The Vibrational Spectrum and Thermodynamic Functions of Acrylonitrile

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The infra-red spectra of gaseous and liquid acrylonitrile have been studied from 2.5μ to 25μ with a spectrometer using LiF, CaF_2, NaCl, and KBr prisms. The Raman spectrum of the liquid has been obtained, including intensity and polarization data. A normal coordinate calculation of the non-planar frequencies has been made, using force constants from related molecules. This information permits a complete assignment of the fifteen fundamental frequencies and a calculation of the thermodynamic quantities for the molecule.

I. INTRODUCTION

THE acrylonitrile (or vinyl cyanide) molecule has the structural formula

H   H
 \   /
  C==C
 /   \
H   C≡N
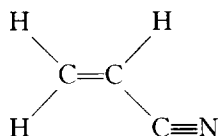
and may be treated as a substituted ethylene. Its vibrational spectrum is of considerable interest since the molecule is small enough to allow a complete assignment of normal vibration frequencies, and yet is large enough to exhibit several interesting features of more complicated molecules. Furthermore, assignment of the fundamental frequencies permits the calculation of thermodynamic functions which should be of extensive use for such a chemically important molecule.

Previous Raman[1,2] and infra-red[3] measurements have been reported for acrylonitrile, but our data are sufficiently different in some cases as to require another choice of normal frequencies.

II. OBSERVED SPECTRUM

The acrylonitrile used for obtaining these spectra had been prepared by the dehydration of hydracrylonitrile, and was purified by vacuum distillation just prior to using. Its index of refraction was $n_D^{22.5} = 1.3902 \pm 0.0002$ and its density was $d_{24} = 0.8024 \pm 0.0003$ g/cc.[4]

Infra-Red Absorption

(a) *Vapor Phase.* The infra-red spectrum shown in Fig. 1 was obtained using a Perkin-Elmer spectrometer Model 12A with LiF, CaF_2, NaCl, and KBr prisms. For the region 4000 to 2000 cm^{-1} a multiple reflection cell with a variable path length of 1, 2, 3, or 4 meters was used, the spectrum in Fig. 1 being that for a 2 meter path. Measurements were made at 27°C with an acrylonitrile partial pressure of about 110 mm of Hg. For the region 2000 to 400 cm^{-1} the small housing of the spectrometer was filled with acrylonitrile vapor at pressures ranging from 110 mm to about 5 mm of Hg, the path length being 40 cm. No absorption bands were observed from 400 to 600 cm^{-1} even at a pressure of 110 mm. The spectrum in Fig. 1 is for a partial pressure of 110 mm, with lower pressure inserts for the bands at 954 and 972 cm^{-1}.

The observed bands are listed in Table I, together with a type designation. Bands are termed type A, B, or C depending on whether the Q branch is observed to be weak, absent, or strong, relative to the P- and R-branches. In some cases overlapping bands (atmospheric water vapor and carbon dioxide) do not permit a sharp distinction, and so the apparent band type is listed as a question mark. In cases where a Q branch is not observed, the band center is taken as the average of the P- and R-branch values.

The P-branch (3115 cm^{-1}) of the band at 3125 cm^{-1} has some asymmetry relative to the R-branch, as though some additional absorption were present other than the single band. A shoulder appears at 2984 cm^{-1} on the P-branch of the strong band at 3042 cm^{-1} when the path

[1] B. Timm and R. Mecke, Zeits. f. Physik **97,** 221 (1935).
[2] A. W. Reitz and R. Skrabal, Monats. f. Chem. **70,** 398 (1937).
[3] H. W. Thompson and P. Torkington, J. Chem. Soc. **1944,** 597.
[4] Literature values are $n_D^{22.5} = 1.3898 \pm 0.0002$ and $d_{24} = 0.8017$ g/cc given by H. S. Davis and O. F. Wiedeman, Ind. Eng. Chem. **37,** 482 (1945).

length is 3 meters, but there is not sufficient structure to determine the band type. It is assumed that the 2984 cm⁻¹ absorption represents a P-branch, and so a band center is estimated at about 2994 cm⁻¹. The P branch of the atmospheric CO_2 band at 2350 cm⁻¹ is overlapped by a weak acrylonitrile band with peaks at 2278 cm⁻¹ and 2295 cm⁻¹. Whether it is an A or B type band is not apparent. The absorption at 1085 cm⁻¹ has the appearance of a weak type C band, superimposed on a type A band at 1096 cm⁻¹.

The absorption bands at 954 cm⁻¹ and 972 cm⁻¹ are very intense so that even a few millimeters pressure with a 40 cm path length causes 50 percent absorption. Part of the fine structure associated with these bands was resolved as shown in Fig. 1, with the frequency values given in Table II. The fine structure frequency values for the analogous band at 683 cm⁻¹ are given in Table III. Measurements down to 655 cm⁻¹ were made with a NaCl prism; below that point a KBr prism was used which did not resolve the fine structure. Although the frequencies in Tables II and III are given to a tenth wave number, the absolute values are good to only ±2 cm⁻¹ and the relative values to only ±0.2 cm⁻¹.

(b) *Liquid Phase.* The spectrum shown in Fig. 2 was obtained using the same spectrometer as for the vapor and using a 0.1 mm cell at room temperature. Other measurements were made in the region 800–900 cm⁻¹ with the cell cooled to about −30°C, but no appreciable changes in intensities of the bands resulted. No discrete absorption bands were found in the region 400–600 cm⁻¹. Band centers are listed in Table I.

RAMAN EFFECT

A number of Raman spectra were obtained using a grating spectrograph and other accessories which have been described previously.[5]
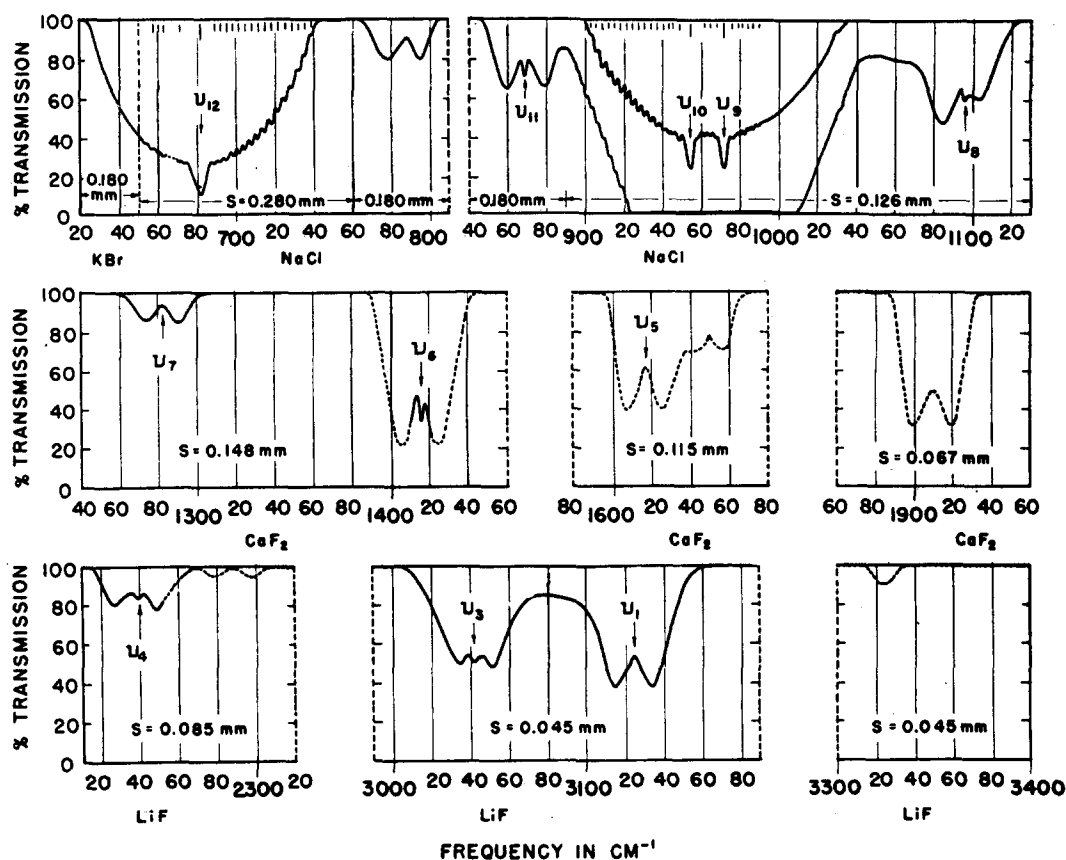

FIG. 1. Infra-red spectrum of acrylonitrile vapor.

[5] R. F. Stamm, Ind. Eng. Chem. Anal. Ed. **17**, 318 (1945).

TABLE I. Observed infra-red absorption by acrylonitrile.

Vapor			Liquid		Vapor			Liquid		Vapor			Liquid	
683	Q	C	690	S	1607	P	B	1609	M	2889	P	B	2885	W
					1625	R				2911	R			
777	P	B	804	W										
794	R				1641	?	?	1648	W	2984	P	?	2990	M
					1658	?				—				
860	P													
869	Q	A	871	M	1899	P	B	1940	S	3035	P			
879	R				1919	R				3042	Q	A	3033	S
										3052	R			
954	Q	C	960 ↕ 980	VS				2174	VW					
972	Q	C											3068	S
					2226	P								
1033	?		1035	W	2239	Q	A	2228	M				3091	W
					2247	R								
1085	Q,P	C								3115	P	B	3125	M
1096	Q	A	1094	M						3134	R			
1104	R				2278	P	?	2280	W				3210	W
					2295	R								
1273	P	B	1288							3330	?	?	3323	W
1291	R							2465	VW					
			1325?	VW				2580	VW				3557	M
			1376?	VW				2697	W					
1406	P													
1416	Q	A	1415	S				2795	VW				~3650	M
1424	R													

Excitation by the indigo triplet (4358, etc.) and the use of Eastman 103-J plates proved sufficient to yield the fundamental frequencies (as well as a few overtones and combinations) in the liquid state. On the long exposures, $\Delta\nu\nu$3032 and 2228 excited by 4047 and 4078 appeared in the 4358 region in spite of the $NaNO_2$ filter.

Polarization measurements were made both by the double and single exposure method. For the former, "Polaroid" cylinders were used.[6] For the latter, two horizontal H-11 arcs backed by machined, Cr plated elliptical reflectors served as a source. The light from the arcs passed through blackened metal slots and then through

TABLE II. Structure on bands at 954 and 972 cm⁻¹.

903.5	943.3
906.1	945.4
909.2	948.7
912.2	954.3 St.
915.2	961.8
918.3	964.6
921.4	967.6
924.5	971.5 St.
927.7	975.7
930.9	979.7
934.1	981.1
937.3	984.1
940.5	986.7
	989.5

TABLE III. Structure on band at 683 cm⁻¹.

657.8	705.0
660.1	708.3
663.0	711.6
—	715.0
671.3	718.4
682.8 St.	721.8
689.2	725.5
692.3	729.0
695.5	732.3
698.5	735.8
701.7	739.6

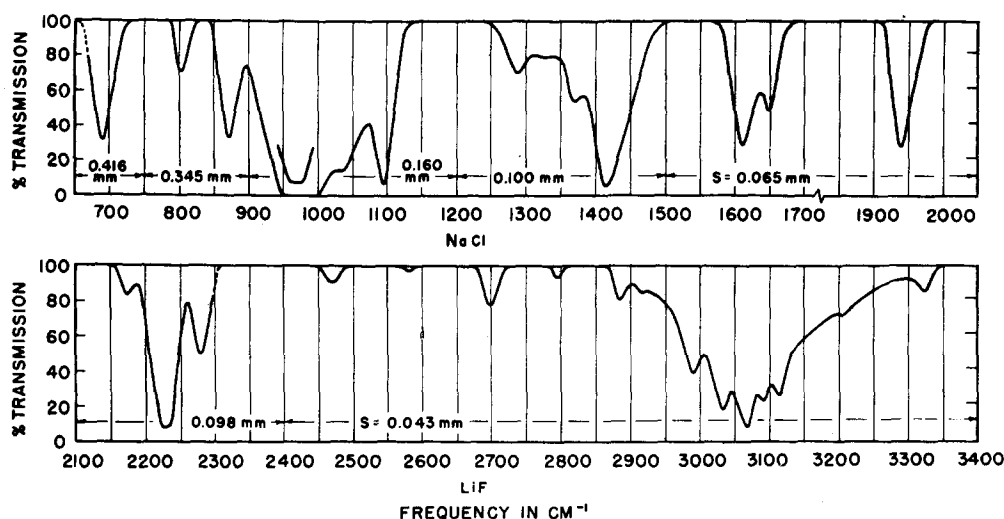[6] B. L. Crawford, Jr., and W. Horwitz, J. Chem. Phys. 15, 268 (1947).

FIG. 2. Infra-red spectrum of liquid acrylonitrile.

glass filters to the liquid which was contained in a horizontal tube of square cross section with a strain-free window of good optical quality fused onto the end. Between the condensing lens and the slit was placed a Wollaston prism (made of $NH_4H_2PO_4$) having an aperture 4 cm $\times$ 4 cm and a semi-angle of divergence of 0.04 radian at 4400A. No depolarizer was used between the Wollaston and the slit. Instead, the polarizing properties of the spectrograph were determined at $\lambda\lambda 4471$, 4713, and 5016A using a fairly large bore He tube as a source in conjunction with the condensing lens and Wollaston prism. The appropriate correction factors were then applied to the experimentally-determined, single-exposure ρ values to obtain the corrected values. No value was obtained for $\Delta\nu 362$. The values for $\Delta\nu\nu 970$ and 1094 are larger than the theoretical limit of 6/7 (0.86) even though 1094 is supposed to be polarized. This is occasioned by their low intensities and diffuse characters. (An additional reason for the high ρ value for 1094 will be mentioned later.)

The Raman frequencies are given in Table V. These values are corrected for vacuum and are accurate to within ± 2 cm^{-1}. The intensities (determined microphotometrically) are given on a scale of 1 to 100 with 2228 being given a value of 100; they have not been corrected for irregularities in plate sensitivity.

Enlarged reproductions of the Raman spectrum and of the single-exposure polarized spectra

are given in Fig. 3 along with the corresponding microphotometer tracings. The two spectra which show $\Delta\nu 362$ have too much background to be suitable for reproduction.

III. THEORETICAL CONSIDERATIONS

The acrylonitrile molecule is presumably, planar, belonging to symmetry point group C_s, and having fifteen normal vibrational degrees of freedom. The representation of this point group (which has the vibrational motions as its basis) in terms of its irreducible components, is $\Gamma_{\text{vib}} = 11A' + 4A''$, where type A' is symmetric and type A'' is antisymmetric with respect to reflection in the molecular plane. Selection rules permit all the vibrational frequencies to be active both in infra-red absorption and in the Raman effect.

Although no data are available for the molecular parameters, estimates can be made which are sufficiently accurate for qualitative discussions. A diagram of the molecule is given in Fig. 4, together with abbreviations used to designate the atoms and angles involved. For our purposes we assume

$$r(C-H) = 1.08A, \quad r(C=C) = 1.35A,$$
$$r(C-C) = 1.49A, \quad r(C\equiv N) = 1.17A$$

and $\alpha_3 = \beta_{56} = 120°$. These dimensions yield as the principal moments of inertia $I_A \simeq 19$, $I_B \simeq 174$, and $I_C = I_A + I_B \simeq 193$ (in units of 10^{-40} g cm^2) about the axes designated as A and B in Fig. 4,

and the C-axes perpendicular to the molecular plane. These moments are only approximate, although I_A seems about right for the observed rotational spacing.

The infra-red absorption bands for the vapor should have contours characteristic of the orientation of the vibrating electric moment with respect to the principal axes. A description of

the band envelopes for this type of molecule may be obtained from the computations of Badger and Zumwalt[7] on unsymmetrical rotator molecules. For a planar molecule with $I_A \ll I_B$, I_C, vibrations in which the electric moment change is parallel to the A-axis should give rise to type "A" bands with three peaks, the central one being weak relative to the others. Vibrations in
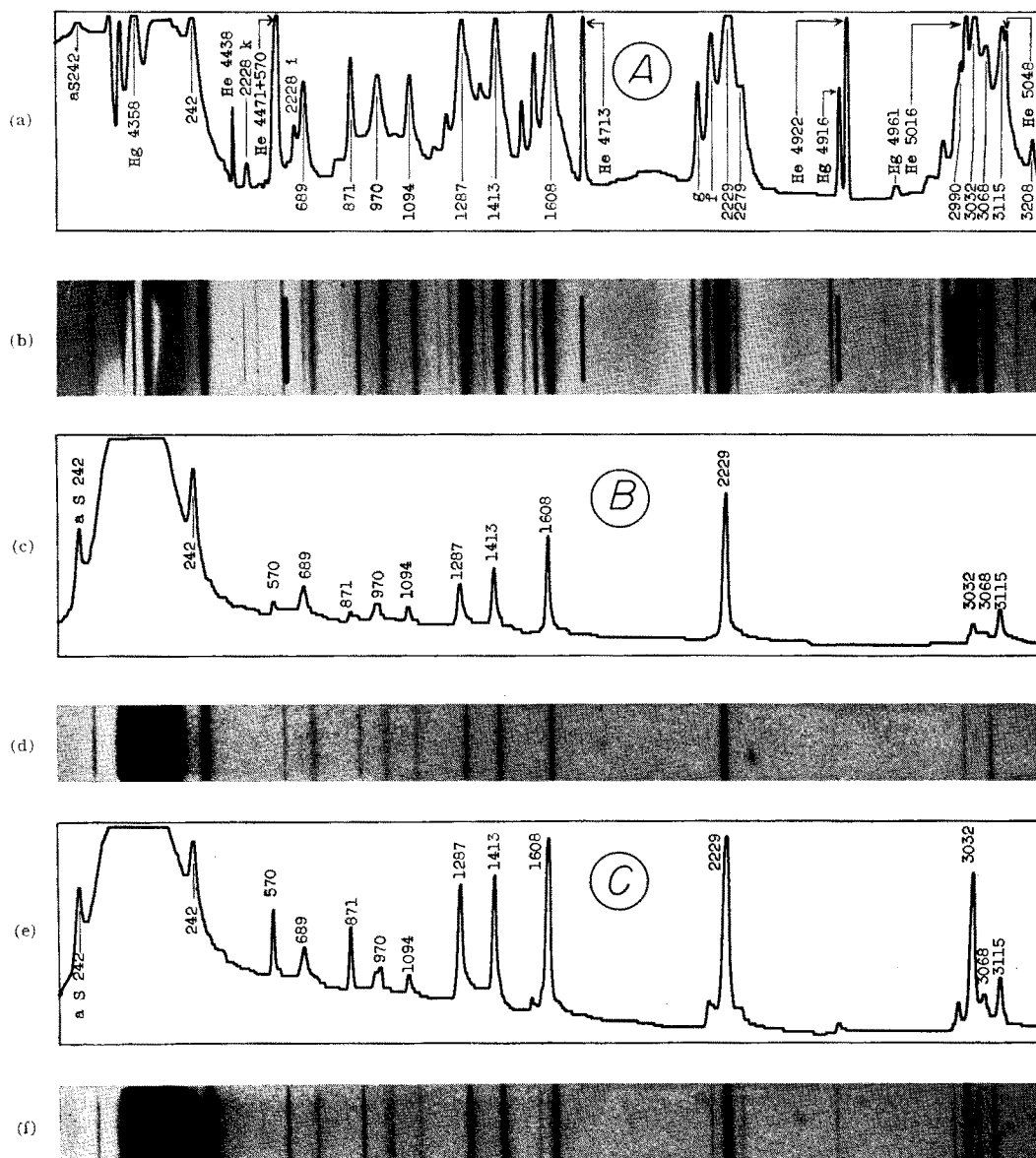

FIG. 3. Raman spectra of acrylonitrile (liquid). (A) Spectrum with helium reference spectrum. The stronger lines are excited by Hg e, f, and g. (B) and (C) are polarized spectra using natural light incident on sample and represent i_σ and I_π, respectively, with $\rho_n = i_\sigma / I_\pi$.

[7] R. M. Badger and L. R. Zumwalt, J. Chem. Phys. 6, 711 (1938).

which the moment is parallel to the B-axis should yield type "B" bands with two peaks and a minimum between them. Vibrations in which the moment is parallel to the C-axis should yield type "C" bands with three peaks, the central one being very strong relative to the other two. And finally, vibrations in which the moment makes an arbitrary angle with the principal axes should yield band envelopes which are linear combinations of the A, B and C type intensity distributions, with coefficients proportional to the squares of the components of the moments along the respective axes; these are termed hybrid bands. Consequently the a'' vibrations[8] should give rise to pure type C bands, while the a' vibrations may give rise to types A or B, or hybrids of the two, depending on the particular vibrations. Hybrid bands, however, may appear to be type B bands because of the low intensity of the Q branch and because of incomplete resolution. Perhaps the purest type A band is the one at 2239 cm^{-1} caused primarily by a stretching of the C≡N bond. Bands at 786 and 1282 cm^{-1} do not show Q branches, although run under conditions which resolve the peaks for bands at 869 and 1416 cm^{-1}.

In the Raman effect lines arising from a'' vibrations should be completely depolarized, i.e., should show a depolarization factor of 6/7 when unpolarized incident light is used, and scattering is observed at 90°. Raman lines arising from a' vibrations, however, may show any depolarization factor, ρ_n, $\leqslant 6/7$, although pure deformation vibrations are expected to show a relatively high factor.[9]
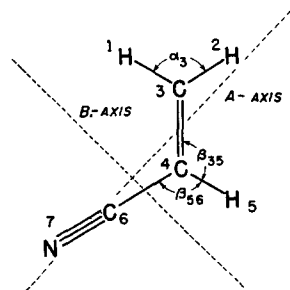

FIG. 4. Structural parameters for acrylonitrile.

FIG. 5. G matrix for non-planar vibrations of acrylonitrile assuming $\alpha_3 = \beta_{56} = 120°$ (symmetrical about diagonal).

A normal coordinate treatment of the a' (planar) vibrations would involve an equation of eleventh degree which is too large to handle conveniently. The a'' (non-planar) vibrations, however, require only a fourth degree equation which is amenable to treatment. Furthermore, an indication of the frequency values of the out-of-plane vibrations will be of material help in assigning some of the low frequency vibrations. As valence force coordinates (VFC) for such a treatment, we take the angle between the bisector of the HC^{3}H angle and the C=C axis (χ_3), the analogous angle between the bisector of the HC^{4}C^6 angle and the C=C axis (χ_4), the angle of torsion about the C=C bond (ψ), and the C−C≡N angle (ϕ). Wilson's technique[10] was used for setting up the secular equation, and the G matrix ($2T = \dot{S}'G^{-1}\dot{S}$, where S represents the VFC) obtained is given in Fig. 5. The F matrix ($2V = S'FS$) used with the G matrix in obtaining the secular equation, $|GF - \lambda E| = 0$, for the a'' vibrations of the acrylonitrile molecule is given in Fig. 6.

Approximate values of the force constants in the F matrix may be estimated from values for related molecules. F_{33} is taken as 0.23×10^{-11},

FIG. 6. F matrix for non-planar vibrations of acrylonitrile.

[8] Small letters are used for the symmetry species of a normal vibration, corresponding to the capital letter for the general symmetry class.

[9] M. Wolkenstein and M. Eliashevich, C. R. Acad. Sci. U.R.S.S. **41**, 366 (1943). The fuzziness and high depolarization factor of the lowest lying Raman line in acrylonitrile supplies some experimental support for these theoretical considerations.

[10] E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939); **9**, 76 (1941).

TABLE IV. Probable regions for vibrational frequencies.

Type	Description	Approximate region	Description	Approximate region
A'	3 C—H stretching	3000 cm^{-1}	1 C=CH$_2$ wagging	1100 cm^{-1}
	1 C≡N stretching	2240 cm^{-1}	1 C—C stretching	900 cm^{-1}
	1 C=C stretching	1630 cm^{-1}	1 C=C—C bending	450 cm^{-1}
	1 =C—H$_2$ deformation	1400 cm^{-1}	1 C—C≡N bending	360 cm^{-1}
	1 C=C—R bending	1290 cm^{-1}		
A''	1 C=CH$_2$ wagging (χ_3)	940 cm^{-1}	1 C=C HR wagging (χ_4) ⎫	⎰964 cm^{-1}
	1 C—C≡N bending (ϕ)	357 cm^{-1}	1 C=C torsion (ψ) ⎭	⎱632 cm^{-1}

F_{44} as 0.25×10^{-11} and f_{34} as $+0.03 \times 10^{-11}$ ergs per radian^2 from the values for vinyl chloride.[11] $F_{\psi\psi}$ is taken as 0.47×10^{-11} ergs per radian,^{2} an average of the values for ethylene dibromide[12] and vinyl chloride.[11] $F_{\phi\phi}$ is taken as 0.344×10^{-11} ergs per radian^2 as given for methyl cyanide.[13] All interaction constants except f_{34} are neglected since no consistent data are available for them. With these values for the force constants, the frequencies calculated for the a'' vibrations are those given in Table IV. Exact agreement between these calculated frequencies and the observed ones should not be expected, since force constants were only estimated and interaction constants were neglected.

Probable spectral regions for the frequencies of the fifteen normal vibrations of acrylonitrile are given in Table IV, together with a description of the principal mode of motion involved in each. In some cases, of course, two or more of these modes may be interacting strongly. For example, the modes designated as the C=CHR out-of-plane wagging (referred to later as ν_9) and the C=C bond torsion (ν_{12}) involve both coordinates χ_4 and ψ to a large extent, with χ_4 making the slightly larger contribution to ν_9 (about 8 percent larger) and *vice versa* for ν_{12}.

IV. ASSIGNMENT OF OBSERVED FREQUENCIES

We shall designate the fifteen normal vibrations arranged in order of descending frequencies by the numbers one to fifteen. Thus the first three will be those associated primarily with the

[11] K. S. Pitzer and N. K. Freeman, J. Chem. Phys. **14**, 586 (1946).
[12] C. Manneback as quoted by M. de Hemptinne, Trans. Faraday Soc. **42**, 5 (1946).
[13] B. L. Crawford and S. R. Brinkley, J. Chem. Phys. **9**, 69 (1941).

stretching of the C—H bonds, which are expected to have frequencies in the vicinity of 3000 cm^{-1}. The two strong vapor phase infra-red bands at 3125 cm^{-1} and 3042 cm^{-1} are assigned to the fundamental vibrations ν_1 and ν_3, respectively. Each of these bands shifts downward about 10 cm^{-1} on going to the liquid. In view of this, the fundamental ν_2 is taken to be 3068 cm^{-1} for the liquid, and estimated at about 3078 cm^{-1} for the vapor (perhaps accounting for the asymmetry in the "P" branch of the band at 3125 cm^{-1}). The variations in intensities of absorption by these vibrations on going from the vapor to the liquid state are also indicative of rather strong intermolecular forces.

The band at 2239 cm^{-1} in the vapor (at 2229 cm^{-1} in the liquid) must be associated with ν_4, the stretching of the C≡N bond. An absorption band with a similar contour occurs at 869 cm^{-1}, which must be caused by a vibration with its transition moment in the same direction. This latter band is assigned to ν_{11}, the stretching of the C—C bond. Little or no shift is observed for this band on going to the liquid state (logical behavior for stretching of an internal bond).

The stretching of the C=C bond, ν_5, is assigned to the band at 1615 cm^{-1}, which also shows little shift with a change of state (1608 cm^{-1} in the liquid). The CH$_2$ deformation, ν_6, is assigned the frequency 1416 cm^{-1}. The vibration ν_7, essentially the in-plane wagging of the olefinic C—H group (involving changes in β_{56} and β_{35} of Fig. 4), is associated with the vapor band at 1282 cm^{-1} and the slightly higher liquid frequency, 1287 cm^{-1} (average of 1286 and 1288 cm^{-1}).

The in-plane wagging of the CH$_2$ group, ν_8, is assigned the frequency 1094 cm^{-1} in the liquid

TABLE V. Vibrational assignments for acrylonitrile.

Descriptive assignments†	Gas Infra-red		Liquid Infra-red		Raman			Average	Infra-red T & T* Gas	Liquid	Raman** Liquid
ν_{15} a' C$-$C$\equiv$N bend					242	.72	16	242	ν_{14}		238
ν_{14} a'' C$-$C$\equiv$N bend					362	—	—	362	ν_{15}		305
ν_{13} a' C$=$C$-$C bend					570	.18	4.1	570	ν_{12}		517
											561
											628
ν_{12} a'' C$=$C torsion	683	C S	690	S	688	.875	3.0	689	ν_{13} 690		688
A' $\nu_{13}+\nu_{15}$	786	B W	804	M				804	791	805	
ν_{11} a' C$-$C stretch	869	A M	871	M	871	.22	4.7	871	870	873	878
										907	
ν_{10} a'' H$_2$C$=$C wag	954	C V.S.}								954	
			960–980	VS	970	.94	2.8	970		960–980	965
ν_{9} a'' HRC$=$C wag	972	C V.S.}								971	
A' $\nu_{14}+\nu_{12}$	1033	? ?	1035	W				1035		1038	
A'' $3\nu_{14}$	1085	C S									
			1094	S	1094	.91	2.8	1094	ν_{8} 1095	1097	1099
ν_{8} a' CH$_2$ rock	1096	A W }									
											1205
ν_{7} a' C$-$H rock	1282	B W	1288	M	1286	.31	14	1287	ν_{7}	1288	1275
A' $\nu_{10}+\nu_{14}$			1325?	VW				1325		1330	
$2\nu_{12}$			1376?	VW				1376		1372	
ν_{6} a' CH$_2$def.	1416	A M	1415	S	1412	.34	20	1413	ν_{6} 1421	1420	1406
A' $\nu_{11}+2\nu_{14}$					1588	P		1588			
ν_{5} a' C$=$C stretch	1615	B M	1609	S	1607	.23	36	1608		1610	1607
A' $\nu_{6}+\nu_{15}$	1650	? W	1648	M	1648	D		1648		1650	
A' $\nu_{9}+\nu_{10}$	1909	B M	1940	M				1940			
A' $2\nu_{8}$			2174	W				2174			
ν_{4} a' C$\equiv$N stretch	2239	A W	2228	S	2228	.30	100	2228	ν_{4}	2232	2224
A' $\nu_{6}+\nu_{11}$	2286	? V.W.	2280	M	2278	P		2279		2283	
A' $\nu_{4}+\nu_{15}$			2465	VW				2465			
A'' $\nu_{5}+\nu_{9}$			2580	VW				2580			
A' $\nu_{6}+\nu_{7}$			2697	W				2697			
A' $\nu_{4}+\nu_{13}$			2795	VW				2795			
	2894	B	2885	W				2885			
	2994	?	2990	W	2989	P		2990			2989
ν_{3} a' C$-$H stretch	3042	A S	3033	S	3032	.21	45	3032			3036
ν_{2} a' C$-$H stretch	(3078?)	?	3068	S	3068	.51	7.5	3068			
A' $\nu_{4}+\nu_{11}$			3091					3091			
ν_{1} a' C$-$H stretch	3125	B S	3114	S	3116	.80	14	3115			3115
A' $2\nu_{5}$			3210		3207			3208			
A' $\nu_{4}+\nu_{8}$	3330	? W	3323					3323			
A' $\nu_{5}+\nu_{9}+\nu_{10}$			3557±7					3557			
			3650±7					3650			

† Present paper.
* Thompson and Torkington, reference 3.
** References 1 and 2.

and 1096 cm^{-1} in the vapor. This is complicated by the appearance of a weak type C band at 1085 cm^{-1}, which is believed to be the third harmonic of a fundamental at 362 cm^{-1} (symmetry A'') lying on top of the fundamental ν_8 (symmetry a'). The A'' harmonic probably gains some intensity by interaction with the intense type "C" bands at 972 cm^{-1} and 954 cm^{-1}. In the Raman spectrum, however, the line at 1094 is comparable in intensity to the doublet at 960–980 cm^{-1}, and presumably is caused by the fundamental itself. This super positioning of A'' and a' frequencies could cause ρ to be high (as high as 0.86) if A'' has considerable intensity.

However, it seems better to say that the third harmonic of 362 will be very weak in Raman effect and that the erroneous value for ρ is

TABLE VI. Thermodynamic functions for acrylonitrile.

Absolute temperature	C_P^0	$(H^0-H_0^0)/T$	$-(F^0-H_0^0)/T$	S^0
298.16	15.24	10.79	54.68	65.47
300	15.30	10.82	54.75	65.56
400	18.36	12.33	58.07	70.40
500	20.95	13.80	60.97	74.78
600	23.11	15.18	63.61	78.79
700	24.90	16.44	66.05	82.49
800	26.43	17.60	68.31	85.91
900	27.75	18.66	70.46	89.12
1000	28.88	19.62	72.49	92.11

caused by experimental difficulties. We therefore disregard the value of ρ for this line and assign 1094 to an a' frequency.

The bands at 972 cm^{-1} and 954 cm^{-1} are extremely intense type C bands in infra-red absorption, and are assigned to ν_9 ($C = CHC$ wagging) and ν_{10} ($C = CH_2$ wagging) respectively, corresponding to the calculations in Table IV. In the liquid the bands occur at slightly higher frequencies. This very intense infra-red absorption by out-of-plane $C - H$ wagging vibrations is compatible with a relatively polar $C - H$ bond[14] as well as the increase in frequency on going to the liquid state. The frequency ν_{12}, torsion about the $C = C$ bond, is assigned to the strong type C band at 683 cm^{-1}. Its intensity is reasonable when compared to the intense bands for ν_9 and ν_{10}, and when consideration is given to the interaction of coordinates ψ and χ_4 in producing ν_{12} and ν_9. The polarized Raman lines at 570 cm^{-1} and 242 cm^{-1} must be assigned to the planar vibrations ν_{13} ($C = C - C$ bending) and ν_{15} ($C - C \equiv N$ bending), respectively. This leaves 362 cm^{-1} as the frequency of the out-of-plane $C - C \equiv N$ bending vibration, ν_{14}. The combination of $\nu_{13} + \nu_{15}$ explains the infra-red band in the liquid at 805 cm^{-1} very nicely. In the vapor, however, this band appears at a lower frequency,

786 cm^{-1}, and if the same assignment is to hold, one or both of ν_{13} and ν_{15} must be lower in the vapor phase. In view of the intermolecular forces present, such a shift is reasonable for bending vibrations.

Our assignment of observed frequencies, together with a comparison of data given by other observers, is given in Table V. Only the band centers are listed.

V. THERMODYNAMIC FUNCTIONS

Since the fundamental frequencies have been determined, and since the moments of inertia have been estimated, the thermodynamic functions for the vapor may be calculated. Values obtained for the temperature range 298.16–1000°K using the tables given by Aston,[15] are given in Table VI in terms of calories per mole per degree. The translational and rotational contributions were obtained using the working equations given by Wagman et al.[16] Values of 560, 362, and 238 cm^{-1} were estimated for the vapor phase frequencies ν_{13}, ν_{14}, and ν_{15} for use in the calculations, and $I_A \cdot I_B \cdot I_C$ was taken as 634×10^{-117} g^3 cm^6.

[14] G. W. Wheland, *The Theory of Resonance* (John Wiley and Sons, Inc., New York, New York, 1944), pp. 135–136.

[15] J. G. Aston, in Taylor and Glasstone, *Treatise on Physical Chemistry* (D. Van Nostrand Company, Inc., New York, New York, 1942), Vol. 1, pp. 655–658.

[16] D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, J. Research Nat. Bur. Stand. **34**, 143 (1945).