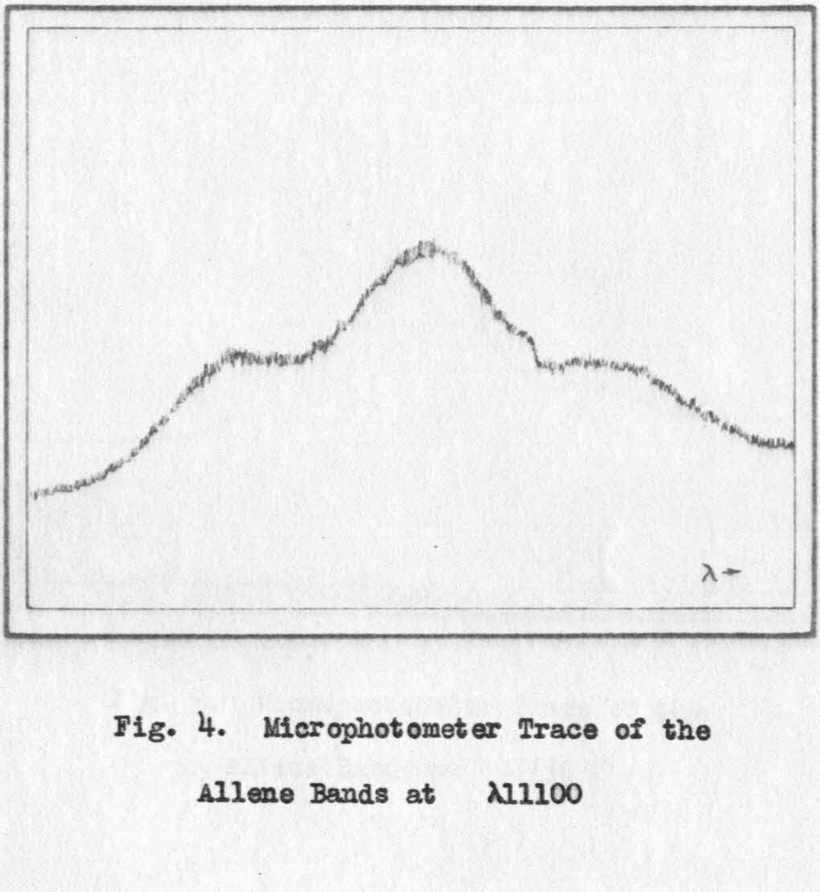


Fig. 4. Microphotometer Trace of the Allene Bands at λ11100

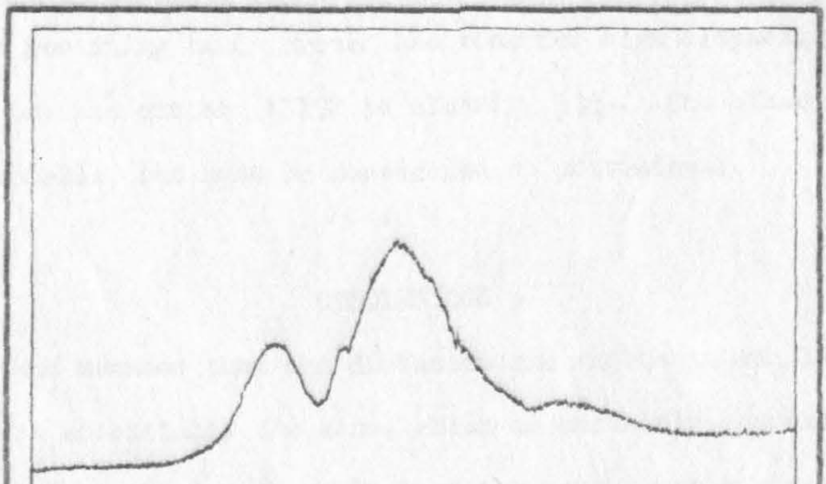


Fig. 5. Microphotometer Trace of the

Allene Bands at λ8758

a more complete treatment of the vibration rotation interaction is required for a quantitative explanation of the band structure, but the photographic data seem far too meagre to warrant a theoretical treatment at present. The author proposes, however, to investigate in the near future the fundamentals of the degenerate frequencies of allene, which should be sufficiently intense to yield, under high dispersion, detailed information concerning this interesting band type.

The remaining bands proved too weak for high dispersion investigation, but the one at $\lambda 7192$ is clearly $5\nu_4$. The other assignments are reasonable, but must be considered as provisional.

CONCLUSIONS

If one assumes that the distances and angles in ethylene and allene are essentially the same, which is certainly approximately true, then one can determine the values of the carbon-carbon double bond distance, of the carbon-hydrogen bond distance, and of the HCH bond angle most consistent with the three independent moments of inertia now known for these two molecules. The most satisfactory values seem to be:

C-H = 1.07 A.   C=C = 1.333 A.   HCH = 117°

The spectrum of allene demonstrates very clearly that in spectra of the more complicated molecules in the photographic region, resonance doublets may become annoyingly common, producing, as in Fig. 4, bands whose envelopes bear small resemblance to those of single vibration rotation bands. This fact may also contribute to an understanding of the very common occurrence, in this region, of bands presenting envelopes which are mere featureless humps. The complicated structure of the perpendicular band, although it must remain unexplained for the present, suggests further investigation of such bands in a more favorable region of the spectrum, and also the need for extending the theory of vibration rotation interactions to explain this interesting rotational structure.

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THE EXPERIMENTAL DETERMINATION OF THE BAND ENVELOPES OF THE ASYMMETRIC ROTATORS, ETHYLENE OXIDE, SULFIDE, AND IMINE

INTRODUCTION

Since most real molecules containing more than two atoms fall neither in the category of spherical nor even of symmetric rotators, but rather in that of asymmetric rotators, and since, moreover, discrete rotational lines can scarcely be said to exist for the heavier molecules at pressures used in ordinary spectroscopic investigations, it has been felt of interest to calculate the envelopes of rotation vibration bands of asymmetric rotators for sufficiently various molecular constants to provide a means for interpreting band envelopes in terms of the moments of inertia of the absorbing molecules. This program of calculations, initiated by Professor Badger, has been recently completed in this laboratory with the assistance of Mr. Zumwalt, and is to be published shortly. In the following report are presented experimental determinations of such band envelopes for three asymmetric rotators, ethylene oxide, ethylene sulfide, and ethylene imine. The special purpose of these investigations has been to ascertain the extent to which the calculated envelopes correspond to those observed in the laboratory, and to study their value in the determination of approximate molecular constants.

EXPERIMENTAL

The ethylene oxide employed in these experiments was a commercial product obtained from the Ohio Chemical Company, and has been used directly from the tank. Some of the same sample was subsequently fractionated by Mr. Lévy, for electron diffraction study, and was found to be of reasonable purity. Photographs were taken at pressures ranging from 1.5 atmospheres to 120 mm. in a six meter absorption tube, and at a pressure of one atmosphere in the seventy-two foot absorption tube of this laboratory.

The ethylene sulfide was prepared from ethylene dithiocyanate kindly furnished by Dr. Buchman, according to the method of Delépine and Eschenbrenner[1]. The product was simply distilled, as it is decomposed by the ordinary drying agents, and photographed at a pressure of 220 mm. in the six meter tube.

The ethylene imine was prepared from redistilled monoethanolamine by the method of Wenker[2], and the product, twice redistilled and dried with metallic sodium, was photographed in the six meter tube at pressures ranging from 240 mm. to 40 mm. A second sample, kindly prepared by Mr. Sargent according to the same method, was photographed at a pressure of one atmosphere in a three meter absorption tube.

Low dispersion spectrograms were first taken in the usual way, and the stronger bands were then rephotographed under the high dispersion of the grating spectrograph.

VIBRATIONAL STRUCTURE

Since the H_2CCH_2 group in these three molecules approximates the ethylene structure, it is not surprising that the photographic spectra, which are due principally to this group except in ethylene imine, where the N-H frequencies also appear, are very similar to the ethylene spectrum, as shown by the corrected microphotometer traces of low dispersion plates (Fig. 1). The selection rules for ethylene oxide and ethylene sulfide,

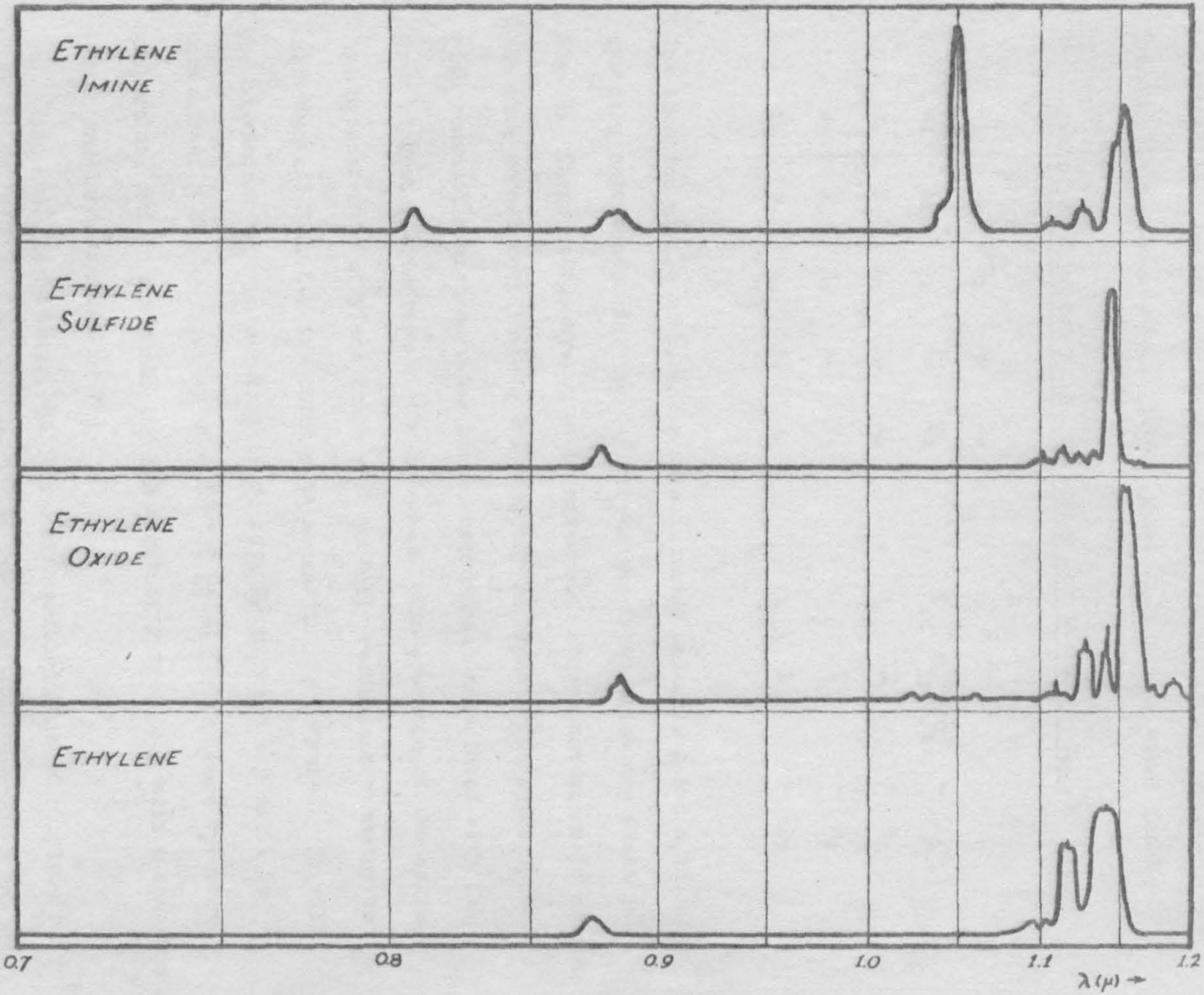


Fig. 1. Corrected Low Dispersion Microphotometer Traces

whose equilibrium configurations have the point group symmetry C_{2v}, are given by the transformation properties of the electric moment and polarizability tensor components, and the multiplication table for the irreducible representations of the group C_{2v}, in the usual fashion.

Table I. Symmetry Selection Rules for the Group C_{2v}

·	A_1	B_1	A_2	B_2
A_1	A_1	B_1	A_2	B_2
B_1	B_1	A_1	B_2	A_2
A_2	A_2	B_2	A_1	B_1
B_2	B_2	A_2	B_1	A_1

$\alpha_{xx}, \alpha_{yy}, \alpha_{zz} \sim A_1$

$\alpha_{xz}, M_x \sim B_1$

$\alpha_{xy}, M_z \sim A_2$

$\alpha_{yz}, M_y \sim B_2$

The location of the x, y, and z axes in these molecules, and a set of symmetry coordinates for the C-H stretching frequencies are shown in Fig. 2. These coordinates must be mixed with others not shown to obtain the true normal coordinates, but they may be expected to approximate, with reasonable accuracy, the normal coordinates associated with the four highest frequencies of the molecule. The presence of the extra hydrogen atom in ethylene imine will probably reduce the symmetry to C_s, allowing all four C-H frequencies to appear in the infrared. It will be convenient to consider that these four frequencies may still be associated with the symmetry coordinates given for the more symmetric molecules, and to associate the N-H stretching frequency with a coordinate which may be designated as ν_5.

The most recent Raman and infrared investigations of ethylene oxide[3] are only capable of placing ν_1 and ν_2 at approximately 3000 and ν_3 and ν_4 at about 3060 cm.$^{-1}$, so the only assignments which can

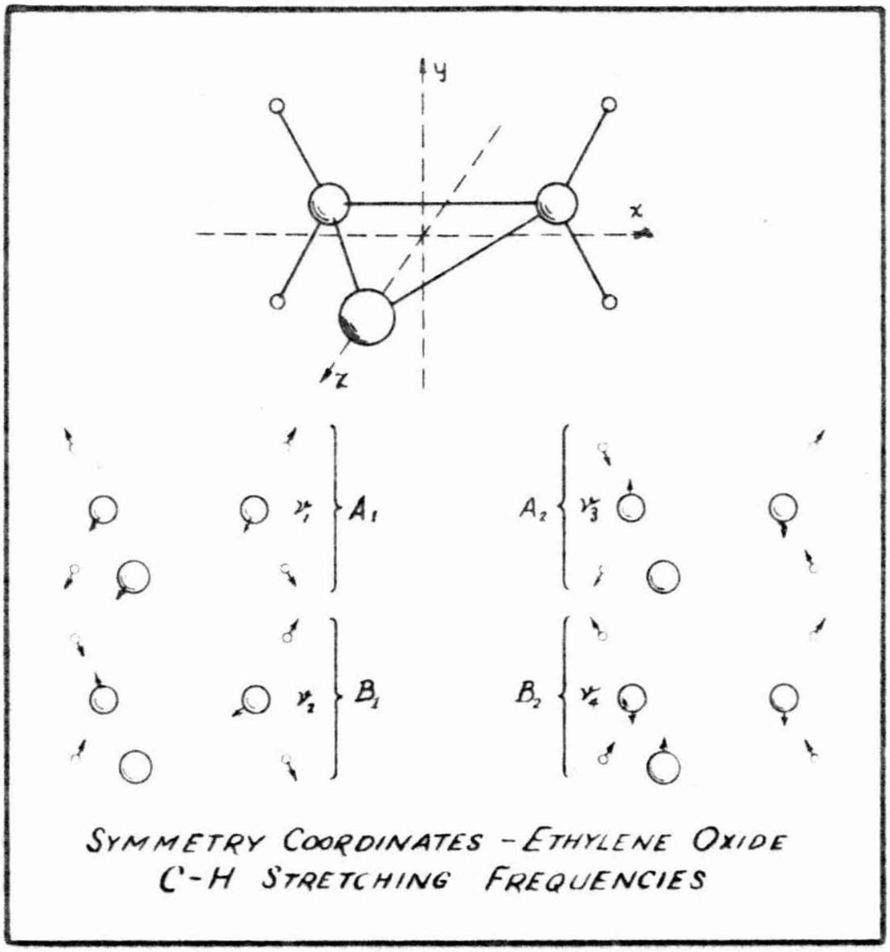


Fig. 2. Symmetry Coordinates for the C-H Stretching Frequencies of Ethylene Oxide

be made with any confidence at all depend on the observed rotational structures. The observed bands and a few provisional assignments of frequencies are given in the following tables:

Table II. Bands of Ethylene Oxide in the Photographic Infrared

Wavelength (A.)	Frequency (cm.$^{-1}$)	Assignment and Band Type
12000	8333	-
11812	8466	-
11625.0	8602.1	A or C
11538.0	8667.0	B, $3\nu_2$
11406.0	8767.3	C
11397.6	8773.8	A, $3\nu_2$
11361.3	8815.8	B
11317.5	8835.8	C
11259.6	8881.3	A
11084.4	9021.7	C, $3\nu_4$
10545	9483	-
10305	9704	-
10197	9807	-
8824	11333	complex

Table III. Bands of Ethylene Sulfide in the Photographic Infrared

Wavelength (A.)	Frequency (cm.$^{-1}$)	Assignment and Band Type
11578	8637	A, $3\nu_1$
11400.6	8771.9	B, $3\nu_2$
11320.2	8833.8	A
11224	8909	-
11133	8982	-
11013.0	9080.2	C, $3\nu_4$
8762	11413	-

Table IV. Bands of Ethylene Imine in the Photographic Infrared

Wavelength (A.)	Frequency (cm.$^{-1}$)	Assignment and Band Type
11571.0	8642.3	B, $3\nu_1$
11396	8775.0	A, $3\nu_2$
11210	8921	-
11017.0	9065.3	C, $3\nu_4$
10468.5	9552.5	hybrid, $3\nu_5$
8780	11390	-
8050	12420	$4\nu_5$

It is of interest to note that the very strong band in each of these three molecules seems to be associated, not with a given normal mode, but with a given band type, namely type B.

BAND ENVELOPES

When the normal modes of vibration of an asymmetric rotator are such that the changes of electric moment are along single principal axes of inertia of the molecule, the resulting rotational structures may be said to be of pure types, and are conveniently characterized as of types A, B, or C, as the electric moment change is along the minor, intermediate, or major axis of the inertial ellipsoid. In molecules of lower symmetry, where the change of electric moment may have components along more than one axis, bands of a twofold or threefold hybrid type will appear, whose envelopes may be described as linear combinations of the intensity distribution functions for the three related pure band types, with coefficients proportional to the squares of the components of the change of electric moment along the corresponding principal axes.

The vibration rotation bands of ethylene oxide and ethylene sulfide should all be of pure types because of the symmetry of these molecules. Approximate moments of inertia, obtained from the electron diffraction distances[4], show that the band types will be related to the irreducible representations of the normal modes as follows:

Ethylene Oxide: $A \sim B_1$, $B \sim A_1$, $C \sim B_2$.

Ethylene Sulfide: $A \sim A_1$, $B \sim B_1$, $C \sim B_2$.

In ethylene imine, where the moments of inertia are very similar to those of ethylene oxide, deviations from pure band types should be expected to be imperceptible in the C-H bands, since the extra hydrogen atom will cause only a very small shift of the z and y axes from their positions in and normal to the plane of the ring. The N-H bands, on the other hand, would be expected to present a twofold hybrid structure involving the band types B and C in a ratio determined essentially by the angle between the N-H bond and the plane of the ring.

These predictions are confirmed in every respect by the observed band envelopes. The ethylene oxide bands at λ11538, λ11260, and λ11084 (Figs. 3 to 5) are clearly of three different types. These microphotometer traces were then corrected for change in plate sensitivity and the presence of superposed water lines, and to make the observed envelopes comparable with the calculated ones, the resulting smoothed microphotometer deflections were plotted on a scale of x, a quantity related to the frequency by the expression:

$$x = (\nu - \nu_0)\sqrt{\frac{2B}{kT}} \quad ,$$

where the value of B, the intermediate moment of inertia was taken from the electron diffraction structure. The observed bands, however, are still not symmetric about the origin because the effective moments of

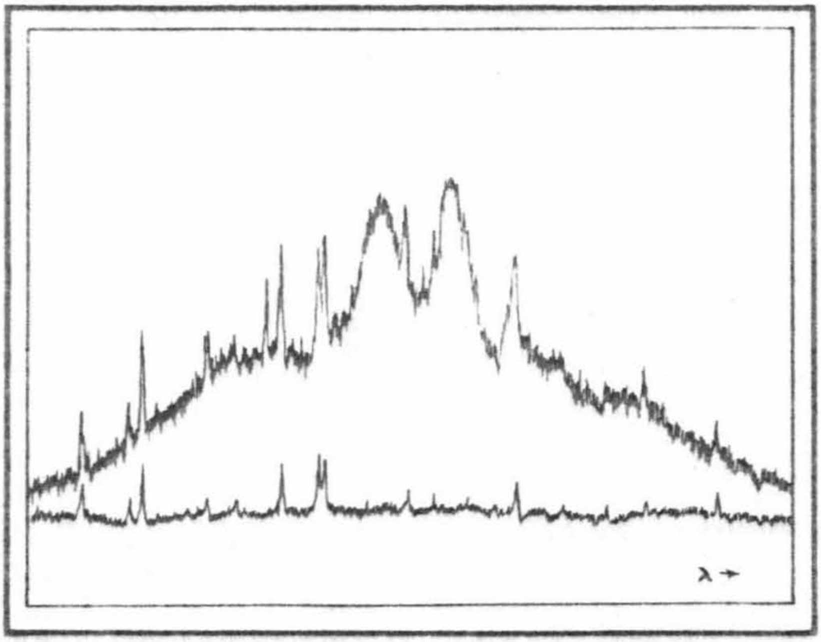


Fig. 3. Microphotometer Trace of the Band of Ethylene Oxide at λ11538, and of the Water Lines in this Region.

Fig. 4. Microphotometer Trace of the Band of Ethylene Oxide at λ11260, and of the Water Lines in this Region

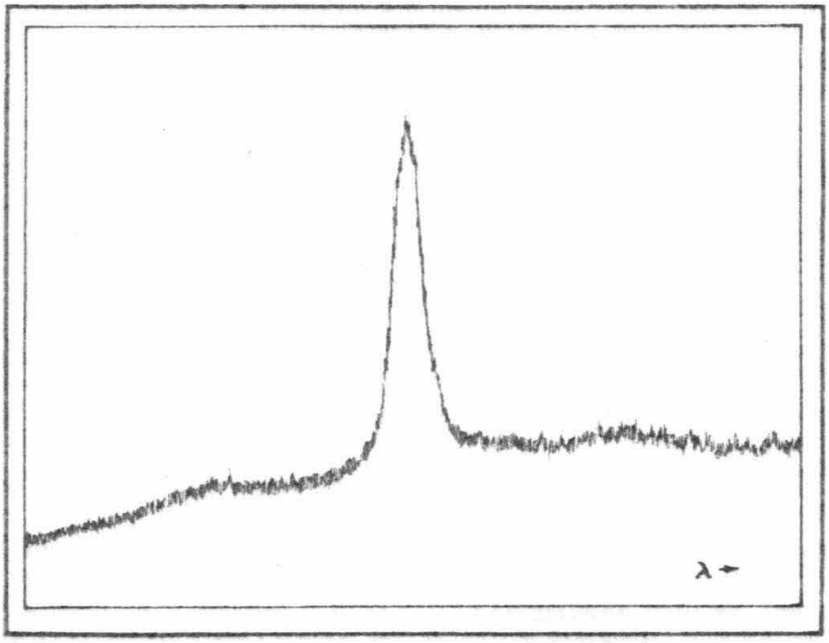


Fig. 5. Microphotometer Trace of the Ethylene Oxide Band at λ11084.

inertia in the two vibrational states will, in general, be different. In the bands of diatomic molecules, the corresponding lines $R(J-1)$ and $P(J)$, which would be found at equal distances from ν_0 when $B' = B''$, will both be displaced from this position by the amount $(B'-B'')J^2$ in the general case. To symmetrize band envelopes only moderately distorted in this simple manner, it is sufficient to reflect the P branch through the band origin and average the P and R branch envelopes, which then gives the correct appearance for the R branch of a symmetric band involving a B which is the average of the actual B' and B". Though this distortion effect in polyatomic molecules, which may have three different moments of inertia, is much more complicated, a similar procedure has been followed here. Having assumed the position of the band origin, and having transformed to the scale of x, the average of the two microphotometer deflections for each absolute value of x was then plotted against x, to give the symmetrized half-envelopes which are shown in Fig. 7 for the ethylene oxide bands and the strong ethylene sulfide band at λ11400. The values of the constants ρ and S, which determine the shapes of the bands are, from the approximate moments of inertia:

Ethylene oxide: $\rho = 0.572$; $S = +0.178$

Ethylene sulfide: $\rho = 1.194$; $S = -0.557$

The band types have then been determined by comparison with the theoretical curves, for the appropriate values of S and ρ, and indeed the corrected envelopes for ethylene oxide do approximate the theoretical ones in a satisfactory fashion, except that in the type B bands, as might be expected, the intensity does not fall to zero at the origin,

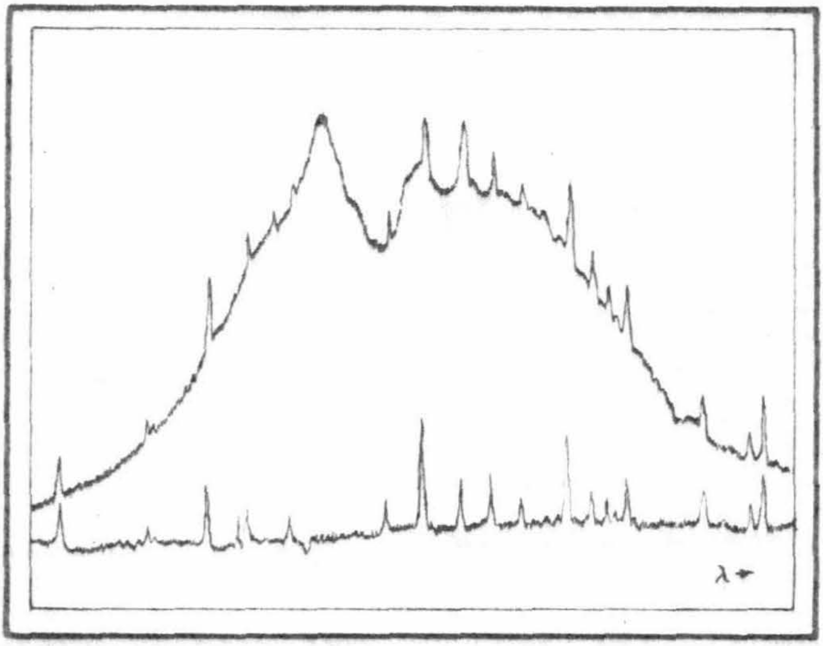
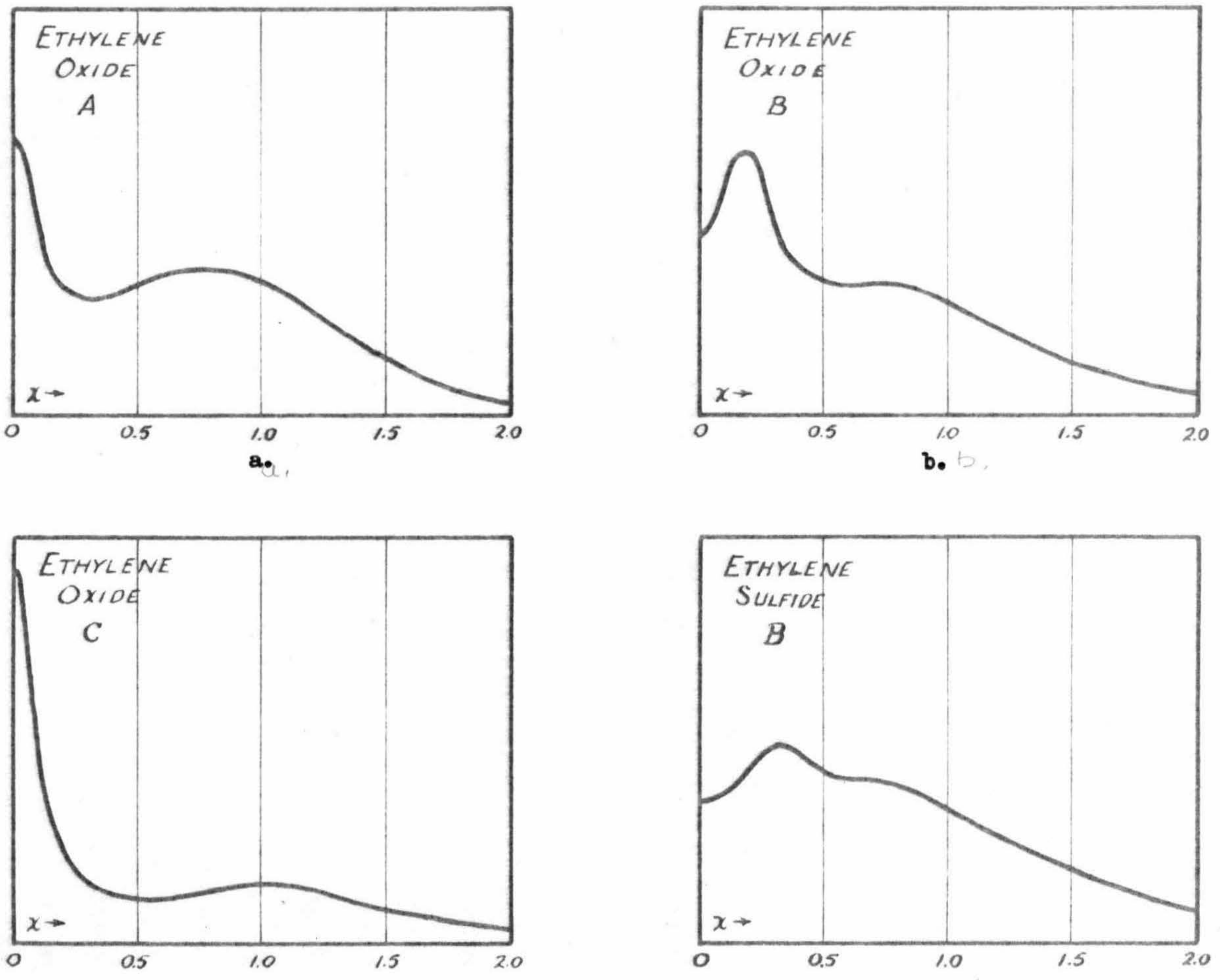


Fig. 6. Microphotometer Trace of the Ethylene Sulfide Band at λ11400, and of the Water Lines in this Region.



a. a,

b. b,

c.

d.

Fig. 7. Symmetrized Band Envelopes of Ethylene Oxide and Sulfide. They may be compared with the uncorrected traces as follows: a) Fig. 4, b) Fig. 3, c) Fig. 5, d) Fig. 6

and the ordinates, which are microphotometer deflections instead of percentage absorptions, do not, of course, correspond quantitatively to the calculated curves. For this reason, and because of the extensive and rather arbitrary corrections which have been applied to the observed traces, it seems unsuitable to attempt to make any quantitative correlations between the envelopes and moments of inertia at this time. The theoretical curves corresponding to the values of ρ and S for ethylene sulfide have not been completed, but the observed envelope differs from that of ethylene oxide in the expected manner. The type A and C bands of ethylene sulfide and ethylene imine are too weak to permit such analysis, and the type B band of ethylene imine, which is very similar in appearance to the corresponding ethylene oxide band, is so badly overlapped on the high frequency side by another band that it also could not be treated in detail.

The N-H band of ethylene imine at $\lambda 10469$ (Fig. 8), does indeed have the predicted hybrid structure, as can be seen by comparing it with the corresponding pure bands of ethylene oxide (Figs. 3 and 5), remembering that the dispersion is less in the N-H region. The low frequency maximum does seem a little too high, but it may be strengthened by an accidental superposition of a weak band of type A. This view is supported by the doubling observable in this maximum. The surprising feature of the band is the low intensity of the type C Q branch, which means that the contribution of the type C structure is remarkably small. If it were feasible to determine intensities in this region, the contributions of the two components could be determined with some precision, since we would then know the intensity distribution functions for the pure bands experimentally, from the spectrum of the very similar ethylene oxide.

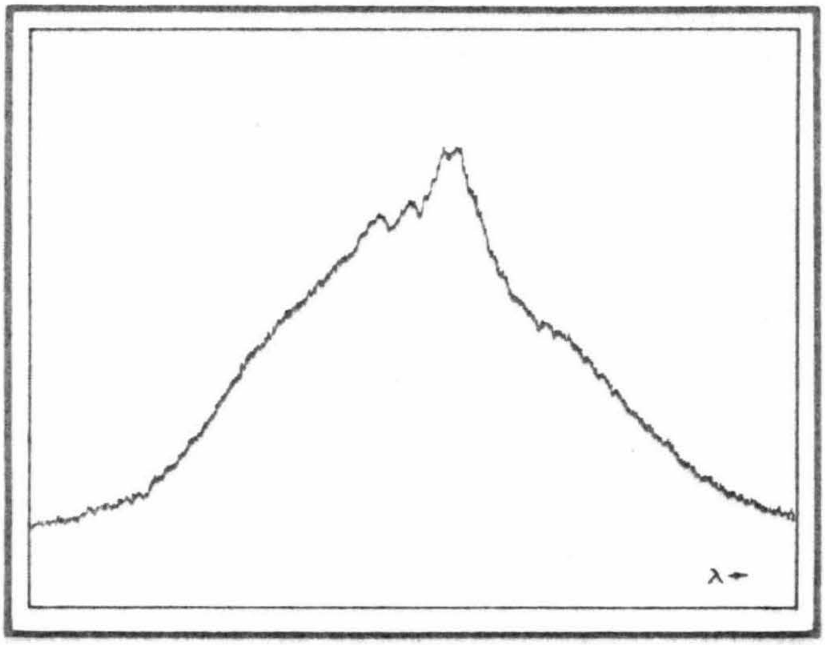


Fig. 8. Microphotometer Trace of the Ethylene Imine Band at λ10469.

If it were then possible to be certain that the electric moment change took place along the line of the N-H bond, the angle between this bond and the plane of the ring could be determined with considerable accuracy. The problem is a complicated one, but it surely appears that this angle is much smaller than the 64° angle between the N-H bond in NH_3 and the plane of the other two N-H bonds. The structure of N-methyl ethylene imine is being studied by electron diffraction methods by Mr. Lévy, to see if the analogous angle in this compound can be definitely determined.

It is of interest to observe that in all these molecules analogues of the famous ethylene band at $\lambda 8720$ are found. Although relatively weak, the ethylene oxide band at $\lambda 8824$ was photographed at a pressure of one atmosphere in the 72 foot tube. Its rotational structure (Fig. 9) is found to be most complex, and is undoubtedly the result of the superposition of two or more combinations of C-H bending and stretching frequencies, as was found in allene, though the frequencies in this case need not belong to the same irreducible representation.

The other bands of Table II to IV were too weak for high dispersion study, and were simply measured on the low dispersion plates.

CONCLUSIONS

If the electron diffraction structures of these molecules be assumed their true ones, then their observed band envelopes are in satisfactory agreement with those calculated by Badger and Zumwalt, but it is unfortunately true that until actual intensity measurements can be made in this region, quantitative determinations of molecular constants are out of the question. The difficulties which prevent the use of any of the ordinary methods of photographic photometry arise chiefly from the lack of uniformity in the hypersensitized plates, and from the fact

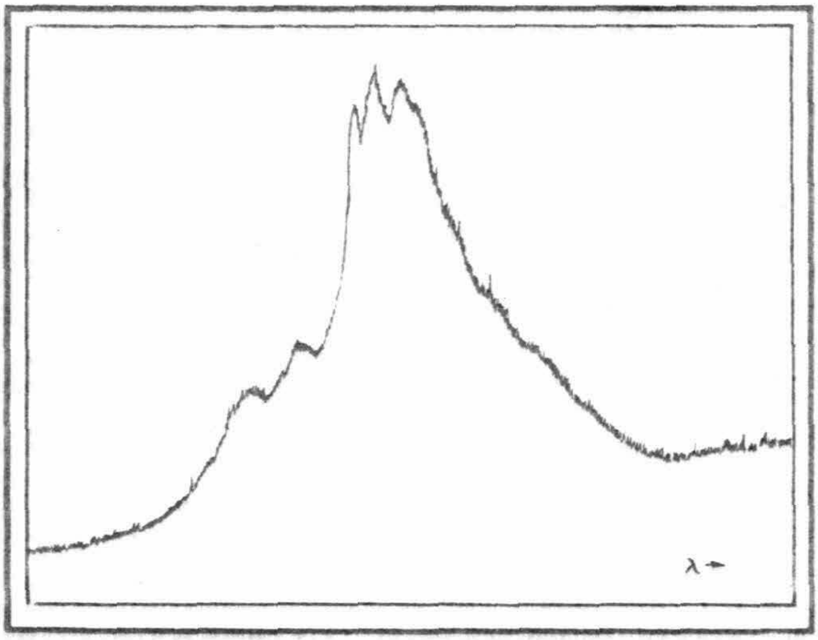


Fig. 9. Microphotometer Trace of the Ethylene Oxide Band at λ8824.

that with present infrared sensitizations exposures of 48 hours are required for high dispersion photographs in the region between 10500 and 12000A. Unless great improvements in plates and spectrograph speeds are made, it seems that some quite different methods of intensity determination must be found.

It would appear that if such intensity measurements become available, the relative intensity of the components of hybrid bands, which could be determined with the aid of approximate moments of inertia obtained from electron diffraction and the corresponding theoretical intensity distribution functions for the pure band types, would furnish information concerning structural details, such as bond angles, involving light atoms, which are at present inaccessible to other methods of structure determination. This seems a more useful application than the determination of approximate moments of inertia, which would in any case become practically impossible in the absence of pure bands. Such an application, however, requires careful analysis, to make certain that the change of electric moment can be actually associated with a given bond in the molecule. If, for example, the vibration producing the λ10469 band of ethylene imine involves a considerable amount of stretching of C-H bonds, as well as of the N-H bond, an N-H bond angle calculated by too naïve a method would correspond to no bond at all, but merely to the resultant of the simultaneous electric moment changes along many bond directions.

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THE ROTATIONAL STRUCTURES OF HYBRID BANDS OF SPINDLE MOLECULES

INTRODUCTION

Although it has long been realized that in molecules of low symmetry the observed rotational band structures should correspond to no pure band types[1], this fact appears to have been overlooked in a number of recent interpretations of the spectra of molecules which would be expected from general structural theory to be of a bent spindle type. Consequently one of these, hydrazoic acid, has been rephotographed under high dispersion in this laboratory, and the spectrum of mono vinyl acetylene, another molecule of this type, has also been studied, in an attempt to reconcile the observed rotational band structures with the expected structures of the molecules.

EXPERIMENTAL

The hydrazoic acid was prepared from recrystallized sodium azide, furnished through the kindness of Dr. C. D. Coryell, by the usual methods, the gas being passed through a 50 cm. $CaCl_2$ drying tube before freezing out in liquid air. The receiver could be fitted to either the generator or the six meter absorption tube by means of interchangeable Pyrex ground joints, and was handled only when its explosive contents were at liquid air temperatures. The spectrum was photographed at the vapor pressure of the liquid at room temperature.

The mono vinyl acetylene was kindly provided by Dr. W. S. Calcott, Director of the Jackson Laboratory of E. I. du Pont de Nemours and Company, as a stabilized 30 percent solution in Xylene. Since the mono vinyl acetylene boils at 5.5°C., the gas was simple allowed to flow from the cylinder into the evacuated six meter tube. High dispersion photographs were taken at a pressure of one atmosphere. Although the strongest band of acetylene in this region appeared weakly, it caused no difficulty.

ROTATIONAL STRUCTURE

A. Hydrazoic Acid

If one accepts the very reasonable structure of methyl azide determined by electron diffraction by Pauling and Brockway,[2] and assumes that that of hydrazoic acid can be obtained from it by merely replacing the methyl group by a hydrogen atom, then the molecular constants assume the following values:

$A = 1.13 \text{ g.cm.}^2 \times 10^{-40}$ $\qquad \alpha = 24.5 \text{ cm.}^{-1}$

$B = 58.7 \text{ g.cm.}^2 \times 10^{-40}$ $\qquad \beta = 0.472 \text{ cm.}^{-1}$

$C = 59.8 \text{ g.cm.}^2 \times 10^{-40}$ $\qquad \gamma = 0.462 \text{ cm.}^{-1}$

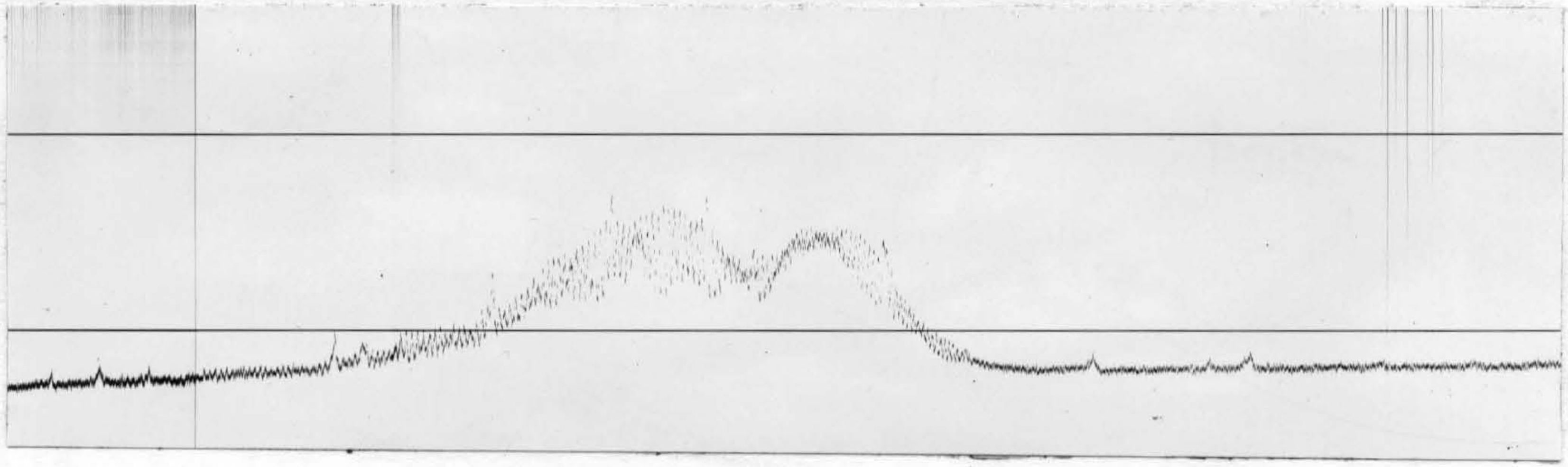
$$S = -0.999$$

$$\rho = 51$$

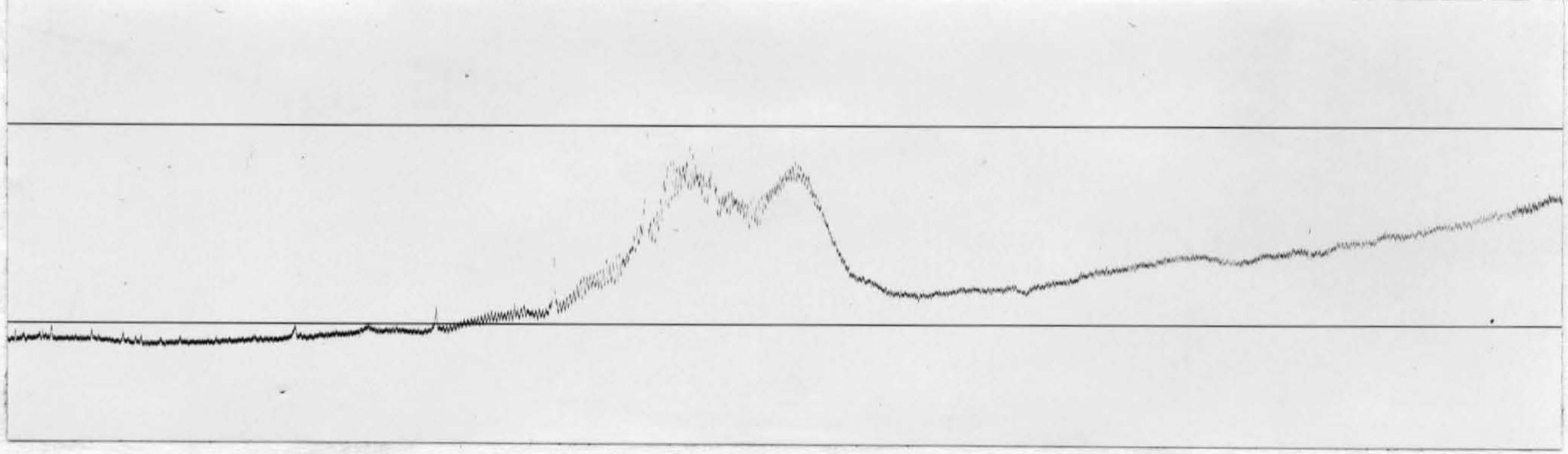
S and ρ are the constants defined for asymmetric rotators by Badger and Zumwalt[3], the constants A, B, and C are the three moments of inertia of the molecule, and α, β, and γ are the spectroscopic constants defined as:

$$\alpha = \frac{h}{8\pi^2 Ac} \;; \qquad \beta = \frac{h}{8\pi^2 Bc} \;; \qquad \gamma = \frac{h}{8\pi^2 Cc}$$

Thus it is seen that the molecule would be of an extreme spindle type ($\rho \gg 1$; $S < 0$), and approximates a symmetric rotator ($S = -1$) to a high degree. Although the axis of the nitrogens makes an angle of only about two degrees with the minor axis of inertia, so that the bands arising from vibrations of the azide group might be expected to differ only imperceptibly from the pure types, quite the opposite will be true of bands due to vibrations of the N-H bond, which makes an angle of about 60° with the minor axis. If the electric moment change associated with the N-H stretching frequency coincides in direction with this bond, the ratio of intensities of the perpendicular and parallel components of the resulting hybrid will be about 8 to 3. The observed bands at 9547.8 and 12412.8 cm.$^{-1}$ correspond to the third and fourth harmonics of such a vibration, with $\omega_e = 3500.2$ cm.$^{-1}$, and $\omega_e x_e = 79.4$ cm.$^{-1}$. Their complicated rotational structure is well resolved, as can be seen from Fig. 1, which shows the microphotometer traces of these bands. The difference of dispersion in the two regions of the spectrum is responsible for the apparent difference in the close spacing, which is actually identical in the two bands. The principal intensity in these bands seems indeed to be due to the parallel components of the hybrids, in which no deviations from symmetric rotator structure can be detected. The coarse structure due to the perpendicular component is most curious, apparently forming a head near the origin, toward the high frequency side, as though the small moment of inertia increased greatly with vibrational quantum number. The detailed rotational analysis has not yet been made, as the band has been only recently obtained, but it certainly appears to be possible, and promises to yield interesting and novel information. It can only be said at present that the conclusion that these bands are produced by two different kinds of molecules, linear and bent ones, reached by Herzberg, Patat, and Verleger[4], is unjustified, and that they are rather to be considered as twofold hybrids of a very nearly symmetric rotator. It is planned to complete the detailed analysis in the near future.



The Hydrazoic Acid Band at 9547.8 cm.$^{-1}$



The Hydrazoic Acid Band at 12412.8 cm.$^{-1}$

Fig. 1

B. Mono vinyl acetylene.

With the aid of the available structures of ethylene and acetylene, it was possible to formulate a reasonably reliable approximate structure for mono vinyl acetylene. The ethylene and acetylene parameters were the accepted ones and the C-C bond joining these two components of the molecule was assumed to be shortened by a single-double bond resonance to 1.43 A. With this structure, the molecular constants become, when expressed in the units used in A:

$A = 21.8$ $\alpha = 1.270$

$B = 175.2$ $\beta = 0.158$

$C = 197.0$ $\gamma = 0.140$

$$S = -0.968$$

$$\rho = 7.15$$

It is seen that the molecule is again a pseudo-symmetric rotator of the spindle type. The acetylenic C-H bond makes an angle of about 24° with the minor axis of the molecule, and if the electric moment change coincides with this bond direction in the acetylenic C-H bands, the intensity ratio of the parallel and perpendicular components of the hybrid will be about 13 to 6. Of course the parallel structure will not be resolvable, but the Q branches of the perpendicular component should be about 2.5 $cm.^{-1}$ apart, and hence easily resolvable. The observed band at λ10222 (Fig. 2) shows absolutely no trace of the perpendicular component, nor can it be found on high magnification microphotometer traces of the low dispersion plates, which usually are more effective in locating weak absorption. Since it is unthinkable that this C-H bond even approximately coincides with the minor axis of inertia of the molecule, one can

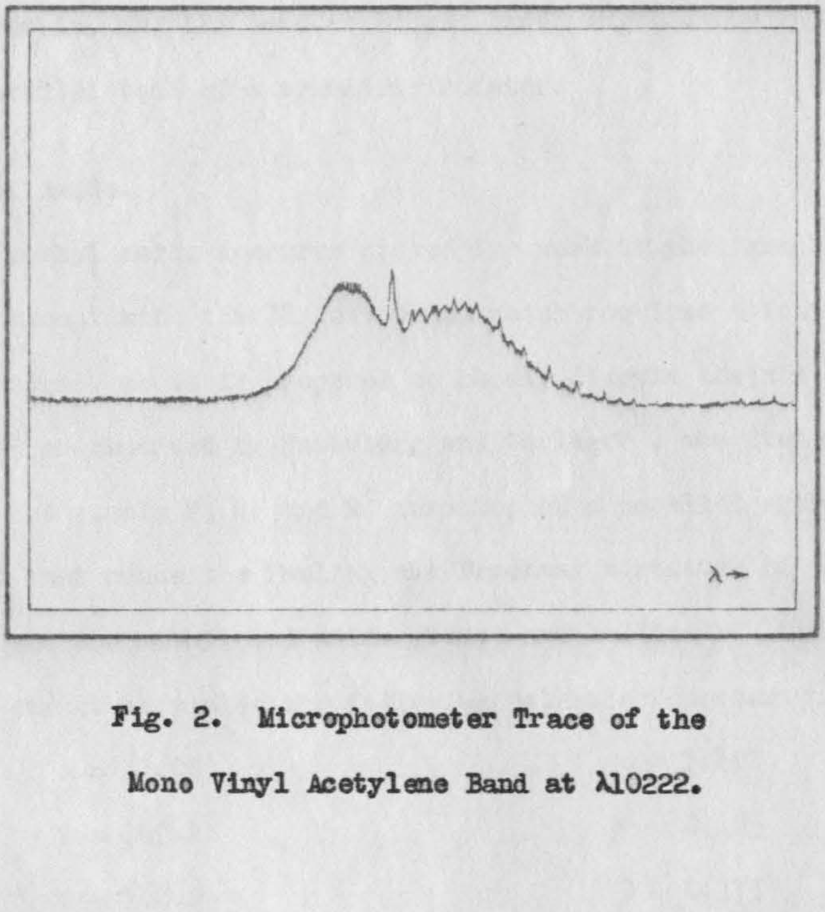


Fig. 2. Microphotometer Trace of the Mono Vinyl Acetylene Band at λ10222.

only conclude that the perpendicular component, which in a molecule with so large a value of ρ will have a very wide and flat envelope, and whose total intensity is expected to be only half that of the compact parallel component, is present but produces too low an absorption in any given frequency interval to be observable above the sensitizer fog. It is also of interest to note that although the parallel component is actually a type B band of an asymmetric rotator, no Q branch splitting appears to have set in, and the band is indeed indistinguishable in every respect from a parallel band of a symmetric rotator.

C. Methyl Azide.

The methyl azide spectrum proved too weak to photograph in high dispersion, except with the 72 foot tube, which requires extremely long exposure times, so it is proposed to merely discuss the structure of the $\lambda 9480$ band as reported by Hertzberg and Verleger[4], who state that this band has the simple P, Q, and R branches of a parallel symmetric rotator band, and that hence the Pauling and Brockway structure of the molecule is wrong and the methyl and azide groups are collinear. The Pauling and Brockway structure yields the following molecular constants:

$A = 17.08$ $\qquad$ $\alpha = 1.621$

$B = 149.2$ $\qquad$ $\beta = 0.185$

$C = 160.2$ $\qquad$ $\gamma = 0.173$

$S = -0.985$

$\rho = 7.84$

It is unfortunately not possible to decide the origin of the $\lambda 9480$ band, and since it must be some complicated combination, prediction of the intensity ratio of a hybrid band would be most difficult. Since this molecule has a value of β very nearly the same as that of mono vinyl acetylene, it may be concluded that a perpendicular component of considerable total intensity might well have been unobservable. Since this structure is even more nearly that of a symmetric rotator than is that of mono vinyl acetylene, it is not surprising that the band had all the appearance of a symmetric rotator band, and it must be concluded that Pauling and Brockway structure is not in disagreement with the spectroscopic data. It is possible that investigation of some of the many weaker bands of this molecule might reveal one in which a real hybrid could be observed, thus establishing the bent structure by spectroscopic methods alone.

CONCLUSIONS

The above considerations clearly show the importance the general recognition of the existence of hybrid bands, and the usefulness of the general concepts and results of structural chemistry in the interpretation of bands to which the formal methods of detailed rotational analysis cannot be applied. Although twofold hybrids involving types B and A or types B and C can be easily recognized in molecules having low values of ρ , there are cases in which hybrids cannot be detected with certainty. This will be the case even for low ρ values when types A and C are the components of a twofold hybrid, and for large values of ρ , where the flat envelopes of type B and C components may well escape observation, and where their absence is a most unreliable criterion of symmetry. It is also to be stressed that all rotators of large ρ values will be pseudo symmetric, and though their type B and C bands, which may then be called pseudo parallel bands, show no deviation from the appearance of the parallel bands of symmetric rotators, it is quite unjustified to then conclude that the molecules are actually symmetric.

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LOW DISPERSION INVESTIGATIONS OF MISCELLANEOUS SPECTRA

INTRODUCTION

In the search for well resolved rotational structures, one invariably discovers many rich spectra which are unfortunately too weak to be conveniently investigated under high dispersion with available apparatus. In the process of these investigations several such spectra have been photographed and measured on low dispersion plates, and these results, together with brief experimental details in the case of molecules not already discussed, will now be given in the hope that they may prove useful at some future time, when better plates, faster spectrographs, and more powerful sources make possible the use of longer absorption tubes than are at present convenient. Tables of frequencies will be supplemented with corrected microphotometer traces, which should be considered only of qualitative significance.

EXPERIMENTAL RESULTS

A. Hydrazoic Acid

In addition to the strong bands already mentioned here and by Herzberg, Patat, and Verleger two other bands were observed (Fig. 1).

Wavelength (A.)	Frequency (cm.$^{-1}$)
11361	8802
9353	10690

B. Hydrazine

The anhydrous product was prepared by repeated vacuum fractionation of redistilled hydrazine hydrate, b.p. 118.5° (E. K. Co.), off fused potassium hydroxide, and low dispersion photographs were taken with the sample in the 3 meter tube at its vapor pressure at 100°C. The spectrum

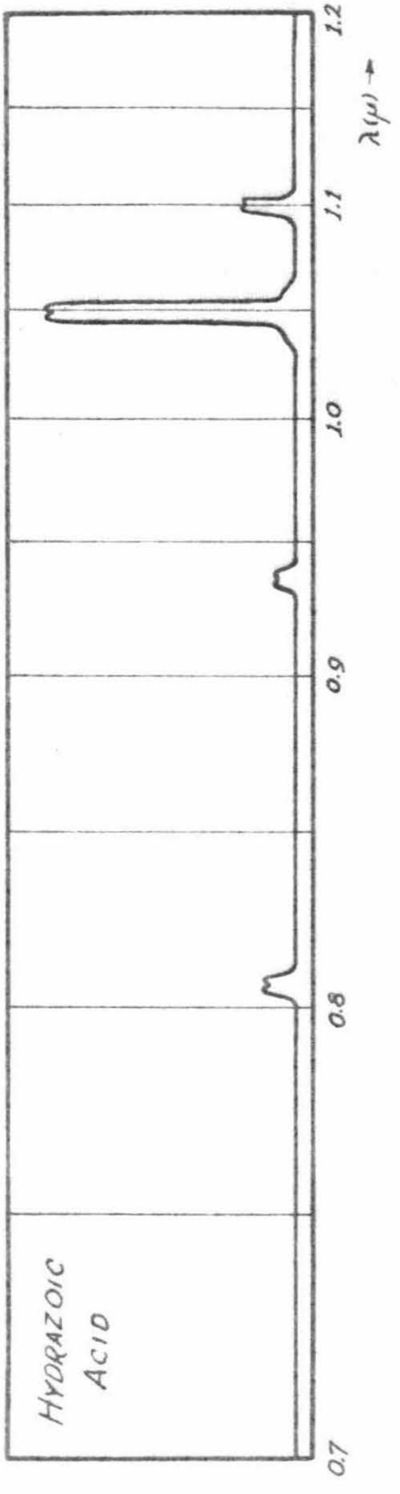

Fig. 1

of the hydrate was also photographed under the same conditions, but appeared to be simply the superposition of the Hydrazine and water spectra. The bands are shown in Fig. 2.

Wavelength (A.)	Frequency (cm.$^{-1}$)
10552	9477
10388	9626

C. Acetaldehyde

The sample used was the redistilled Eastman Kodak Co. preparation, which was studied at its vapor pressure at room temperature in the six meter tube (Fig. 3).

Wavelength (A.)	Frequency (cm.$^{-1}$)
11900	8403
11732	8524
11553	8656
11028	9068
10930	9149
9788	10217
9023	11080

D. Mono Vinyl Acetylene

In addition to the bands already mentioned, several others were observed (Fig. 3) and those at λ11310 and λ11030 were actually photographed on high dispersion, where, however, they gave rather featureless humps.

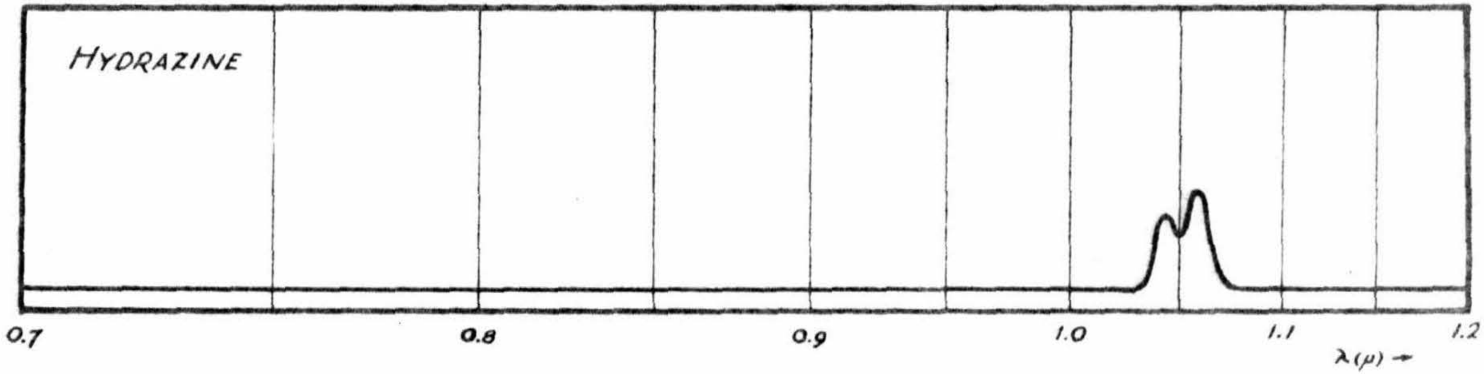

Fig. 2

Wavelength (A.)	Frequency (cm.$^{-1}$)
11528	8675
11432	8747
11310	8842
11030	9066
10851	9216

E. Methyl Azide

The methyl azide was prepared by methylation of sodium azide with dimethyl sulfate, the dried and redistilled product being studied at its vapor pressure at room temperature in the six meter tube. The bands reported by Herzberg and Verleger, and a number of other weaker ones were found (Fig. 3).

Wavelength (A.)	Frequency (cm.$^{-1}$)
11950	8369
11824	8457
11620	8606
11453	8731
11341	8818
9480	10550
9367	10676
9102	10987
8938	11118

F. Vinyl Fluoride

The sample used was kindly furnished by Dr. L. O. Brockway, and the gas was used at a pressure of about one atmosphere in the six meter tube. It is interesting to note that when one of the hydrogen

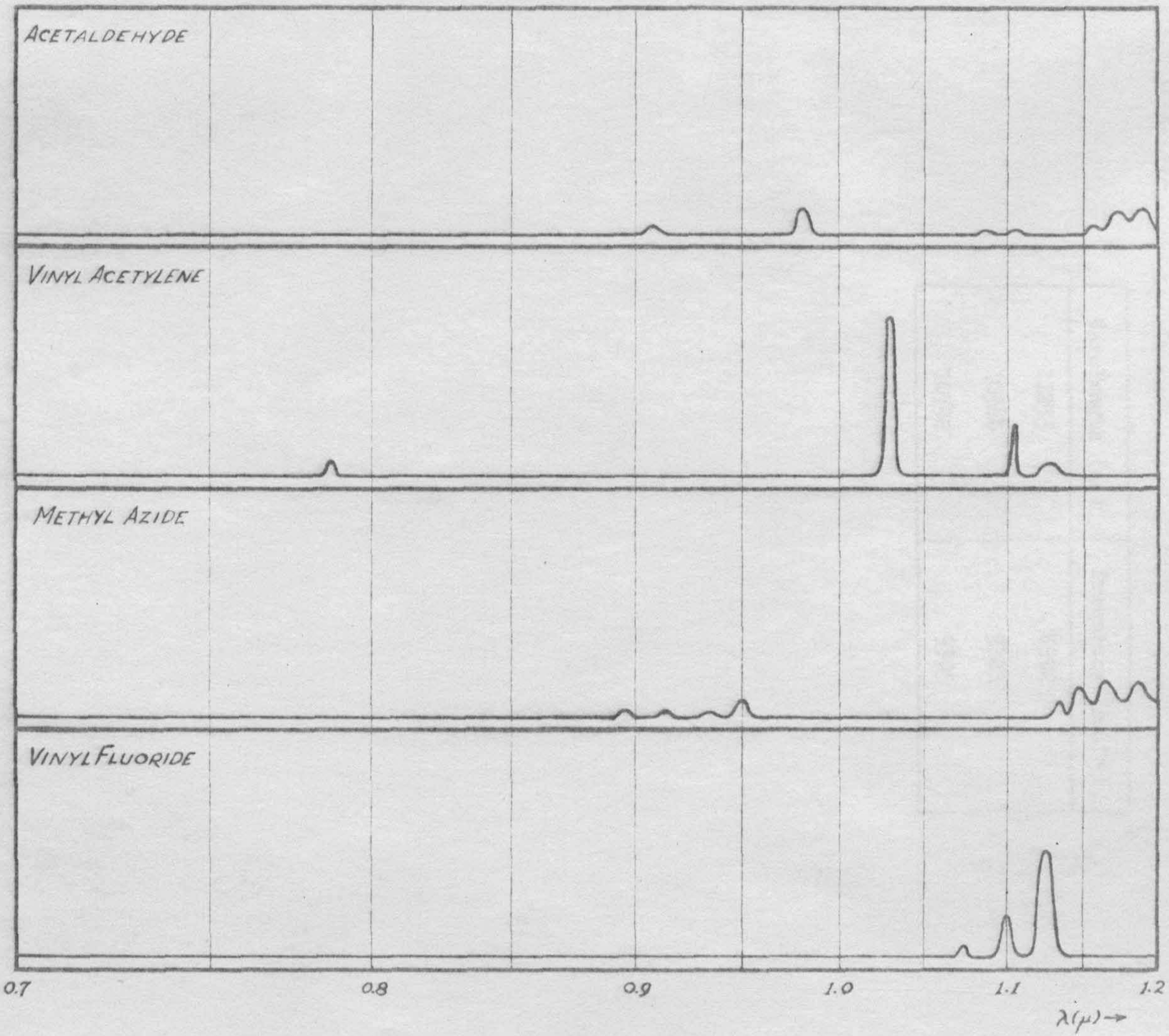
ACETALDEHYDE
VINYL ACETYLENE
METHYL AZIDE
VINYL FLUORIDE
0.7
0.8
0.9
1.0
1.1
1.2
λ(μ)→

Fig. 3

atoms of ethylene is replaced by fluorine, the band at λ8720 disappears (Fig. 3).

Wavelength (A.)	Frequency (cm.$^{-1}$)
11233	8902
10964	9121
10742	9309

SUMMARY

I. The visible and ultraviolet bands of silicon fluoride have been analyzed, correcting previous errors, and determining vibrational constants, internuclear distances, and term identifications for three of the electronic states of the molecule.

II. Existing suggestions which attribute certain broad stationary lines observed in stellar spectra to definite molecules in interstellar space have been critically examined and declared unjustified. A careful survey of observed terrestrial molecular spectra has revealed no known molecular bands which could account for these lines.

III. The spectrum of allene in the photographic infrared has been studied, the observed bands being assigned as combinations and harmonics of the fundamental frequencies, which were obtained from existing Raman and near infrared data. The large moment of inertia was determined from the rotational structure of a $\parallel$ type band, and an anomalous but very weak $\perp$ type band was found.

IV. The envelopes of the bands of ethylene oxide, sulfide, and imine have been determined in this same spectral region, and found to be in qualitative agreement with the theoretical calculations of Badger and Zumwalt. The hybrid band of ethylene imine suggests that the N-H bond makes an angle of no greater than 30° with the plane of the ring.

V. The spectrum of hydrazoic acid has been photographed under high dispersion, and though the complete rotational analysis has not yet been made, the conclusions of Herzberg, Patat, and Verleger concerning its structure appear to be incorrect. The observed spectrum of mono vinyl acetylene leads to conclusions concerning the bands of bent spindle rotators which reconcile the appearance of the methyl azide band of Herzberg and Verleger with Pauling and Brockway's structure determination of this molecule

VI. The low dispersion spectra of a number of molecules are briefly described, in the hope that they may in the future be investigated under high dispersion.

ACKNOWLEDGMENTS

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It has been my privilege to see the theoretical calculations of the envelopes of asymmetric rotator bands in advance of publication, through the kindness of Professor R. M. Badger and Mr. L. R. Zumwalt. For the preliminary results of the electron diffraction investigations of ethylene oxide, ethylene imine, and ethylene sulfide, I am indebted to Mr. H. A. Lévy. Dr. J. W. Linnet has very kindly placed at my disposal the unpublished results of his recent Raman and near infrared studies of allene and ethylene oxide.

I wish also to thank Mr. V. F. H. Schomaker, and my colleagues in the spectroscopic laboratory, Dr. S. H. Bauer and Mr. L. R. Zumwalt for their assistance on numerous occasions, and for interminable discussions of spectroscopic matters.

It is, finally, a pleasure to acknowledge my great indebtedness to Professor R. M. Badger, under whose direction these investigations have been carried out, for his continuous assistance through both experimental and theoretical difficulties.

PROPOSITIONS

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1) Contrary to previous assumptions[1,2], the α system of SiF is emitted in a ${}^2\Pi_{\text{case b}} \rightarrow {}^2\Pi_{\text{case a}}$ transition; both the coupling and the vibrational frequency in the upper state are to be considered anomalous.

2) The famous ethylene band at $\lambda 8720$ [3] has analogs in the spectra of allene, ethylene oxide, ethylene sulfide, and ethylene imine. These bands are to be attributed to the approximate coincidence of stretching and bending frequencies of the carbon-hydrogen bonds; specific assignments can be made in the case of ethylene and allene.

3) Neilsen's theory of the rotation-vibration interaction for nearly degenerate frequencies of molecules which approximate symmetric rotators [4] appears incorrect, for:
   a) It fails to explain the intensity distribution in the formaldehyde bands[5] for which it was specifically devised,
   b) Its predictions for the analogous ν_9 and ν_{10} bands of the ethylene molecule[6] are completely incompatible with the observed structures.[7]

The spectra of ketene and diazomethane would furnish similar nearly degenerate pairs to test this theory.

4) Calculation of the integral absorption coefficient and the half-width due to collision broadening indicates that the phosphine absorption predicted[8] to occur near 14 meters would be too broad and weak to be observed with the standard resonance methods used

in the 3 to 300 meter region. All spectroscopic investigations of gases in this range will be attended by extreme difficulty, unless it is possible to measure the energy lost to the gas over a frequency range comparable to the half width of the absorption lines or bands. Since at present only sources of monochromatic radiation are available in this region, the only method which offers promise is the measurement of the anomalous dispersion by the extremely sensitive beat frequency method.

5) The spectra of the rare earth hydrides in emission constitute a most interesting field for investigation, because:
   a) There is evidence that they would be observable, and the fine structure could be easily resolved.
   b) They would furnish examples of electronic states of higher multiplicities and Λ -values than any molecules known at present.
   c) The coupling of the f electrons and the rest of the molecule should differ from the usual cases, and might be expected to furnish information concerning the coupling in the rare-earth atoms.

6) Reports of the efficiency of so-called "optical catalyzers" in producing Raman-like scattering of unusual intensity[9] are erroneous.

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7) The strong interstellar lines not of atomic origin, reported by Merrill[10], cannot be identified with any known molecular spectra, and the assignments which have been made[11,12] are erroneous.

8) Nebular counts out to a given red-shift, the type of greatest theoretical interest, could be made with reasonable accuracy and speed with the projected 72 inch Schmidt telescope, if it were equipped with an objective prism.

9) If it be assumed that an acceptable general relativistic quantum theory for single particles reduce in proper coordinates to the Dirac theory, then, for a general metric, not only will the special relativistic uncertainty relations persist, but there will also appear absolute uncertainties in the proper momenta and in the proper energy, which will be determined by the metric and will vanish as this become Euclidean. Should Born's recent theory[13] prove correct, there would also exist symmetrical absolute uncertainties in the proper coordinates and in the proper time, determined by the metric in the reciprocal momentum-energy space.

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10) Existing conclusions[14] concerning the structures of the hydrazoic acid and methyl azide molecules, based on their absorption spectra in the photographic infrared, appear entirely unjustified upon a further examination of these bands.

11) The moments of inertia of ethylene and allene can be satisfactorily interpreted by assuming equal distances and angles in the two molecules, which means that considerable differences in the heats of hydrogenation of carbon-carbon double bonds need not be accompanied by related differences in bond distances.

12) From the envelope of the hybrid[15] band of ethylene imine at λ10500 one may tentatively conclude that the angle between the N-H bond and the plane of the ring is at most about 30°. This conclusion can best be tested by electron diffraction studies of N-methyl ethylene imine, which are being made.

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