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The Far Ultraviolet Absorption Spectra of Simple Alkyl Amines*

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A quantitative study of the absorption spectra of ammonia, the three methyl and the three ethyl amines, has been made in the region 39 000 to 63 000 cm^{-1} . Three electronic transitions have been observed in most cases. The first is of low intensity particularly in the secondary amines, the second is of higher intensity and increases from the primary to the tertiary compound, and the third, which is only partially covered by these measurements, is of intermediate intensity. The positions of all transitions, particularly the second, are influenced by alkyl substitution. These transitions are discussed in relation to the spectrum of ammonia. Vibrational structure, present in ethyl amine, methyl amine, and dimethyl amine, has been analyzed in part.

INTRODUCTION

THE investigation of the far ultraviolet spectra of the simple aliphatic amines was undertaken to obtain fundamental information concerning the electronic transitions that occur in these molecules and, if possible, to correlate the spectra with the chemical reactivity of the compounds. Thompson and Duncan,¹ who reported oscillator strengths and positions of bands for the spectrum of ammonia, the parent compound of these series, were able to measure four electronic transitions in the range of 45 000 cm^{-1} to 120 000 cm^{-1} . These four transitions were assigned as being transitions of one electron of the unshared pair: $2p_z-3s$, $2p_z-3d_z$, $2p_z-4s$, and $2p_z-5s$. The assignment of the second transition was, however, tentative, and it was pointed out that another possibility involved an NH bonding electron; a $N-V$, bonding to antibonding, or a $(\pi e)-(\pi e)'$, bonding to bonding, transition being consistent with the position and intensity of the observed band. These possible assignments were based on an electron configuration proposed by Mulliken.²

EXPERIMENTAL

Purification of Compounds

Methods of purification of amine samples obtained from Eastman Kodak Company are summarized as follows: (1) direct distillation of the free amine: ethyl and triethyl amine; (2) direct distillation of an aqueous solution of the amine: methyl and dimethyl amine; (3) fractional crystallization of the hydrochloride from absolute alcohol or ether followed by treatment with base and distillation: ethyl, methyl, diethyl, and dimethyl amine; (4) free amine refluxed with acetic anhydride and distilled: triethyl and trimethyl amine; (5) treatment with Hinsberg reagent followed by distillation: trimethyl amine. All distillations were carried

out in an atmosphere of nitrogen. Compounds whose boiling points are above room temperature were refluxed with a drying agent and fractionally distilled through a modified Fenske column. Fractions boiling within a 0.1°C range were used for the measurements. More volatile compounds were distilled over a long column of soda lime or other drying agent.

Diethyl amine was also prepared by the acid hydrolysis of a purified sample of diethyl cyanamide which was prepared in this laboratory.

Ammonia was prepared from Baker's cp ammonium sulfate by heating in a nitrogen atmosphere and passing the vapor over potassium hydroxide pellets.

The flowing vapor method used for intensity measurements provides a criterion of purity more sensitive than any available chemical method. The impurity will become more or less concentrated in the course of a series of measurements depending on the relative vapor pressures of compound and contaminant, and can be detected by noting any drift in the values of the extinction coefficient obtained. The agreement between measurements on different samples provided an additional assurance of purity.

TABLE I. Summary of experimental details.

	Vacuum Spectrograph	Quartz Spectrograph	Beckman Spectrophotometer
Region	2300-1600A	3000-2100A	3000-2100A
Source	flowing hydrogen lamp	standard hydrogen lamp	standard hydrogen lamp
Exposure time	3 and 4 min	2 and 3 min	
Cell length	32.5 cm 31.0 cm	5.0 cm 12.5 cm 15.5 cm	1.00 cm 10.00 cm
Pressure of the amine vapor	0.01-1.8 mm	5-500 mm	1.5-120 mm
State of sample	flowing vapor	static vapor	static vapor
Measurements made	extinction coefficient and band position	band position	extinction coefficient
Plates	Ilford Q1	Eastman No. 50	

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[§] Presented in partial fulfillment of the degree of Master of Arts, 1949.

¹ R. J. Thompson and A. B. F. Duncan, *J. Chem. Phys.* **14**, 573 (1946).

² R. S. Mulliken, *J. Chem. Phys.* **3**, 506 (1935).

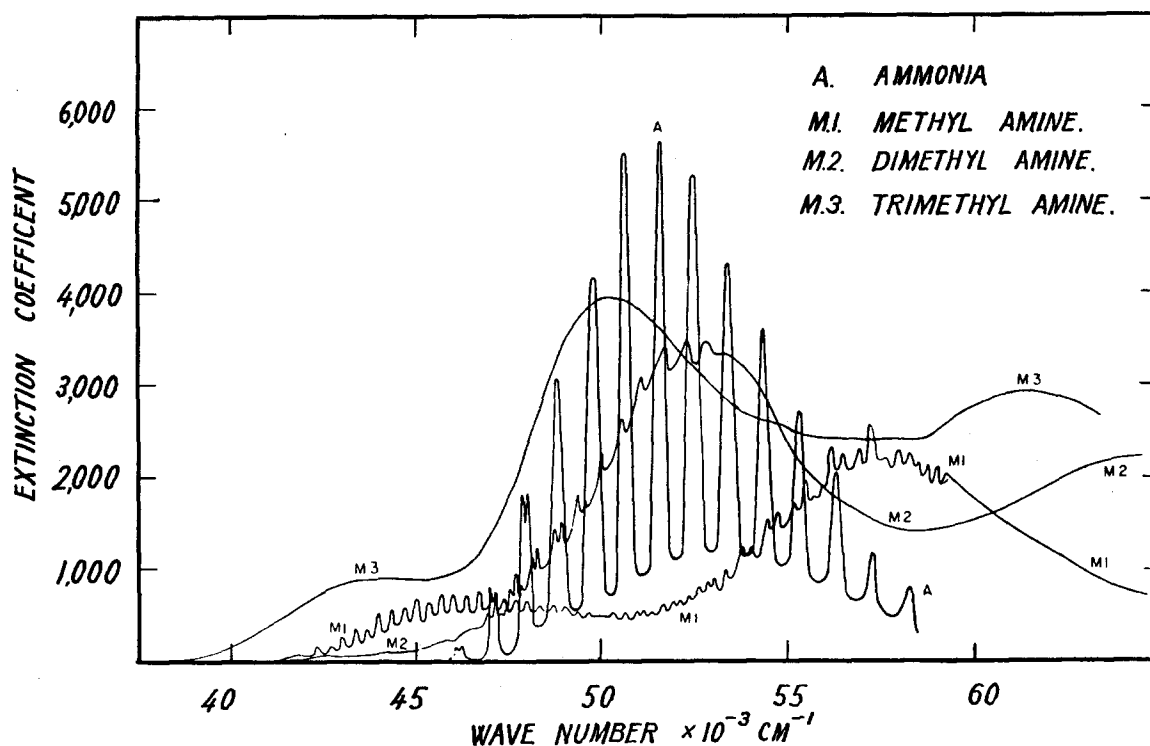


FIG. 1. Methyl series absorption curves. The molar extinction coefficient is defined by the relation: $\epsilon c L = \log_{10}(I_0/I)$ where c is concentration in moles per liter, L is path length in cm.

Spectrographic Measurements

The experimental details of measurement are summarized in Table I. The apparatus and flowing vapor method for intensity measurements have been previously described.³ Modification of the apparatus for low temperature studies involved the adaptation of a condenser for use as an absorption tube. The method used for intensity measurements is based on time calibration. The data for ammonia, the least extensively studied compound of the group, were determined from 8 plates. For each of the other compounds, the curves are based on data taken from between ten and sixteen plates.

With the exception of ammonia, the precision of the measurements of log epsilon on both the Beckman spectrophotometer and the vacuum spectrograph was usually not greater than 0.02 with an occasional average deviation of 0.05. In the region in which two instruments overlapped, from 42 500–47 500 cm^{-1} , intensity measurements determined on the two instruments checked within 0.02. The band positions, as measured on a Hilger comparator and from microphotometer tracings of plates taken at low temperatures, were determined with a precision of 20 cm^{-1} . A superimposed copper-silver spark and the mercury absorption line were used as the wavelength standards. The hydrogen emission lines were used in the region from 59 700 cm^{-1} to 65 000 cm^{-1} . For this reason, any fine structure that

the spectra of these compounds may have in this region could not be determined.

The measurement of the spectrum of ammonia was not originally considered as a part of this problem since band positions and oscillator strengths had been reported previously. However, a plot of the spectrum was desirable for comparison with the other curves and a series of measurements were made. The unusual height of vibrational band structure made measurements more difficult and accentuated experimental errors. For example, measurements with the Beckman spectrophotometer indicated that slit width and scattered light were both too large a factor in the region from 220 $\text{m}\mu$ to 210 $\text{m}\mu$ to make reliable intensity measurements on this compound. The results of measurements with the vacuum spectrograph showed only a slightly greater average deviation than those of other compounds. However, the height of the bands is so great that only two or three values of epsilon were obtained at most of the maxima and minima with the eight plates which were taken. Since in this case, the width of the band becomes an appreciable factor in determining the area under the curves, the width of each band was measured at two or three points between each maximum and minimum.

The positions of the vibrational bands have been extensively studied by Duncan⁴ using a grating instrument of high dispersion. Our band positions which are necessarily less precise are in substantial agreement with

³ Harrison, Gaddis, and Coffin, *J. Chem. Phys.* **18**, 221 (1950).

⁴ A. B. F. Duncan, *Phys. Rev.* **47**, 822 (1935); **50**, 700 (1936).

his reported values. However, our value of the oscillator strength of the first band was found to be 0.079 as compared with 0.13 reported by Thompson and Duncan. In both cases, the estimated precision was of the order of ten percent. The methods of measurement are so different that it is difficult to account satisfactorily for the discrepancy between the two f values. Under the conditions of their experiments (carried out on static samples at a pressure of 0.4–0.5 mm Hg, a cell length of 17.2 cm, and an exposure time of 40–60 minutes), they obtained a smooth curve⁶ with no evidence of vibrational structure between 50 000–60 000 cm^{-1} . Our measurements were made at comparable pressures on flowing vapor samples and exposure times of four minutes.

DISCUSSION OF THE ABSORPTION CURVES

The absorption curves of corresponding members of the ethyl and methyl series show striking similarities (see Figs. 1 and 2). Ethyl and methyl amine both have a shallow band extending from about 40 000 cm^{-1} to about 50 000 cm^{-1} followed by a second broad band of more intense absorption. In each of these spectra both bands are rich in vibrational structure. A third band is beginning to appear in the spectrum of ethyl amine between 57 000 and 60 000 cm^{-1} .

Dimethyl and diethyl amine have an extremely shallow region of absorption beginning at about 46 000 cm^{-1} , and another region of intense absorption begin-

ning at about 57 000 cm^{-1} . The maximum of the third band is beyond the range of the spectral measurements.

The spectrum of trimethyl amine consists of three bands, the first beginning at about 39 000 cm^{-1} , the second at about 46 000 cm^{-1} , and the third at about 56 000 cm^{-1} . The spectrum of triethyl amine consists of two well-defined bands, the first of which is probably composed of two overlapping bands corresponding to the first two bands in trimethyl amine. There is a suggestion of this in the slope of the curve in the region from about 40 000 cm^{-1} to about 45 000 cm^{-1} . The band with a maximum at about 57 000 cm^{-1} corresponds to the third transition in trimethyl amine.

The essential characteristics of the first two bands are summarized in Table II. Data on the third band are not sufficiently complete to warrant inclusion in the table. Values in parentheses are somewhat uncertain due to overlapping of two bands. In the case of triethyl amine, the first band is so completely obscured by the second that the characteristics of the first band could not be determined. The values of oscillator strength are based on the assumption that one band ends and the next begins at a minimum in the absorption curves. The exact values selected are given in the table. By dividing the curves of the amines into these three general regions of absorption, they are found to form an ordered pattern, each region exhibiting a characteristic behavior towards alkyl substitution through each series from

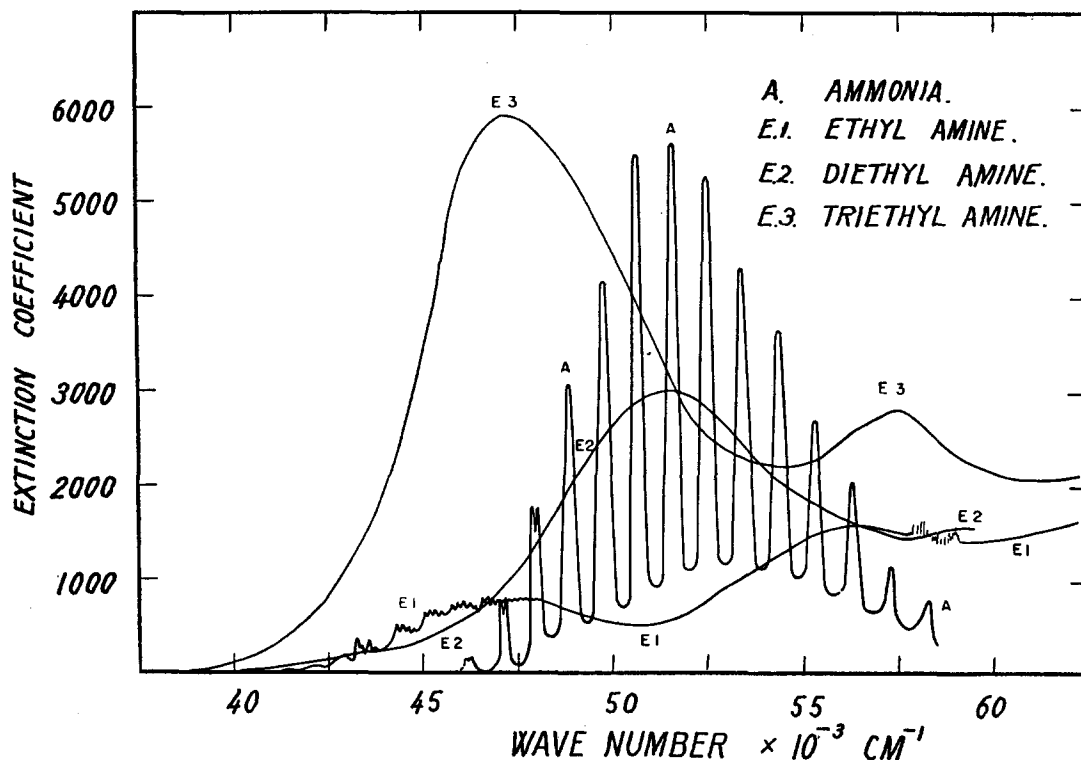


FIG. 2. Ethyl series absorption curves. The diffuse structure of the ethyl amine curve out to 55 000 cm^{-1} is not shown. The sharp bands at about 58 000 cm^{-1} has been indicated by vertical lines drawn at the band positions.

⁶ A. B. F. Duncan, private communication.

TABLE II.

	Ammonia	Methyl amine	Dimethyl amine	Trimethyl amine	Ethyl amine	Diethyl amine	Triethyl amine
Pressure range mm Hg	0.0676-0.501	0.0895-1.53	0.0925-0.630	0.0799-0.311	0.190-0.805		
Wave number extrapolated $\log \epsilon = 1.0$	45 700	40 800	40 500	37 800	41 300	39 700	37 700
FIRST BAND							
(1) Position of max cm^{-1}	51 500	46 500	(45 000)	44 000	47 000	(45 000)	...
(2) Maximum ϵ	5600	600	(100)	900	800	(300)	...
(3) Oscillator strength	0.079	0.017	(0.0017)	0.016	0.019	(0.0028)	...
(4) Wave number range	46 000-60 000	41 000-50 500	40 000-46 000	38 000-45 500	41 000-50 500	40 000-45 000	
(5) Position of 0-0	46 140	41 690			42 870		
SECOND BAND							
(1) Position of max cm^{-1}	66 000*	57 500	52 500	50 250	56 500	51 500	(47 250)
(2) Maximum ϵ		2200	3300	3950	1600	3000	(5900)
(3) Oscillator strength	0.0095*	0.084	0.10	0.13	0.050	0.10	(0.18)
(4) Wave number range		50 500-65 000	46 000-58 500	45 500-56 500	50 500-60 000	45 000-57 500	38 500-54 000
(5) Position of 0-0	60 135*	(50 360)	45 870				
Difference between maxima of first and second bands in cm^{-1}	14 500	11 000	7500	6250	9500	6500	...

* See reference 3.

primary to tertiary amine. The first band in all of the amines is of low intensity and is shifted only slightly with alkyl substitution. All the amines begin absorption between $38\,000\text{ cm}^{-1}$ and $41\,000\text{ cm}^{-1}$, that is, within a range of only 3000 cm^{-1} , which is also the separation between the first maximum of methyl and trimethyl amine. Comparing either the beginning of absorption or the maximum of the first band, the shift from ammonia to ethyl or methyl amine is about 5000 cm^{-1} . The second band, on the other hand, is strikingly influenced by alkyl substitution, ethyl substitution being more effective than methyl substitution. The total spread in position of maxima is about 9000 cm^{-1} in contrast to the 3000 cm^{-1} of the first band. The shift in position of the second maximum towards the visible through the series from primary to tertiary amine is accompanied by an increase in intensity. The fact that the second band shifts by large increments while the first band shifts only about 1000 cm^{-1} from one member of the series to the next makes reasonable the assumption that the first and second bands of triethyl amine almost completely overlap.

Generalizations about the characteristics of the third band are less certain since it extends, in most cases, beyond the limit of the spectral measurements. However, the band appears to shift to the visible and increase in intensity from primary to tertiary amine, and probably has an oscillator strength of value between that of the first and second transitions. Inspection of the curves indicates that the pattern formed by this band is more nearly like that of the second band than the first.

VIBRATIONAL ANALYSES

Methyl Amine

The near ultraviolet spectrum of methyl amine and its deuterated forms was determined by Förster and Jungers⁶ who analyzed the structure in terms of two frequencies, 650 cm^{-1} and 1000 cm^{-1} , with the 0-0 transition at $41\,680\text{ cm}^{-1}$. The 650 cm^{-1} frequency was associated with the amino group and the 1000 cm^{-1} was found to be influenced more by substitution of deuterium on the methyl group. The results of this investigation are in essential agreement with the above and extend the measurements out to 65000 cm^{-1} . All the bands to about 50000 cm^{-1} were accounted for by the following equation:

$$\nu = 41\,690\text{ cm}^{-1} + 660\nu_1' + 1000\nu_2', \\ \nu_1' = 0, 1, \dots, 6; \quad \nu_2' = 0, 1, 2, \dots, 8.$$

The frequency assignments of the individual bands are listed in Table III. One weak band was found 770 cm^{-1} on the long wave side of the 0-0 transition. This frequency is in good agreement with the value of 783 cm^{-1} as determined by a number of investigators⁷ from infrared data corresponding to a ground state NH bending vibration, and is most probably the same type of vibration as the 660 cm^{-1} of the excited state. Similarly, it is reasonable to correlate the 1000 cm^{-1} of the excited state with the strong CN vibration (1045 cm^{-1}) of the

⁶ T. Förster and J. C. Jungers, Z. physik. Chem. **B36**, 387 (1937).

⁷ A. P. Cleaves and E. K. Plyler, J. Chem. Phys. **7**, 563 (1939); Bailey, Carson, and Daly, Proc. Roy. Soc. (London) **A173**, 339 (1939); R. G. Owens and E. F. Barker, J. Chem. Phys. **8**, 229 (1940).

ground electronic state found in the infrared. The structure in the region from about 50 000 cm^{-1} to about 60 000 cm^{-1} forms a pattern different in appearance from that below 50 000 cm^{-1} and is probably associated with a different electronic transition. The structure may actually continue beyond 60 000 cm^{-1} , but intensity measurements in the hydrogen line region of the spectrum are not sufficiently sensitive to detect it. From inspection of the microphotometer records, the 0-0 of the second transition appears to be a band at 50 360 cm^{-1} . However, no attempt has been made, to analyze the structure in this region, and the appearance of the microphotometer record can often be misleading.

Ethyl Amine

The spectrum of ethyl amine is very much like that of methyl amine in many respects. The general shape of the two curves is the same and both have a marked amount of structure. The structure of ethyl amine consists of very narrow bands which become somewhat diffuse at about 45 000 cm^{-1} and gradually go over into a continuum. At about 58 000 cm^{-1} another short series of very sharp narrow bands begins unlike the first series. The bands very probably mark the beginning of a third electronic transition. The details of the structure cannot be shown on a plot the size of Fig. 2, which

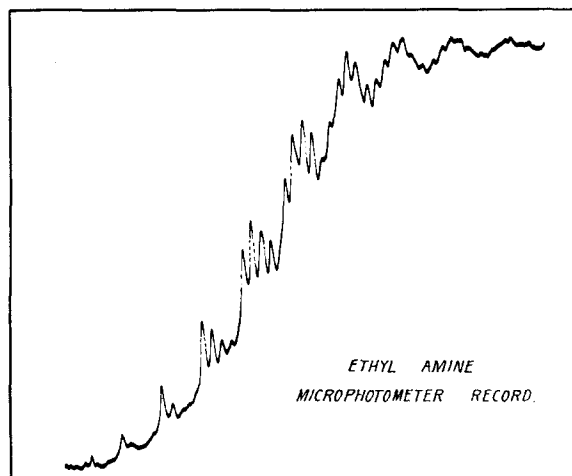


Fig. 3. Microphotometer tracing of ethyl amine in the region from 42 500 cm^{-1} to 48 000 cm^{-1} showing the details of the structure.

indicates only the most prominent bands. Figure 3 shows a microphotometer tracing of part of the spectrum indicating clearly the details of the structure. In Fig. 4 the structure has been schematically represented by vertical lines drawn above the curve where the maxima occur.

The vibrational structure was analyzed by determining the temperature dependence of the intensity of the bands. The method consisted of confining a constant amount of sample in the absorption tube by means of a stopcock situated at the entrance to the tube, and taking successive photographic exposures as the temperature was changed from -35° to 70° .⁸ At low temperatures, the bands became sharper and their relative intensities were altered. The peak at 42 870 cm^{-1} increased whereas the bands on either side of it were lowered. Figure 5 illustrates this effect, showing two superimposed microphotometer tracings of the portion of the spectrum at the two indicated temperatures. This peak was identified as the 0-0. All the most prominent bands were accounted for by the equation

$$\nu = 42\,870\text{ cm}^{-1} - 620\nu_1'' + 740\nu_1' - 1500\nu_2'' + 1620\nu_2',$$

$\nu_1'' = 0, 1, 2, 3$; $\nu_1' = 0, 1, \dots, 8$; $\nu_2'' = 0, 1$; $\nu_2' = 0, 1, 2, 3$. Although this equation accounts both for the position and expected relative intensities of the bands (see Table IV), it is a questionable assignment since it lacks corroborative evidence from other sources. First of all, one would expect the vibrational frequencies of ethyl amine to be analogous to those of methyl amine, where the vibrations in the excited electronic state so clearly parallel the skeletal vibrations of the molecule found in the infrared, but this is not the case. Furthermore, the methyl amine frequencies originate almost entirely from

⁸ Photodecomposition was not a factor here since the wavelength region was restricted by the use of quartz equipment. The lower limit of temperature is determined by the vapor pressure of the compound and the length of the tube.

TABLE III. Methyl amine—vibrational analysis.

Wave no. Exptl	Wave no. Calc	ν_1' 660 cm^{-1}	ν_2' 1000 cm^{-1}	ν_1'' 770 cm^{-1}
40 920	40 920	0	0	1
41 690	41 690	0	0	0
42 350	42 350	1	0	0
42 710	42 690	0	1	0
43 000	43 010	2	0	0
43 350	43 350	1	1	0
43 680	43 690	0	2	0
	43 670	3	0	0
44 000	44 010	2	1	0
44 350	44 330	4	0	0
	44 350	1	2	0
44 680	44 690	0	3	0
	44 670	3	1	0
45 015	45 010	2	2	0
	44 990	5	0	0
45 350	45 350	1	3	0
	45 330	4	1	0
45 690	45 690	0	5	0
	45 670	3	2	0
45 980	45 990	5	1	0
46 370	46 350	1	4	0
47 700	47 690	0	6	0
	47 670	3	4	0
48 010	48 010	2	5	0
	47 990	5	3	0
48 370	48 330	4	4	0
48 670	48 690	0	7	0
	48 670	3	5	0
	48 650	6	3	0
49 010	49 010	2	6	0
	48 990	5	4	0
49 340	49 350	1	7	0
	49 330	4	5	0
49 640	49 650	6	3	0
	49 690	0	8	0

the ground vibrational level, whereas many of the frequencies of ethyl amine are assigned as originating from excited vibrational states of the ground electronic state. Also, the frequencies on the long wave side of the 0-0 do not check convincingly those found in the infrared and Raman spectra.⁹ Despite repeated attempts to find another pattern more consistent with the other data, none could be found to account for all of the most prominent bands.

Earlier work¹⁰ reported on the near ultraviolet spectrum of this compound was done on smaller spectrographs which were unable to resolve as much of the fine structure as has been here determined.

Dimethyl Amine

The spectrum of dimethyl amine is characterized by a sharp series of vibrational bands beginning at 45 130 cm^{-1} . It is notable that the region of absorption from 41 000 cm^{-1} to about 45 000 cm^{-1} is of low intensity and completely devoid of structure in contrast to the two primary amines which have such pronounced structure from the very beginning of absorption.

The vibrational bands were analyzed by exactly the same method as was the structure of ethyl amine. The peak at 45 870 cm^{-1} was, in this way, identified as the 0-0 transition. Most of the bands were described by a formula involving one ground frequency and one upper state frequency as follows:

$$45\,870\text{ cm}^{-1} - 750\nu'' + 605\nu', \\ \nu'' = 0, 1; \quad \nu' = 0, 1, 2, \dots 6.$$

Listed in Table V are the individual frequency assignments.

No information could be found in the literature on the infrared spectrum of dimethyl amine to check the 750 cm^{-1} frequency. A frequency of 794 cm^{-1} is reported in the Raman spectrum,¹¹ but the difference between these values is beyond experimental error.

INTERPRETATION OF RESULTS

It is reasonable to assume that the observed transitions of the alkyl amines are analogous to those of ammonia. The first transition, a $2p_z-3s$, is progressively

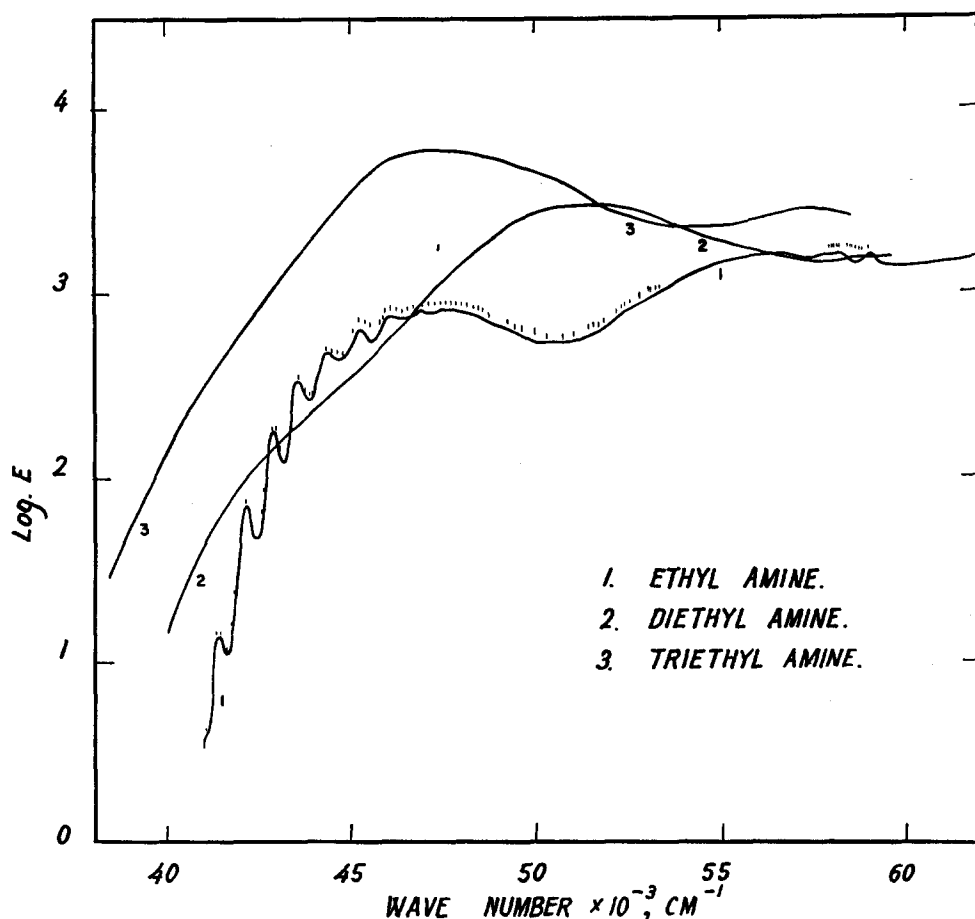


FIG. 4. Log epsilon plot of the ethyl amine series of absorption curves. All of the ethyl amine vibrational structure has been schematically represented by vertical lines drawn above the band positions.

⁹ E. Frolich, Calco Division, American Cyanamid Corporation, private communication; J. T. Edsall, J. Chem. Phys. 5, 225 (1937); K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (J. Springer, Berlin, 1931), p. 312.

¹⁰ H. J. Emeleus and L. J. Jolley, J. Chem. Soc. 1612 (1935); S. Vencov, Bull. sect. sci. acad. Roumaine 26, 89 (1943).

¹¹ J. S. Kirby-Smith and L. G. Bonner, Phys. Rev. 55, 1113 (1939).

TABLE IV. Ethyl amine—vibrational analysis.

Wave no. Exptl		Wave no. Calc	ν'' 620	ν' 740	ν'' 1500	ν' 1620	Wave no. Exptl		Wave no. Calc	ν'' 620	ν' 740	ν'' 1500	ν' 1620
40 760	vw ^a	40 750	1	0	1	0	46 120	s	46 090	1	3	0	1
41 070	vw	41 010	3	0	0	0	46 270	s	46 230	1	1	0	2
41 370	w	41 370	0	0	1	0	46 410	w					
41 490	w	41 490	1	1	1	0	46 575	m	46 550	0	7	1	0
41 640	vw	41 630	2	0	0	0			46 570	0	5	0	0
41 770	vw	41 750	3	1	0	0			46 690	0	5	1	1
41 860	vw						46 720	s	46 710	0	3	0	1
42 180	w	42 110	0	1	1	0			46 690	1	6	0	0
42 265	w	42 250	1	0	0	0	46 840	s	46 830	1	4	0	1
42 610	vw	42 230	1	2	1	0			46 850	0	1	0	2
42 660	vw						46 990	s	46 970	1	2	0	2
42 870	s	42 870	0	0	0	0			46 970	0	1	1	3
		42 850	0	2	1	0	47 160	w	47 110	1	0	0	3
42 995	m	42 990	0	0	1	1	47 320	m	47 310	0	6	0	0
		42 990	1	1	0	0			47 450	0	4	0	1
43 100	w	43 110	1	1	1	1	47 440	s	47 430	1	7	0	0
		43 110	2	2	0	0			47 430	0	6	1	1
43 610	s	43 610	0	1	0	0	47 590	s	47 570	1	5	0	1
		43 590	0	3	1	0			47 570	0	2	0	2
43 785	m	43 730	1	2	0	0	47 730	s	47 730	0	0	0	3
43 920	w	43 870	1	0	0	1			47 700	1	3	0	2
43 970	vw	43 990	2	1	0	1	47 870	m	47 850	1	1	0	3
44 345	s	44 330	0	4	1	0	48 030	w	48 050	0	7	0	0
		44 350	0	2	0	0	48 165	w	48 170	0	7	1	1
		44 490	0	0	0	1	48 350	m	48 330	0	3	0	2
44 510	s	44 470	1	3	0	0	48 485	s	48 450	1	4	0	2
		44 470	0	2	1	1			48 490	0	1	0	3
44 660	m	44 610	0	0	1	2	48 600	m	48 590	1	2	0	3
		44 610	1	1	0	1	48 770	w	48 790	0	8	0	0
44 810	w						48 290						
45 070	m	45 070	0	5	1	0	49 445						
		45 090	0	3	0	0	49 655						
		45 230	0	1	0	1	49 990						
45 220	s	45 210	1	4	0	0	50 305						
		45 210	0	3	1	1	50 760						
45 380	s	45 350	1	2	0	1	51 050						
45 530	m						51 440						
45 805	m	45 810	0	6	1	0	51 580						
		45 830	0	4	0	0	51 720						
		45 970	0	2	0	1	etc.						
45 945	s	45 950	0	5	0	1							
		45 950	0	4	1	1							

^a Relative vibrations are indicated as: strong, s; medium, m; weak, w; and very weak, vw.

displaced to smaller wave numbers by alkyl substitution as measured by the beginning of absorption; the first alkyl group giving a displacement of about 5000 cm^{-1} and each additional group a displacement of about 1000 cm^{-1} . Methyl and ethyl groups seem to be about equally effective. The low oscillator strength of the dimethyl and diethyl amine seems to be an anomaly. However, the first band of dipropyl amine,¹² of piperidine,¹³ and pyrrolidine¹⁵ is very similar in both position and intensity and seems to be characteristic of secondary amines. It seems possible that these low oscillator strengths may be related to the high base strength of these compounds: The greater the probability that the pair of electrons may enter into a chemical reaction, the lower the probability that one of the electrons be excited to a higher energy level.

The second transition is more sensitive to alkyl

¹² Preliminary determination in this laboratory.

¹³ L. W. Pickett, *et al.*, final Report, ONR, Contract N8onr-74100, Project NR-055-160, 37 (1950).

substitution. The displacement to smaller wave numbers is 18 500, 5000, and 2250 cm^{-1} for 1, 2, and 3 methyl groups, respectively, and 19 500, 5500, and 4250 cm^{-1} for the corresponding ethyl groups. Throughout both series there is a marked increase in oscillator strength, the increase being most pronounced in the ethyl series. These characteristics strongly indicate that this transition is closely related to the alkyl group and might be either a charge transfer of an unshared electron or a transition involving a CN bonding electron. The latter interpretation would support Thompson and Duncan's suggestion that the second transition in ammonia might involve a bonding electron. In an attempt to distinguish between these two interpretations, the effect of protons on this band was investigated. A few exploratory plates made with the quartz spectrograph indicated that although the spectrum of an aqueous solution of trimethyl amine exhibited two regions of absorption (one of low intensity beginning about 44 000 cm^{-1} and another more intense region beginning about

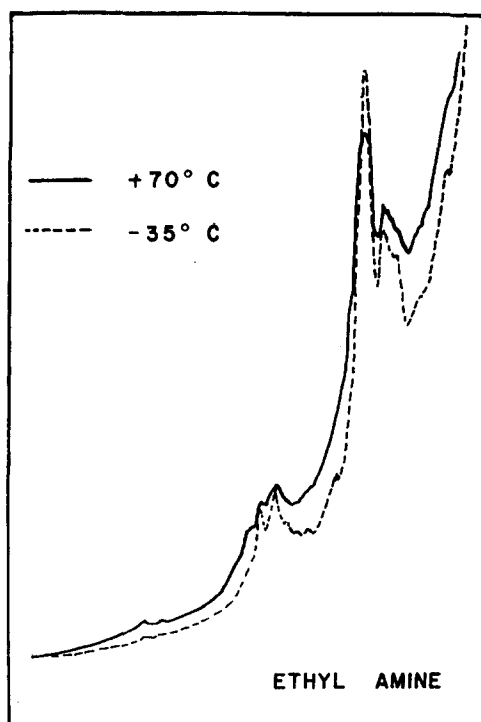


FIG. 5. Two superimposed microphotometer tracings showing the temperature dependence of the intensity of the band at $42\,870\text{ cm}^{-1}$. The exposure was made on a nonflowing sample using the Hilger Quartz Spectrograph.

$46\,500\text{ cm}^{-1}$) an acid solution of the same concentration is practically transparent to the limit of the instrument ($48\,000\text{ cm}^{-1}$). These results strongly indicate that both transitions involve an unshared electron. However, the evidence is not conclusive since it is possible that the presence of a proton might stabilize the CN bonding electrons to such a degree that the transition would not occur below $48\,000\text{ cm}^{-1}$.

Although the third transition is incompletely covered by these measurements, some characteristics seem to be apparent, and the effect of alkyl substitution does not

TABLE V. Vibrational analysis—dimethyl amine.

Wave no. Exptl		Wave no. Calc	ν_1'' (750)	ν_1' (605)
45 130	m ^a	45 120	1	0
45 290	w			
45 720	m	45 725	1	1
45 870	s	45 870	0	0
46 300	m	46 330	1	2
46 480	s	46 475	0	1
46 590	w			
46 920	m	46 935	1	3
47 080	s	47 080	0	2
47 200	w			
47 550	m	47 540	1	4
47 680	s	47 685	0	3
48 160	m	48 145	1	5
48 290	s	48 290	0	4
48 780	m	48 750	1	6
48 890	s	48 895	0	5
49 420				
49 560		49 500	0	6
50 030				
50 610				
51 120				
51 700				

^a See reference a, Table IV.

parallel exactly that on either the first or the second transition. Again, alkyl substitution gives progressive displacement to smaller wave numbers. The magnitude of the displacement is greater than that of the first band but less than that of the second and is greater for ethyl substitution than for methyl substitution. The intensity of the transition seems to be greater than that of the first and less than that of the second. Oscillator strengths may have little meaning here since the shape of the curves indicate that this transition may be superimposed upon a broad continuum. Saturated hydrocarbons begin to absorb in this region and other transitions might be expected. There is sufficient pattern indicated by even these incomplete data to suggest that the same transition is involved in all the amines studied. The very sharp bands occurring at $57\,500$ – $58\,500\text{ cm}^{-1}$ in ethyl amine strongly suggest a Rydberg transition and lends support to the analogy with the $2p_z$ – $4s$ assignment in ammonia.