THE VIBRATIONAL SPECTRUM AND STRUCTURE OF ORGANIC CRYSTALS: UREA, THIOUREA, GLYCINE

Thesis by

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R. D. W.

ABSTRACT

Investigations of the infra-red spectra of single crystals of urea, thiourea, glycine, and deuterium derivatives with polarized radiation are presented. The polarization measurements are of value in identifying the normal vibrations.

For urea, evidence is presented that the molecular structure is entirely planar. Frequency assignments are made for 14 of the 18 fundamental vibrations for urea and deutero-urea. A valence force calculation of the skeletal force constants is made. The isotope product rule is applied to the vibrations of 2 symmetry species.

For thiourea, the spectrum is closely related to that of urea. Frequency assignments of fundamental vibrations are made for 15 frequencies of thiourea and 12 frequencies of deutero-thiourea. A valence force calculation of the skeletal force constants is made. The isotope product rule is used to calculate 2 of the unobserved frequencies of deutero-thiourea. Evidence is given in support of a planar or nearly planar molecular structure.

The spectrum of glycine yields polarization data giving the orientation of the transition moment of individual vibrations. This is applied to the analysis of the observed frequencies. The polarizations of the absorption bands associated with stretching vibrations of the NH_3^+ group are compatible with restricted rotation of that group about the C-N bond.

The relation between vibrational frequency and hydrogen bonding is discussed. The use of partially deuterated glycine permits the study of the effects of individual hydrogen bonds on the frequency and band shape of ND stretching vibrations.

Some features of the polarization technique are used to predict group orientations in the l-leucine crystal.

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GENERAL EXPERIMENTAL METHODS

The infra-red spectra reported in the following exposition were recorded from three instruments. The low dispersion work in the rocksalt region, from 700-5000 cm^{-1}, was performed with a Beckman Infra-red Spectrophotometer, model IR-2, operated with a combined wavelength and slit drive permitting automatic recording. Investigations at longer wavelengths were carried out with a KBr prism vacuum spectrograph donated by the Shell Development Co. This instrument in its original form was described by Brattain (1). Recent modifications include AC amplification, and an electrical slit control. The accessible spectrum was extended to 400 cm^{-1} with this spectrograph. For high dispersion work in the 3000 cm^{-1} region, a vacuum grating instrument was used. This machine, employing a PbS photo-cell cooled with solid CO_2, has been described previously.(2) Gratings with 7500 and 4500 lines per inch were used in first order. The radiation source for the latter two spectrographs was the customary globar.

The wavelength calibration of the prism instruments was verified with the water vapor, carbon dioxide, ammonia, and methanol bands. The frequencies reported in the low dispersion traces are probably accurate within the limits tabulated below. Fluctuations in temperature was the chief cause of variations in band positions.

TABLE I

Instrumental Error in Frequency

Frequency	Error
5000 cm^{-1}	$\pm$ 100 cm^{-1}
3000	30
2000	10
1500	5
1250	3
< 1000	1.5

The calibration of the gratings was effected by measurement of the 1.4 and 1.9μ water bands as reported by Nelson (3). The limiting factor in the measurement of wavelengths on this instrument was the slit width necessary for the operation of the microscope. The theoretical slit width at 50 % transmission varied from 1.9 to 7 cm^{-1} in the 3000-3500 cm^{-1} region.

The crystal specimens were illuminated with a reflecting microscope (4) designed to match the optics of the Beckman instrument. The use of the microscope enabled one to effect approximately a twenty-fold linear reduction in sample dimensions from the size of the monochromator slit. Crystals of less than 1 mm in length and as little as .1-.2 mm in width gave adequate transmission for polarization studies. The determination of the thickness of samples and absolute intensities of absorption was not feasible under the experimental conditions developed for growing and mounting crystal samples. Indeed, the uniformity of thickness for a given sample in some cases was questionable. In general samples under 10 microns (10^{-2}

mm) in thickness were used, with some specimens estimated from comparative intensities to be less than 2 microns thick.

For polarization studies, a transmission polarizer was placed in the collimated beam directly preceding the microscope. The polarizer consisted of three or four plates of AgCl inclined at 65-70° to the optic axis. The intensity of the rejected component is less than 5% of the transmitted component at 5000 cm^{-1} for three plates, and probably does not exceed that figure throughout the spectral region investigated.

After polarization, the beam is twice reflected before reaching the sample which introduces a slight phase shift resulting in elliptic polarization. It can be shown that for long wavelengths and angles of incidence less than 20°, the refractive index n becomes very large and the phase shift between the components parallel and perpendicular to the plane of incidence Δ, is of the order of $\sin\phi / n$ where ϕ is the angle of incidence. This effect is negligible with respect to the incompleteness of polarization.

Since the reflected beam is convergent as it meets the sample, some depolarization occurs due to reflection at oblique azimuths. The extreme ray reflected at 45° from the plane of polarization will be rotated less than 8.5°. The net effect is again insignificant when compared with the polarization inefficiency.

The analysis in the general case of the interaction of radiation with an anisotropic medium is rather complex. Plane-polarized light incident upon quartz is split into circularly polarized components which may be separated by using enantio-

morphic sections. Considerable simplification is possible when elements of symmetry are present in the crystal lattice. Planes or centers of symmetry preclude stereo-optical activity. These elements were present in all of the crystals studied in the following discussions with the exception of l-leucine. Polarizations parallel to symmetry axes or normal to symmetry planes are necessarily preserved since the principal axes of the polarizability ellipsoid must coincide with the symmetry axes of the lattice.

Low temperature spectra were taken with a low temperature sample holder consisting of a copper bar slotted to carry the sample which is attached to a stainless steel dewar jacket. The entire microscope was evacuated with a diffusion pump, and by cooling with liquid N_2, a temperature of about -185° C could be maintained. Ice formation occurs slowly giving rise to broad bands which do not interfere seriously for several hours of operation. The ice line indicated on several of the subsequent figures represents the absorption due to ice on the substrate accumulated after a period several times longer than that involved in taking the sample spectra.

PART I

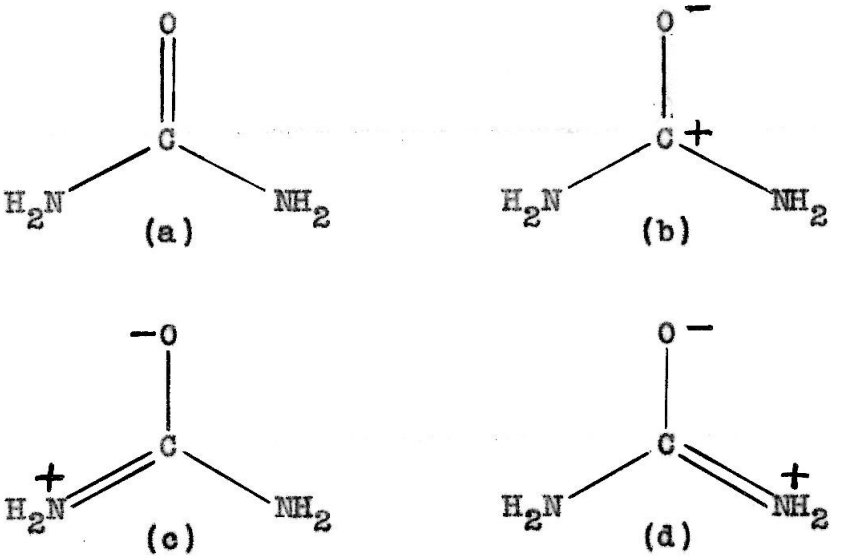
THE VIBRATIONAL SPECTRUM OF UREA

THE VIBRATIONAL SPECTRUM OF UREA

Introduction

The heats of formation of amides and urea are somewhat less than expected for simple covalent bond structures, indicating resonance energy stabilization of the structures. Pauling (5) gives 37 kcal/mole for the resonance energy of urea.

The contributing structures may be represented by the following formulae:



Structure b containing one less valence bond contributes to the stability of aldehydes, ketones, and all other carbonyl groups, and the resonance energy of this form is not included in the value quoted above. The bond strength of the C=N bond in structures c and d is favored by a planar configuration about the nitrogen atom. If the potential barrier for inversion in ammonia is considered as normal, a resonance in-

teraction greater than the barrier energy (2076 cm^{-1}) would be required to induce the planar configuration. It is readily seen that half of the resonance energy (18.5 kcal/mole) is much greater than the 5.9 kcal/mole destabilization of the N bonding.

In the subsequent sections, spectroscopic evidence is presented in verification of the planar structure.

The study of urea was undertaken as part of the institute program of research on proteins and related products. The amide linkage -CONH- is the fundamental binding unit in these natural products, and its presence in urea makes possible its study with the simplification of considerable symmetry.

The infra-red and Raman spectra of urea have been reported previously by several investigators. The Raman spectra of aqueous solutions of urea have been observed by Krishnamurti (6), Pal and Sen-Gupta (7), Dadieu and Schneider (8), Kohlrausch and Pongratz (9), and Otvos and Edsall (10) who also investigated urea in D_2O. The Raman spectrum of crystalline urea was studied by Krishnamurti (6), Ananthakrishnan (11), and Graz (12), and fused urea was examined by Thatte and Joglekar.(13) Infra-red spectra of the crystals have been reported by Kellner (14) and Keller (15).

Kohlrausch, Kellner, and Keller have proposed partial vibrational assignments of the observed frequencies. These assignments will be examined in greater detail in the following text.

In the present investigation, the infra-red spectra of single crystals of urea and deuterium-substituted urea were observed with plane-polarized radiation in low dispersion from 400-5000 cm^{-1} and with high dispersion in the 3000 cm^{-1} region.

Experimental

The physical equipment was described in a preceding section. The samples were prepared by evaporation of a concentrated aqueous solution on AgCl plates about .5 mm thick. At suitable rates of crystallization, the growing needles spread out to widths of .2 mm or more while remaining about 5 microns thick. Some tracings were made with thicker crystals without AgCl backing. The samples were masked with metal foil or opaque cellophane tape and mounted on various sample holders for use in the reflecting microscope. Deuterium substitution was effected by repeated solution and vacuum evaporation of urea in 99.8% D_2O. The final stage of the treatment was performed on a AgCl plate; the sample was evacuated to the vapor pressure of the solution, followed by slow evaporation in the partial vacuum. J. T. Baker CP urea was used throughout.

Discussion

X-ray investigations (16) of urea yield the crystallographic space group V_d^3 ($P\bar{4}2_1m$) which indicates a symmetry of C_{2v} for the heavy atoms. The assumption will be made in the following discussion that the molecule as a whole possesses the same symmetry. (Fixed positions of hydrogen of lower

symmetry are unlikely from crystallographic considerations, while a random arrangement is unlikely in view of the completeness of polarization of the infra-red bands.) Previously Keller (15) and Badger and Waldron (17) have presented evidence in support of an entirely planar structure based on the selection rules for infra-red transitions. The latter reference is reproduced below.

The Planarity of the Urea Molecule*

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February 10, 1950

ARGUMENTS based on infra-red observations were recently presented by W. E. Keller for the planarity of the urea molecule in the crystalline state.[1] Though plausible, we have not found these completely convincing since the statement that in a nonplanar model one of the A_1 hydrogen bending fundamentals should be essentially inactive is based on certain assumptions, and not on a selection rule required by symmetry. The really conclusive evidence is to be found in the 3μ region where the resolving power of the spectrometer employed by Keller seems to have been inadequate. In the planar model four N–H valence frequencies may be active, two of which have the character A_1. In the nonplanar C_{2v} model only three of these fundamentals can be active, and only one of these has the character A_1.

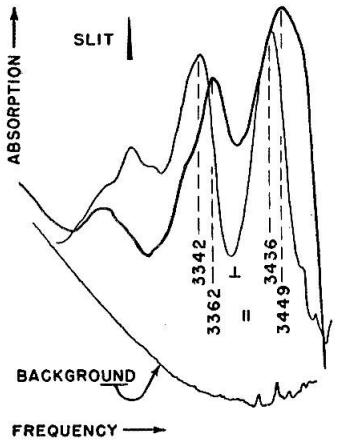


FIG. 1. Recorder tracings of the spectrum of a single urea crystal in polarized infra-red at 2.9μ, obtained with reflecting microscope and vacuum grating spectrometer. Frequencies of the four intense maxima are given. Symbols $\perp$ and $\parallel$ indicate direction of electric vector with respect to the tetragonal axis.

Excellent absorption spectra with very high resolution were recently obtained in this laboratory, using polarized radiation and single micro crystals of urea. These observations were made possible by a reflecting microscope or "microilluminator," with polarizing attachment, designed especially to match the optical systems of both the Beckman IR-2 spectrometer and our large vacuum grating instrument.[2] The latter instrument, with lead sulfide detector cooled by solid CO_2, was used in the work mentioned.

As may be seen in Fig. 1, two pairs of intense bands were observed in the 2.9μ region, accompanied by much weaker bands on the long wave side, which are presumably combination frequencies or overtones. These pairs are incompletely resolved in ordinary light but with polarized radiation each was very definitely shown to consist of two components, one polarized perpendicular, and one parallel to the tetragonal axis. Because of their high intensity we regard it as very probable that the four strong bands are NH stretching fundamentals, and consider that the complete planarity of the urea molecule in the crystal is now reasonably well established by spectroscopic evidence.

* Contribution No. 1391 from the Gates and Crellin Laboratories of Chemistry. The investigation here described was supported in part by the Bureau of Ordnance under Contract N6-ori-102, VI with the ONR.

[1] W. E. Keller, J. Chem. Phys. 16, 1003 (1948).
[2] Badger, Zumwalt, and Giguère, Rev. Sci. Inst. 19, 861 (1948).

The planar structure will be assumed in the following dissertation.

The isolated molecule of urea with eight atoms has $3 \times 8 - 6 = 18$ fundamental frequencies distributed as follows among 4 symmetry species;

TABLE II

Species Classification of Components of Transition Moment (M) and Polarizability (α)

Operation	Species			
	$A_1(M_z, \alpha_{ii})$	$A_2(\alpha_{xy})$	$B_1(M_x, \alpha_{xz})$	$B_2(M_y, \alpha_{yz})$
C_2	+	+	-	-
σ_{xz}	+	-	+	-
σ_{yz}	+	-	-	+
No. of Vibrations	7	2	6	3

The symbol + indicates the component is unchanged, - indicates the component changes sign following the symmetry operation. $\alpha_{ii} = \alpha_{xx}, \alpha_{yy}, \alpha_{zz}$.

Figure 1 gives a perspective view of the crystal structure and illustrates the coordinate axes used in following analysis.

The following spectra show the principal bands in the infra-red above 400 cm^{-1} for urea (Fig. 2, 3)

FIGURE 1

Crystal Structure of Urea

Top: Crystal Habit

m = 110

o = 111

Center: Unit Cell

Dotted lines represent hydrogen bonds with

N···O distances:

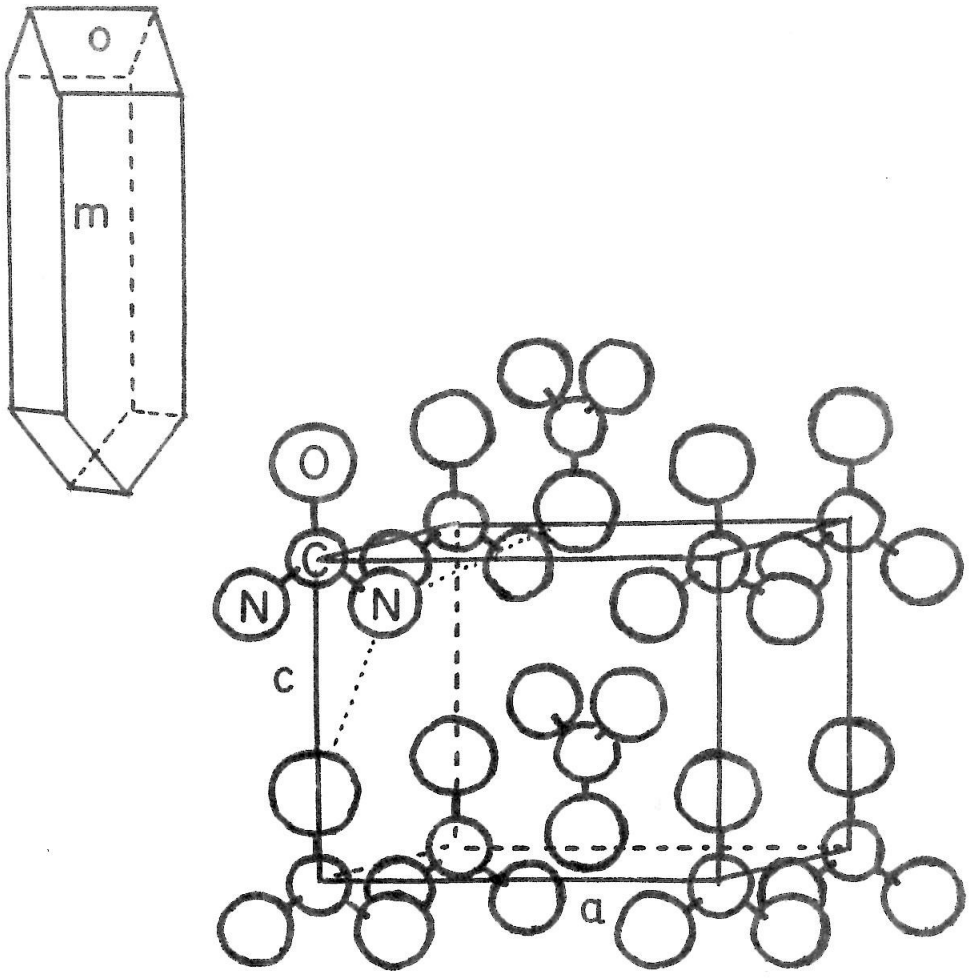
$\parallel c$ 3.00 Å

$\perp c$ 3.07 Å

Bottom: Coordinate Axes

z = 2-fold axis C_2

σ = symmetry plane


o
m
O
C
N
N
c
a

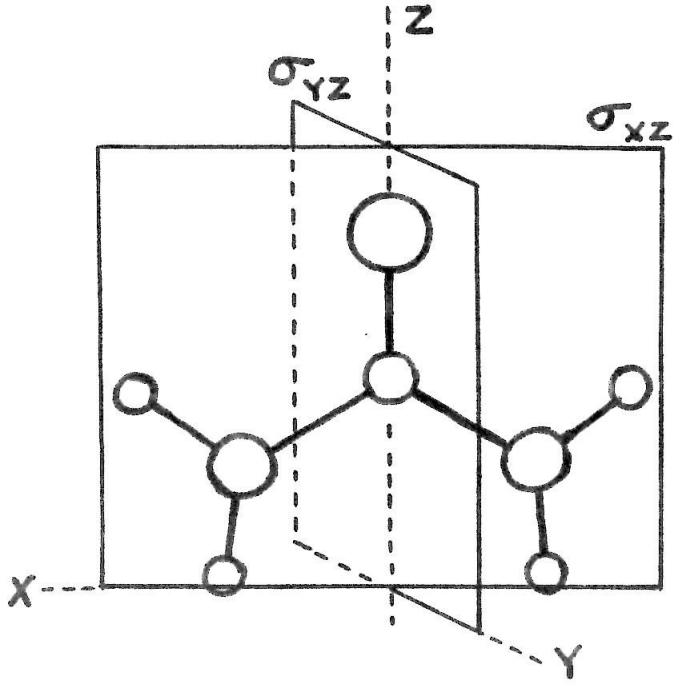

Z
σYZ
σXZ
X
Y

FIGURE 2

Infra-red Spectrum of Urea from 700-5000 cm^{-1}

Abscissa: Frequency in cm^{-1}

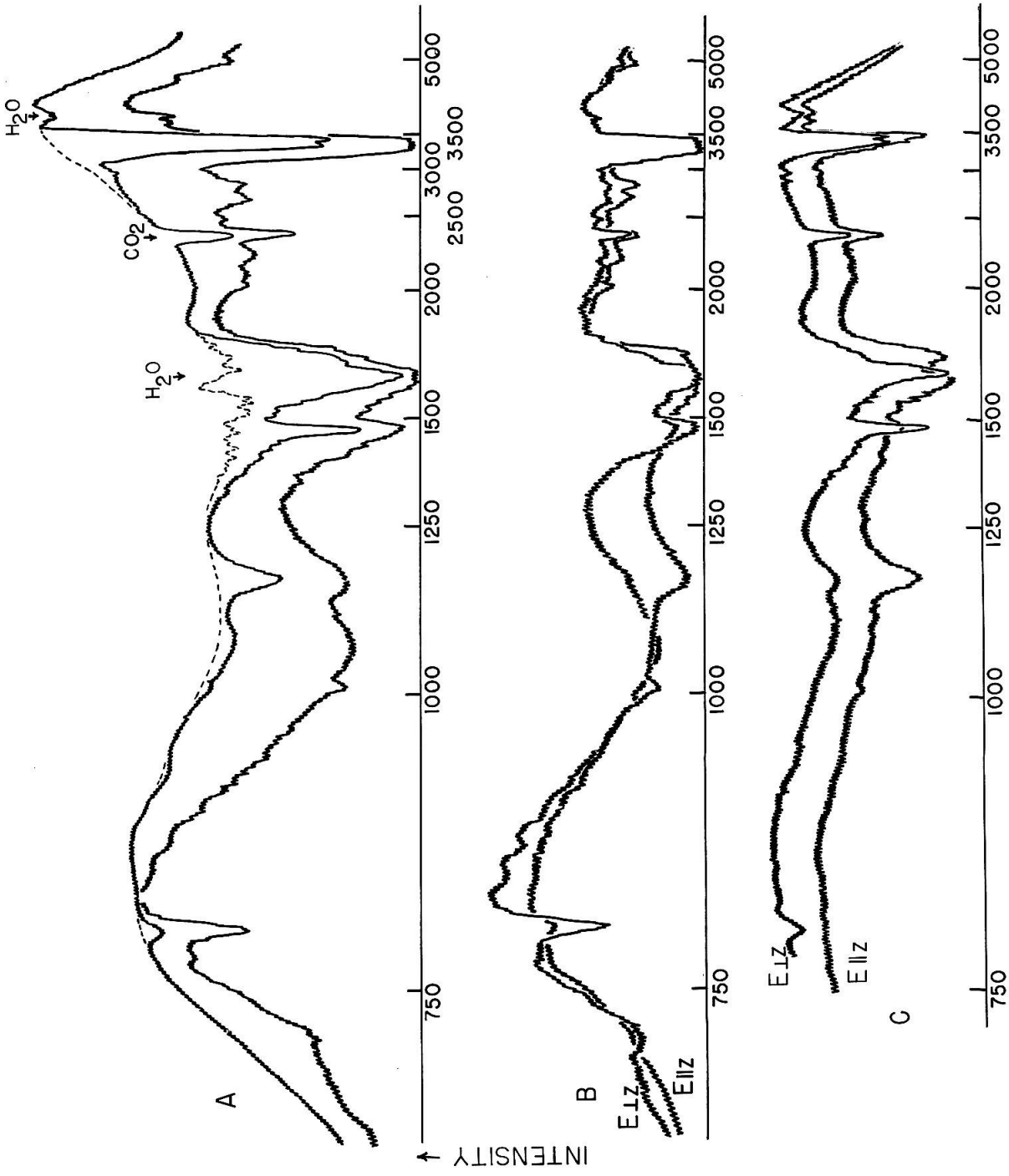
Ordinate: Intensity of transmitted radiation

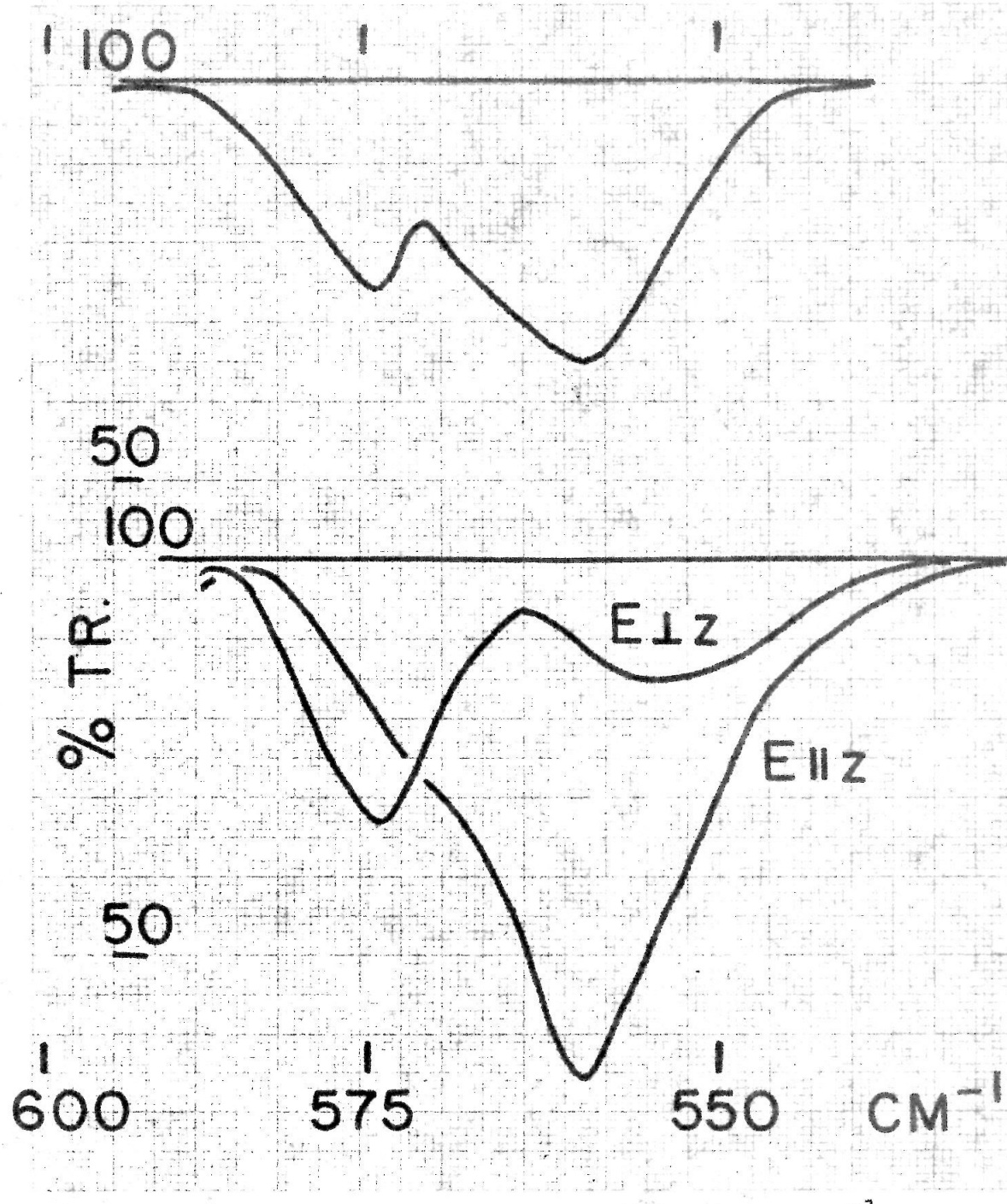
A. Unpolarized Spectrum

Two different sample thicknesses are shown

B. Polarized -- Thick sample

C. Polarized -- Thin sample


H_2O
CO_2
H_2O
A
B
E⊥z
E∥z
C
E⊥z
E∥z
INTENSITY
750
1000
1250
1500
2000
2500
3000
3500
5000



Infra-red Spectrum of Urea below 700 cm^{-1}

Top. Unpolarized Bottom. Polarized

FIGURE 3

The table below lists the frequencies, polarization character, and comparative intensities of the absorption bands. The intensities listed are for incident polarized light, and constitute only a rough approximation to the true values.

TABLE III

Infra-red Absorption Bands of Urea

Frequency	Polarization	Density	Freq.	Pol.	Dens.
5030 cm^{-1}	$\vec{E} \parallel z$	.07	2060	$\vec{E} \perp z$	.07
4550	$\vec{E} \perp z$	.05	2005	$\vec{E} \parallel z$	.20
3449	"	30	1689	"	9
3436	"	15	1630	"	13
3362	"	10	1610	"	13
3342	"	12	1472	"	8
3288	"	3	1160	"	6
3261	"	3	1054	"	1
3226	"	2	1005	"	.35
2820	"	.31	790	"	1
2645	"	.27	718	"	.31
2490	"	.05	574	"	2.9
2210	"	.17	558	"	5.2

In describing the orientation of polarization, we shall refer to the plane of the electric vector $\vec{E}$. Bands which absorb strongly for $\vec{E} \parallel z$ (z is parallel to the tetragonal axis, c) indicate a symmetry species A_1 for the transition. Polarization $\perp z$ may correspond to either species B_1 or B_2. Species

A_2 is inactive in the infra-red.

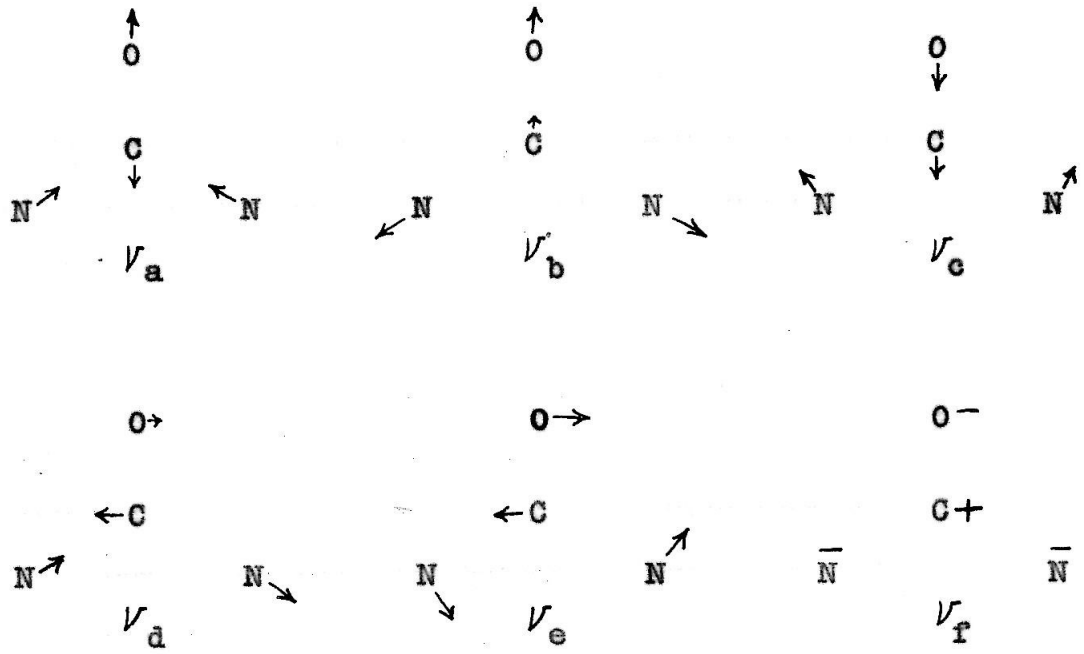
In first approximation one may describe the normal vibrational modes as consisting of hydrogen atom vibrations and "skeletal" vibrations. (The neglect of coupling between skeletal motions and hydrogen bending oscillations leads to some serious difficulties, but is useful for preliminary classification of observed frequencies, simplifies valence force calculations, and aids in visualization of the vibrational modes. The neglect of interaction of molecular vibrations with lattice vibrations should not be too serious for weakly hydrogen-bonded crystals such as urea.)

The 4 hydrogen atoms contribute 12 degrees of freedom giving 4 stretching and 8 bending frequencies. The heavy atom skeleton may be treated as a 4 particle system with 6 fundamental frequencies (analogous to H_2CO and Cl_2CO). The classification according to symmetry class is given below. Figure 4 illustrates the approximate form of the normal vibrations with the symbols used for their description in the material to follow.

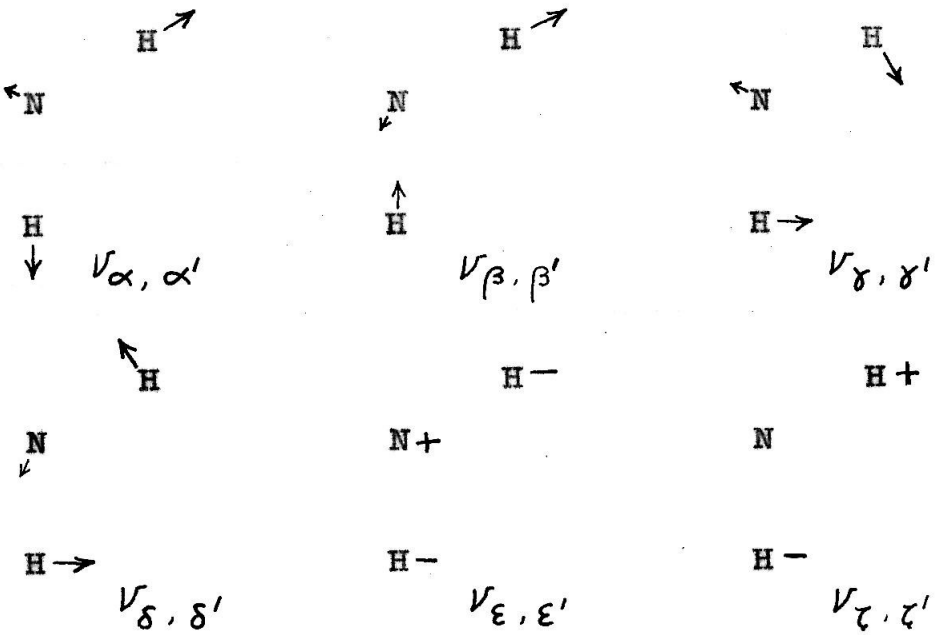
TABLE IV

Species Classification of Hydrogen and Skeletal Vibrations

Species	H stretch.	bend	Skel. stretch.	bend		Designation
A_1	2	2	2	1	(7)	$\nu_1 - \nu_7$
A_2	0	2	0	0	(2)	ν_8, ν_9
B_1	2	2	1	1	(6)	$\nu_{10} - \nu_{15}$
B_2	0	2	0	1	(3)	$\nu_{16} - \nu_{18}$



Skeletal Vibrations (Schematic)



Hydrogen Vibrations (Schematic)

The unprimed subscripts refer to vibrations symmetric with respect to σ_{yz} (A_1 and B_2); the primed subscripts refer to vibrations antisymmetric with respect to σ_{yz} (A_2 and B_1).

FIGURE 4

Assignment of Frequencies

A prerequisite for the correct identification of specific vibrational modes with the observed frequencies is the recognition of the fundamental absorption bands. The selection is made from consideration of the infra-red and Raman intensities and empirical evidence from the spectra of related compounds.

As discussed on p. 9, there are observed 4 fundamentals in the 3000-3500 cm^{-1} region at 3449, 3436, 3362, and 3342 cm^{-1}. The polarization indicates 2 of the bands are of species A_1 and 2 are B_1.

At lower frequencies, intense A_1 bands are observed at 1689, 1610, 1160, and 558 cm^{-1}. 1005 cm^{-1} which is weak in the infra-red gives an intense polarized Raman line. These lines are very probably A_1 fundamentals which completes the identification of the fundamentals of this symmetry species.

For the vibrations of species A_2 and B_2, the elongation of valence bonds is an infinitesimal of higher order than the normal coordinate, and we expect the frequencies to be quite low (pure bending modes). One pair of frequencies, ν_ζ and $\nu_{\zeta'}$, involving essentially torsion of the NH_2 group about the C-N axis is almost certainly of lower frequency than 500 cm^{-1}. (One would expect a frequency considerably lower than in ethylene (1027 cm^{-1}) and approaching that of ethane (290 cm^{-1}) (18).) A second pair, ν_ε and $\nu_{\varepsilon'}$ involving NH_2 wagging normal to the plane of the molecule would probably be much lower than the corresponding pair in ethylene (949 and 943 cm^{-1}) since the transition from a double bond to a single bond $=RH_2$, $-RH_2$

inverts the potential energy surface, i.e. a potential minimum exists for ethylene in the planar position which becomes a maximum for ammonia or primary amines. (The C-N distance of 1.34 Å indicates considerable double bond character for the linkage.) The remaining B_2 vibration is the skeletal bending vibration ν_f.

Of the lower frequency bands observed for $\vec{E} \perp z$, the medium to intense lines at 1630, 1472, 790, and 574 cm^{-1} are considered to be fundamentals. For reasons given in the preceding paragraph, we do not believe a B_2 fundamental would have a frequency as high as the first 2 bands listed; consequently they must be B_1 fundamentals. We consider the band at 790 cm^{-1} the skeletal frequency ν_f, and 574 cm^{-1} the skeletal frequency ν_e of symmetry species B_2 and B_1 respectively.

Five fundamentals remain unidentified; 1 B_1, 2 B_2, and the 2 inactive A_2.

Skeletal Frequencies

To identify the skeletal frequencies, following Kohlrausch (9), we will treat urea as a 4 particle system using, however, somewhat different frequencies. The system, planar XYZ_2 (C_{2v}) has 6 genuine vibrations: 3 A_1, 2 B_1, and 1 B_2 (Fig. 4). In our choice of frequencies we differ from Kohlrausch in the following respects:

TABLE V

Assignment of Skeletal Vibrations

	A_1			B_1		B_2
	ν_a	ν_b	ν_c	ν_d	ν_e	ν_f
Kohlrausch & Pongratz (R)	1655	1000	585	1157	525	
Waldron (I)	1689	1005	558	1472	574	790
" (deutero-urea)	1632	1002	476	1501	512	779

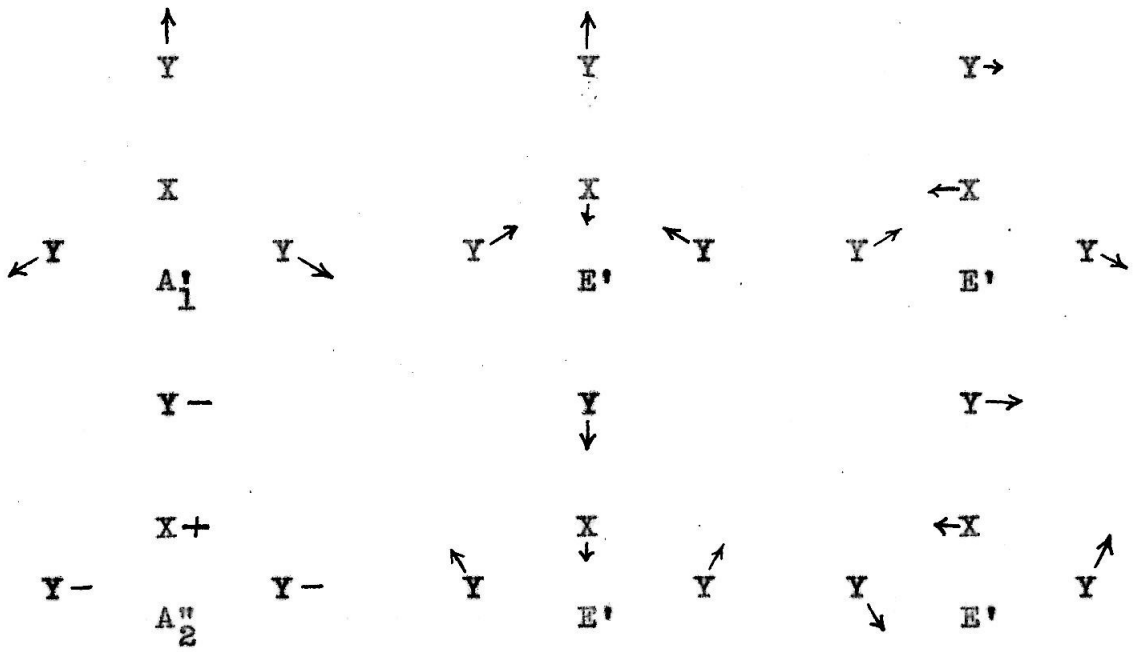
ν_a, ν_b, and ν_c are polarized $\parallel$ z in the infra-red and are essentially in agreement except for the interchange of ν_c and ν_e. (The differences in frequency between the Raman and infra-red are due in part to the transition from solution to the crystal.) 1160 cm^{-1} is also polarized $\parallel$ z and consequently cannot be ν_d. For the B_1 frequencies we choose 1472 and 574 cm^{-1}; for ν_f, 790 cm^{-1}.

The validity in assuming the above frequencies is strengthened by considering the spectrum of deutero-urea. The bands ν_a, ν_b, ν_d, and ν_f persist upon substitution of deuterium for hydrogen with only very slight frequency shifts. ν_c and ν_e exhibit proportionately greater drops in frequency, but even here the shift is much less than one would expect for H bending vibrations.

Additional confirmation of the choice comes from considering the spectra of the carbonate and guanidinium ions, which are iso-electronic with urea. $CO_3^{=}$ with symmetry D_{3h} has only 4 vibrational frequencies, 2 of which are doubly degenerate. Guanidinium ion, $C(NH_2)_3^{+}$, which also has 3-fold symmetry may

be treated as a 4 particle system.

The frequencies of $CO_3^=$ have been positively identified with vibrational modes as given in the table below. For $C(NH_2)_3^+$, the Raman spectrum has been investigated by Gupta (19), Graz (12), and Otvos and Edsall (10) for aqueous solutions of the chloride, and the crystalline state was examined by Graz (12) and Ananthakrishnan (11). The strong polarized line at 1005-15 cm^{-1} must correspond to A_1'. A_2'' is Raman inactive, and the degenerate pair E' probably correspond to the medium intensity lines at 1549-65 and 526-36 cm^{-1} although the high frequency band may be the very weak line at 1462-83 cm^{-1}. Figure 5 illustrates the form of the normal vibrations.



Vibrations of Planar XY_3 (D_{3h})

FIGURE 5

The table below shows the correlation of these frequencies with those of urea.

TABLE VI

Skeletal Frequencies of $CO_3^=$, $C(NH_2)_3^+$, and $(NH_2)_2CO$

	A_1'	A_2''	E'			
$CO_3^=$ (20)	1063	879	1415		680	
$C(NH_2)_3^+$	1008	unobs.	1552 (or 1472)		529	
$(NH_2)_2CO$	1005	790	1689	1472	574	558
	A_1	B_2	A_1	B_1	B_1	A_1

It is seen that the agreement is quite satisfactory considering the approximations involved. ν_e and ν_f which are indistinguishable on the basis of polarization present the chief possibility of error. In addition to the better correlation with the spectrum of $CO_3^=$, we prefer our assignment for several additional reasons: the evaluation of force constants from a valence force potential using 1472 and 790 cm^{-1} as ν_d and ν_e leads to imaginary force constants which deviate widely from real values; since 790 cm^{-1} was not observed in the Raman work, it probably more nearly corresponds to A_2'' of $CO_3^=$; 574 cm^{-1} shows an isotope shift comparable with the other planar bending vibration ν_c; somewhat greater than that of 790 cm^{-1}.

Hydrogen Frequencies

We may now discuss the hydrogen frequencies. The assignment of the hydrogen stretching frequencies offers no particular difficulties. If we assume that the higher frequency

of each symmetry class corresponds to a reciprocating vibration, ν_β and $\nu_{\beta'}$, we obtain the following assignment.

TABLE VII

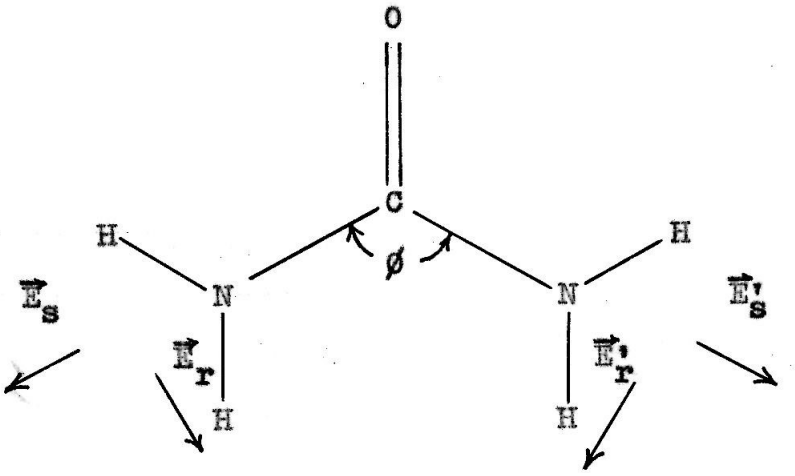
Hydrogen Stretching Vibrations

Vibration	Frequency	Polarization
$\nu_\beta = \nu_1$	3449 cm^{-1}	$\mathbf{E} \parallel z$
$\nu_{\beta'} = \nu_{10}$	3436	$\mathbf{E} \perp z$
$\nu_\alpha = \nu_2$	3362	"
$\nu_{\alpha'} = \nu_{11}$	3342	"

The observed intensities of the stretching fundamentals are in qualitative agreement with those predicted from the known structure of the heavy atom skeleton assuming reasonable bond angles for the hydrogen atoms. The change in dipole moment associated with ν_α and $\nu_{\alpha'}$ is approximately $\vec{E}_s + \vec{E}'_s$ and $\vec{E}_s - \vec{E}'_s$ (Fig. 6). The transition moments associated with ν_β, $\nu_{\beta'}$ are $\vec{E}_r + \vec{E}'_r$ and $\vec{E}_r - \vec{E}'_r$.

Radiation theory yields the result that the absorption coefficient is proportional to the square of the absolute value of the transition moment. Half of the molecules in the lattice will not contribute to absorption intensities for B_1 or B_2 transitions since their transition moments will be parallel to the direction of propagation of the incident radiation. With the assumption that the angle bisectors of the NH_2 groups intersect forming an obtuse angle $\phi > 110^\circ$, then $2|\vec{E}_r + \vec{E}'_r|^2 > |\vec{E}_r - \vec{E}'_r|^2$ and $|\vec{E}_s - \vec{E}'_s|^2 > 2|\vec{E}_s + \vec{E}'_s|^2$. This simple treatment predicts that the intensity of $\nu_1 > \nu_{10}$ and $\nu_2 < \nu_{11}$ in agreement with observation.

The Raman spectra of aqueous solutions show shifts of the valence frequencies due to changes in the nature of the hydrogen bonding, but the crystal spectra are in good agreement with our infra-red measurements.



Components of Transition Moments for Hydrogen Stretching Vibrations (Schematic)

s = synchronous vibrations $\nu_{\alpha,\alpha'}$, r = reciprocating vibrations $\nu_{\beta,\beta'}$.

FIGURE 6

We may now discuss the remaining hydrogen bending modes. The high frequency pair of bands at 1630 and 1610 cm^{-1} correspond to the scissors vibrations, $\nu_{\gamma'}$ and ν_{γ}. The band at 1160 cm^{-1} then represents the last A_1 fundamental, the H rocking vibration ν_{δ}. This completes the assignment of the previously identified fundamentals. $\nu_{\delta'}$ is expected to occur near the frequency of the corresponding symmetric band, 1160 cm^{-1}. A broad diffuse band polarized $\perp z$ extends from about 900-1200 cm^{-1}. The absorption in this region was shown to consist of several components during investigation of the spectrum at

liquid air temperatures. We assign $\nu_{\delta'}$ to the band centered at 1054 cm^{-1} of polarization $\vec{E} \perp z$.

The 4 remaining fundamentals, ν_{ε}, $\nu_{\varepsilon'}$, ν_{ζ}, and $\nu_{\zeta'}$ probably lie below 400 cm^{-1}. Some absorption of undetermined polarization was observed below 410 cm^{-1} which may correspond to ν_{ε}.

The foregoing assignment is recapitulated in the following table together with a tentative assignment of combination and overtone bands compatible with observed frequencies and polarization.

TABLE VIII

Vibrational Assignment

Fundamentals

A_1	A_2	B_1	B_2
3449 = ν_1 = ν_{β}	Unobserved	3436 = ν_{10} = $\nu_{\beta'}$	790 = ν_{16} = ν_f
3362 = ν_2 = ν_{α}	(ν_8, ν_9)	3342 = ν_{11} = $\nu_{\alpha'}$	Unobserved
1689 = ν_3 = ν_a		1630 = ν_{12} = $\nu_{\gamma'}$	(ν_{17}, ν_{18})
1610 = ν_4 = ν_{γ}		1472 = ν_{13} = ν_d	
1160 = ν_5 = ν_{δ}		1054 = ν_{14} = $\nu_{\delta'}$	
1005 = ν_6 = ν_b		574 = ν_{15} = ν_e	
558 = ν_7 = ν_c			

TABLE VIII (CONTINUED)

Combinations and Overtones

5030	$\vec{E} \parallel z$	$\nu_1+\nu_4, \nu_2+\nu_3, \nu_{10}+\nu_{12}$	2645	$\vec{E} \parallel z$	$\nu_4 + \nu_6$
4550	$\vec{E} \perp z$	$\nu_5 + \nu_{10}$	2490	$\vec{E} \perp z$	$\nu_3 + \nu_{16}$
3288	"	$\nu_3 + \nu_{12}$	2210	"	$\nu_5 + \nu_7$
3261	"	$\nu_4 + \nu_{12}$	2060	"	$\nu_6 + \nu_{14}$
3226	"	$2\nu_4$	2005	"	$2\nu_6$
2820	"	$\nu_3 + \nu_5$	718	"	$(\nu_{8,9} + \nu_{17,18})$

DEUTERIUM SUBSTITUTED UREA

We may now turn our attention to the spectrum of deutero-urea. The small amount of residual hydrogen introduces superfluous bands in the spectra, and introduces some uncertainty in the identification of the weak spectral bands. The spectrum of deutero-urea above 400 cm^{-1} is presented in Figures 7 and 8.

The following table lists the frequencies, polarization, and relative intensities of the absorption bands attributed to $(ND_2)_2CO$. Less prominent bands considered to be due to molecules with residual NHD groups will be discussed in the text.

FIGURE 7

Infra-red Spectrum of Deutero-urea from 700-5000 cm^{-1}

Ordinate: Intensity of transmitted radiation

A. Unpolarized Spectrum

B. Polarized Spectrum

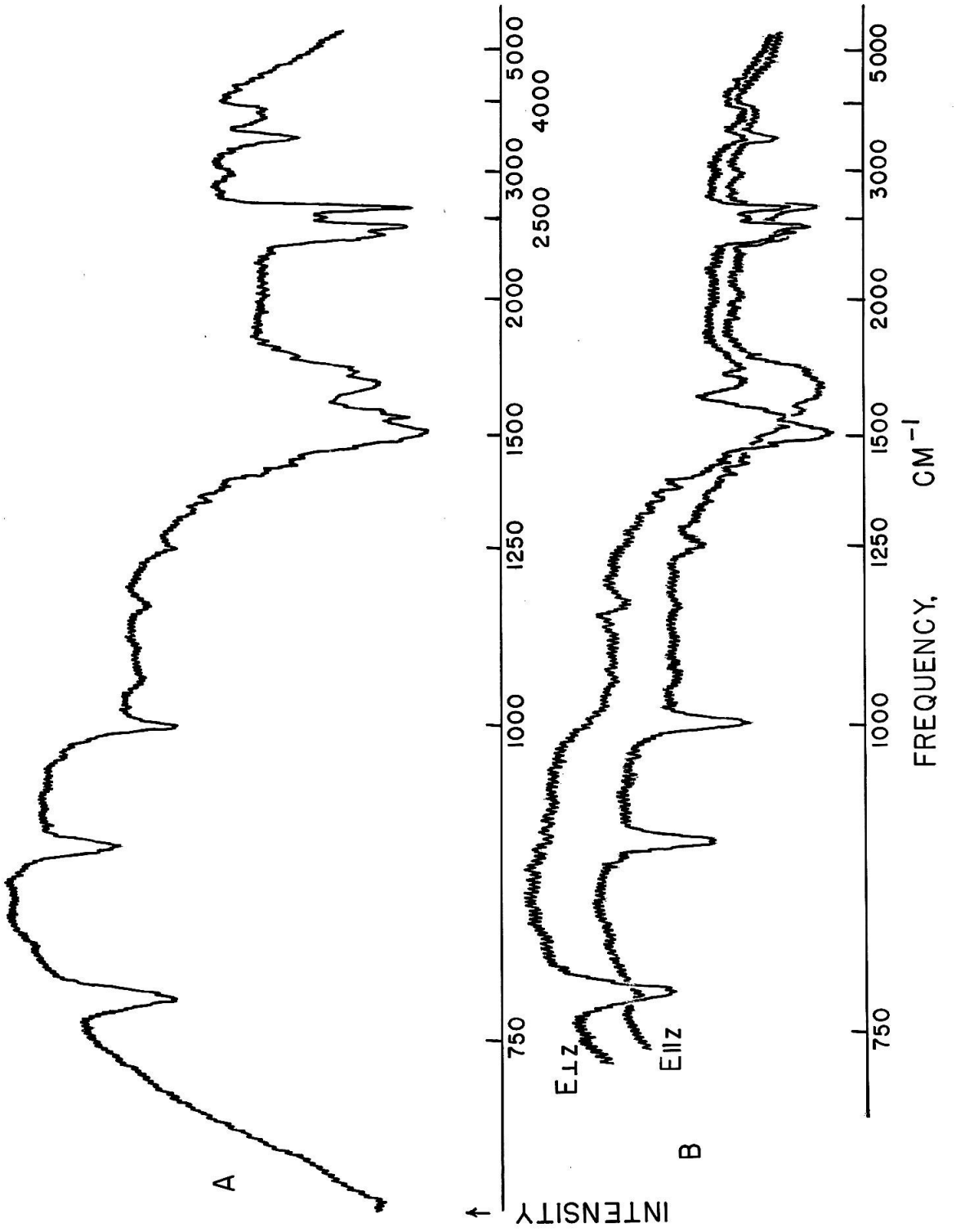

A
B
E⊥z
E∥z
INTENSITY
750
1000
1250
1500
2000
2500
3000
4000
5000
FREQUENCY, CM⁻¹

FIGURE 8

Infra-red Spectrum of Deutero-urea below 700 cm^{-1}

Ordinate: Per cent Transmission

The margin mark — represents 75 % transmission

Top. Unpolarized Spectrum

Bottom. Polarized Spectrum

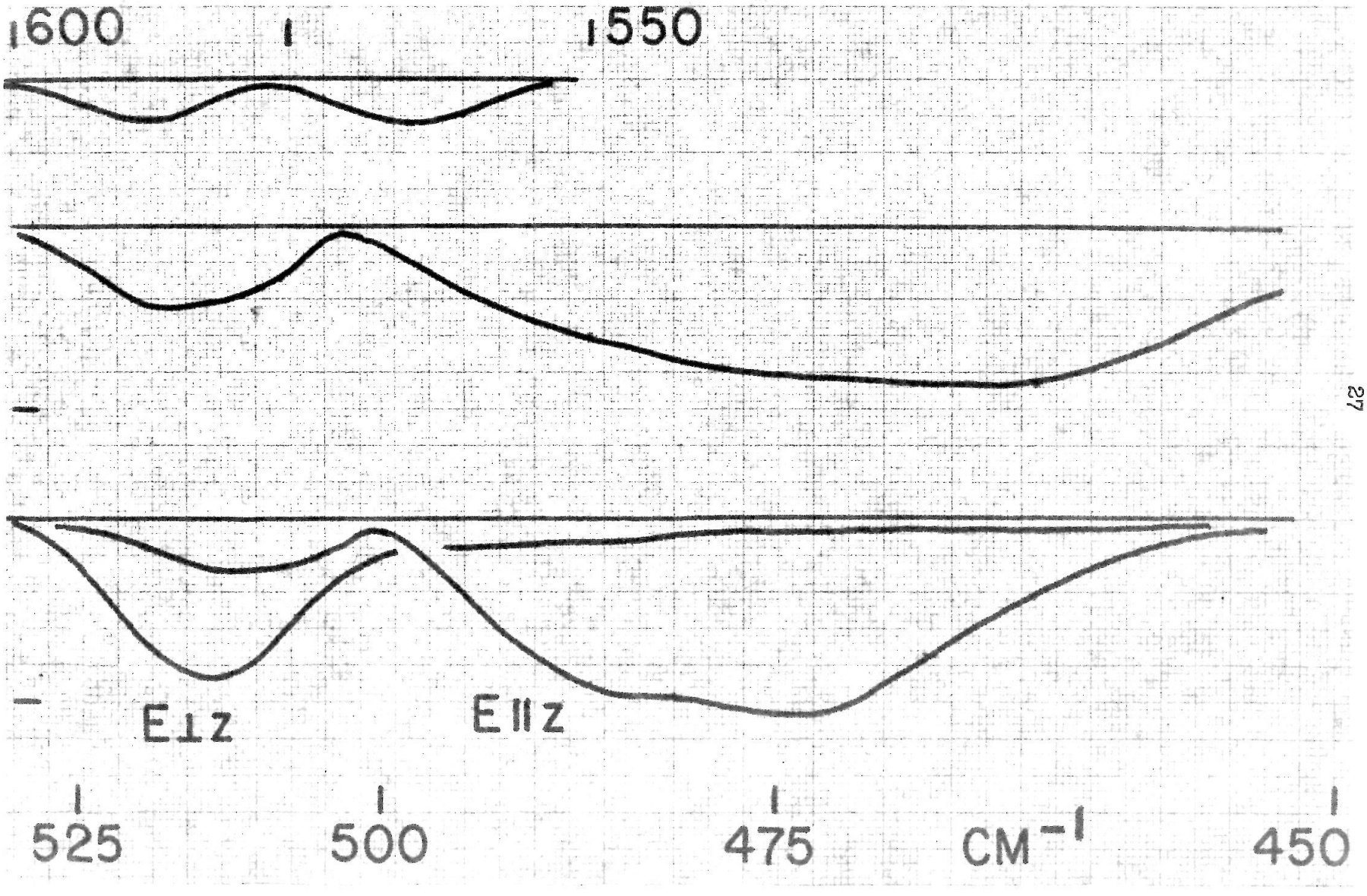

1600
1550
E⊥z
E∥z
525
500
475
CM⁻¹
450

TABLE IX

Infra-red Absorption Bands of Deutero-urea

Frequency	Polarization	Density	Freq.	Pol.	Dens.
2962	$\vec{E} \perp z$	.45	1501	$\vec{E} \perp z$	16
2874	$\vec{E} \parallel z$	.22	1248	$\vec{E} \parallel z$	.30
2732	"	.15	1160	"	.35
2589	"	12	1002	"	2.5
2586	"	8	891	"	2.2
2433	"	11	854	"	.20
2428	"	8	779	"	3.2
1996	"	.20	512	"	2.6
1632	"	13	476	"	5.5

cf. p. 14

Assignment of Frequencies

Proceeding as with urea, we shall first attempt to identify the fundamentals. We expect 4 D stretching vibrations in the 2500 cm^{-1} region corresponding to the H stretching vibrations of urea. Only low dispersion was available in this spectral region, and 2 band envelopes were observed at 2588 and 2431 cm^{-1}. Both envelopes showed mixed polarization which we consider demonstrates the presence of 2 fundamentals associated with each band envelope.

At lower frequencies, intense A_1 bands are observed at 1632, 1002, 891, and 476 cm^{-1} which are considered to be fundamentals.

Intense bands of polarization $\vec{E} \perp z$ appear at 1501, 779,

and 512 cm^{-1}. The band at 779 cm^{-1} is considered a B_2 fundamental, the other two B_1 fundamentals as previously stated (p. 19).

Seven fundamentals remain unidentified; 1 A_1, 2 B_1, 2 B_2, and the 2 inactive A_2.

Skeletal Frequencies

The skeletal frequencies were treated in conjunction with the corresponding vibrations of urea (p. 19). ν_d increases in frequency upon deuteration indicating some interaction of ν_d with $\nu_{\gamma'}$ in normal urea.

Hydrogen Frequencies

By analogy with urea, the high frequency pair of bands are assigned to the reciprocating vibrations, ν_β and $\nu_{\beta'}$, and the low frequency pair of bands are assigned to the synchronous vibrations, ν_α and $\nu_{\alpha'}$. Upon polarization, a slight difference in the positions of the maxima of the band envelopes was observed, but this effect was within the possible range of instrument drift. We thus assign ν_β = 2589, ν_α = 2428, $\nu_{\beta'}$ = 2586, and $\nu_{\alpha'}$ = 2433 cm^{-1}.

ν_δ is assigned to the A_1 fundamental at 891 cm^{-1} giving a frequency ratio ν_δ (H)/ ν_δ (D) = 1.30 . This completes the assignment of the previously identified fundamentals.

In attempting to find the deuterium scissors bending vibrations, ν_γ and $\nu_{\gamma'}$ corresponding to ν_4 and ν_{12} in urea, there are observed only very weak bands in the region expected from normal isotope shifts. We consider the weak band polarized $\parallel$ z at 1248 cm^{-1} as ν_γ, and the weak band polarized

$\perp z$ at 1160 cm^{-1} as $\nu_{\gamma'}$. A polarized line of medium intensity at 1247 cm^{-1} and a weak depolarized line at 1164 cm^{-1} were reported in the Raman spectrum (10). The isotopic frequency ratios $\nu_{\gamma}(H)/\nu_{\gamma}(D) = 1.29$ and $\nu_{\gamma'}(H)/\nu_{\gamma'}(D) = 1.41$ are reasonable since these frequencies may be expected to interact with the high frequency skeletal vibrations, ν_3 and ν_{13} in normal urea. The scissors bending vibrations appear as medium intensity bands at 1196 and 1150 cm^{-1} in the closely related compound, deutero-thiourea.

$\nu_{\delta'}$ is expected to occur near the frequency of the corresponding symmetric band, 891 cm^{-1}. Application of the isotope product rule gives a calculated value of 834 cm^{-1} for $\nu_{\delta'}$. We assign $\nu_{\delta'}$ to the very weak band of polarization $\vec{E} \perp z$ at 854 cm^{-1}.

We attribute the bands at 3400, 1063, 586, and 565 cm^{-1}, as well as the diffuse absorption polarized $\parallel z$ near 1400-1500 cm^{-1}, to vibrations of molecules containing NHD groups.

The following table gives a resume of the foregoing assignments and offers tentative assignments for several weak combination bands observed.

TABLE X

Vibrational Assignment

Fundamentals

A_1	A_2	B_1	B_2
2589 = ν_1 = ν_β	Unobserved	2586 = ν_{10} = $\nu_{\beta'}$	779 = ν_{16} = ν_f
2428 = ν_2 = ν_α	(ν_8, ν_9)	2433 = ν_{11} = $\nu_{\alpha'}$	Unobserved
1632 = ν_3 = ν_a		1501 = ν_{12} = ν_d	(ν_{17}, ν_{18})
1248 = ν_4 = ν_γ		1160 = ν_{13} = $\nu_{\gamma'}$	
1002 = ν_5 = ν_b		854 = ν_{14} = $\nu_{\delta'}$	
891 = ν_6 = ν_δ		512 = ν_{15} = ν_e	
476 = ν_7 = ν_c			

Combinations and Overtones

2962	$\vec{E} \perp z$	$\nu_2 + \nu_{15}$, $\nu_7 + \nu_{10}$	2732	$\vec{E} \perp z$	$\nu_4 + \nu_{12}$
2874	$\vec{E} \parallel z$	$\nu_2 + \nu_7$, $\nu_3 + \nu_4$	1996	$\vec{E} \parallel z$	$2\nu_5$

Two cases of "crossing over" of frequencies may be noted. ν_δ occurs at higher and lower frequencies than ν_b in urea and deutero-urea respectively. Also $\nu_{\delta'}$ occurs at higher and lower frequencies than ν_d in the same manner.

Theoretical Treatment

The assignments postulated in the preceding sections differ from those of Kellner (14) in several respects. A direct comparison would not be too profitable, since a different model was used, and the higher dispersion used in the present work resolved several bands not previously separated.

A. Evaluation of Force Constants

The treatment of resonating molecules by a valence force potential field is not too satisfactory since the interaction energy may be appreciable. Further refinements in the case of the skeletal vibrations of urea are not very significant since the skeletal approximation is a limiting factor in the validity of the force constants obtained. The treatment of $CO_3^=$ and $C(NH_2)_3^+$ will be considered first.

The valence force treatment of planar symmetric XY_3 is given in Herzberg (20). Using a potential energy expressed in the form:

$$2V = k_1(Q_{12}^2+Q_{13}^2+Q_{14}^2) + k_\delta(\delta_{23}^2+\delta_{24}^2+\delta_{34}^2) + k_\Delta(\Delta_{12}^2+\Delta_{13}^2+\Delta_{14}^2)$$

Q_{ij} = displacement coordinate of the bond i-j

δ_{jk} = radian displacement coordinate of the angle j-1-k

Δ_{ij} = " " " of the bond i-j from the plane of the molecule

there are obtained the equations:

1. $\lambda_1 = k_1/ m_y$
2. $\lambda_2 = (1 + 3m_y/ m_x) k_\Delta/ m_y L^2$
3. $\lambda_3 + \lambda_4 = (1 + 3m_y/2m_x)(k_1/ m_y + 3k_\delta/ m_y L^2)$
4. $\lambda_3\lambda_4 = 3(1 + 3m_y/ m_x)(k_1 k_\delta/ m_y^2 L^2)$

m_i = mass of atom i

L = length of bond i-j

$\lambda_i = 4\pi^2\nu_i^2$

For $CO_3^{=}$, the solution of equations 1 and 4 gives:

$$k_1 = 10.65 \times 10^5 \text{ dynes/ cm}$$

$$k_\delta / L^2 = .51 \quad " \quad " \quad "$$

Solution of equations 3 and 4, however, leads to imaginary force constants. An approximate solution satisfying equation 3 and giving the greatest product $\lambda_3 \lambda_4$ consistent with real force constants gives:

$$k_1 = 3.87 \times 10^5 \text{ dynes/ cm}$$

$$k_\delta / L^2 = 1.29 \quad " \quad " \quad "$$

Equation 2 gives:

$$k_\Delta / L^2 = 1.46 \times 10^5 \text{ dynes/ cm}$$

The poor agreement of k_1 and k_δ determined by the alternate methods is indicative of considerable resonance interaction involved in the vibrational motions.

A similar treatment may be carried out with $C(NH_2)_3^{+}$. Due to the uncertainty in the assignment we shall list 2 sets of solutions (for ν_3 = 1552 and 1472 cm^{-1}).

	(1552)	(1472)
	$k_1 = 9.59 \times 10^5$ dynes/ cm ,	same
Equations 1 and 4		
	$k_\delta / L^2 = .42$ " " " ,	$.38 \times 10^5$ dynes/ cm
	$k_1 = 6.65 \times 10^5$ dynes/ cm ,	5.83×10^5 dynes/ cm
Equations 3 and 4		
	$k_\delta / L^2 = .60$ " " " ,	.62 " " "

The interaction energy is again considerable.

Since we have 3 planar frequencies, we may add to the potential function an interaction term of the form

$$2V = 2V_o + 2k_1' (Q_{12}Q_{13} + Q_{12}Q_{14} + Q_{13}Q_{14})$$

where V_o is the valence force potential function. Substitution of this expression yields the original equations 1-4 with k_1 replaced by $k_1 + 2k_1'$ in equation 1, and by $k_1 - k_1'$ in equations 3 and 4.

This gives for $CO_3^=$:

$k_1 = 6.13 \times 10^5$ dynes/ cm

$k_1' = 2.26$ " " "

and for $C(NH_2)_3^+$:

	(1552)	(1472)
k_1 =	7.63×10^5 dynes/ cm ,	7.08×10^5 dynes/ cm
k_1' =	.98 " " " ,	1.25 " " "

The treatment of planar XYZ_2 is also given in Herzberg. The valence force potential function is:

$$2V = k_1 Q_{14}^2 + k_2(Q_{12}^2 + Q_{13}^2) + k_\delta \delta_{23}^2 + k_{\delta'}(\delta_{24}^2 + \delta_{34}^2) + k_\Delta \Delta^2$$

Δ = radian displacement coordinate of the bond X-Y from the plane of YZ_2

from which there are obtained the equations:

1. $\lambda_1 + \lambda_2 + \lambda_3 = k_1(w_x + w_y) + k_2(w_z + 2w_y\cos^2 u) + k_3(w_z + 2w_y\sin^2 u)$

2. $\lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_2\lambda_3 = k_1k_2(w_xw_z + w_yw_z + 2w_xw_y\cos^2 u) + k_1k_3(w_xw_z + w_yw_z + 2w_xw_y\sin^2 u) + k_2k_3(w_z^2 + 2w_yw_z)$

3. $\lambda_1\lambda_2\lambda_3 = k_1k_2k_3(w_xw_z^2 + w_yw_z^2 + 2w_xw_yw_z)$

4. $\lambda_4 + \lambda_5 = k_2(w_z + 2w_y\sin^2u) + k_4(2w_xR + w_z/R + 2w_y[R + 2\cos u + \cos^2u/R])$

5. $\lambda_4\lambda_5 = k_2k_4(2w_xw_zR + w_z^2/R + 2w_yw_z[R + 1/R] + 4w_yw_z\cos u + 4w_x^2R\sin^2u)$

6. $\lambda_6 = k_5\sec^2u\,(\frac{1}{2}w_z + w_xR\cos^2u + w_y[1/R + 2\cos u + R\cos^2u])$

$w_i = 1/m_i$ $\qquad k_3 = \dfrac{2k_\delta + k_{\delta'}}{L_2^2}$

$2u$ = ZYZ angle

$R = L_2/L_1$ $\qquad k_4 = k_{\delta'}/L_1L_2$

L_1 = X-Y bond length

L_2 = Y-Z " " $\qquad k_5 = k_\Delta/L_1L_2$

Equations 1-3 do not give real solutions for urea. An approximate solution satisfying equation 1, an auxiliary equation derived from equations 2 and 3, and giving the greatest product $\lambda_1\lambda_2\lambda_3$ consistent with real force constants gives:

$f_{C-O} = k_1 = 7.4 \times 10^5$ dynes/ cm

$f_{C-N} = k_2 = 9.25$ " " "

$Rk_3 = 2.26$ " " "

Substitution of these constants and solving for the frequencies gives:

	Calculated	Observed
ν_a =	1719 cm^{-1}	1689 cm^{-1}
ν_b =	949	1005
ν_c =	557	558

Similar calculations for deutero-urea lead to considerably imaginary force constants.

The solution of equations 4 and 5 gives:

	Urea	Deutero-urea
k_2 =	5.42×10^5 dynes/ cm,	6.22×10^5 dynes/ cm
k_4 =	.80 " " " ,	.63 " " "

Equation 6 yields:

	Urea	Deutero-urea
k_5 =	$.434 \times 10^5$ dynes/ cm ,	$.428 \times 10^5$ dynes/ cm

One would expect somewhat smaller interaction constants for urea than for $CO_3^=$ ion. It is apparent that the force constant for the C-O bond has a value considerably below that for ketones. (Herzberg lists 12.1 as the characteristic stretching force constant for C-O in ketones.) In contrast, the C-N stretching force constant is larger than that calculated for methylammonium ion, 4.63 (21). These observations are in accord with resonance interaction which transfers some of the double bond character of the C-O bond to the C-N bonds. This is reflected in the interatomic distances which lie intermediate between normal single and double bond values: (5)

	Single Bond	Urea	Double Bond
C-O	1.43 Å	1.24 Å	1.21 Å
C-N	1.47 Å	1.33 Å	1.26 Å

The frequencies of the H stretching vibrations are rather high for a crystal in which hydrogen bonding can occur.

The mean value of the synchronous vibrations $\frac{1}{2}(\nu_2 + \nu_{11})$ = 3352 cm^{-1} while in ammonia ν_1 = 3336 cm^{-1}. For the reciprocating vibrations, $\frac{1}{2}(\nu_1 + \nu_{10})$ = 3442 cm^{-1} compared with ν_3 = 3414 in NH_3. The interatomic distances as calculated from X-ray data are N···O = 3.00 and 3.07 Å which indicate only rather weak hydrogen bonding forces. The C-N···O angle corresponding to the hydrogen bond along the z axis is less than 100° which is also unfavorable for hydrogen bond formation. The weakness of the hydrogen bonds is probably due to a saturation effect at the oxygen atom; it being unable to furnish enough electrons to form 4 strong hydrogen bonds.

In the application of spectroscopy to the prediction of hydrogen bond strength from the frequency of hydrogen stretching vibrations, caution should be exercised in the interpretation of frequency shifts. Unsaturation of the atom to which the hydrogen(s) are attached profoundly affects the stretching frequency as an examination of the spectra of ethane, ethylene, and acetylene reveals. A change in coordination number as in the transition from NH_3 to NH_4^+ also causes alteration of the H stretching frequencies. Either of these effects may cause departures from "normal" H stretching frequencies of several hundred wave numbers-- of the same order of magnitude as hydrogen bonding shifts. It is apparent that for use in determining hydrogen bond strengths, the other variables must be known with some precision.

B. The Isotope Product Rule

The previous observations give sufficient frequencies to apply the Teller-Redlich isotope product theorem (20) to the A_1 and B_1 frequencies.

The general formula is:

$$\prod_S \frac{\omega(i)}{\omega(n)} = \sqrt{\prod_K \left(\frac{m(n)}{m(i)}\right)^f \left(\frac{M(i)}{M(n)}\right)^t \prod_P \left(\frac{I(i)}{I(n)}\right)^r}$$

where: ω = zero order frequency of symmetry species S

m = mass of one atom of the K non-identical sets of atoms; each set consisting of the atoms equivalent by symmetry

f = degrees of freedom of atom m in the symmetry species S

M = molecular weight of the molecule

t = number of translations in symmetry species S

I = moment of inertia of the molecule about one of the P principal axes of inertia

r = number of rotations about axis a in symmetry species S

i and n refer to the isotopic and normal molecule respectively.

Calculation of the right hand side of the equation gives for A_1 .2586; for B_1 .2805. The left hand side of the equation may be approximated by substitution of the fundamental frequencies, ν_i, for the zero order frequencies, ω_i, giving .2653 for A_1 and .2874 for B_1. The left hand side is expect-

ed to be larger than the right when the observed frequencies are used to approximate the zero order terms due to convergence of the energy levels. The deviations amount to about 2.5 % in each case; these values are tolerable considering the number of frequencies involved. A representative calculation of the 3 fundamentals of species A_g in ethylene gives a deviation of 1.6 %. It is surprising that the van der Waals forces in a condensed state do not perturb the convergence of the lower vibrational levels sufficiently to influence the deviations of the isotopic frequency ratios from the theoretical values.

PART II

THE VIBRATIONAL SPECTRUM OF THIOUREA

THE VIBRATIONAL SPECTRUM OF THIOUREA

Introduction

An investigation of thiourea was undertaken to supplement the study of urea in addition to providing information of intrinsic value. In its relation to urea, the spectroscopic behavior of the hydrogen frequencies and its relation to the change in hydrogen bonding of the two crystals is of special interest.

The same resonance forms which contribute to the stability of urea (p. 6) are also possible for thiourea. A comparison of the observed heat of formation (solid) (22) with the value calculated* for the non-resonating structure (model (a), p. 6 with O replaced by S) for the vapor phase gives an excess energy of 62 kcal/ mole. This may be compared with 67 kcal/ mole for urea. The resonance energies are these values less the heats of sublimation of the crystals. If the heats of sublimation of thiourea and urea are approximately equal, the resonance energy of thiourea must be nearly as great as for urea; i.e. about 30 kcal/ mole.

This leads to the prediction that thiourea, like urea, is a planar molecule.

---

* The calculation was made with the use of tables of empirical values of bond energies as given by Pauling (5) following the method developed in this reference.

The Raman spectrum of crystalline thiourea has been investigated by Kohlrausch and Wagner (23), while Edsall (24) has studied the compound in aqueous solution. No previous infra-red studies have been reported to the knowledge of the author. Kohlrausch briefly discussed the assignments of some of the Raman lines; these will be reviewed in subsequent sections.

In the present investigation, the infra-red spectra of single crystals of thiourea and deuterium substituted thiourea were obtained from 400-5000 cm^{-1} with low dispersion prism spectrographs, and with a high dispersion grating spectrograph in the 3000-3500 cm^{-1} region. Polarization measurements parallel to the 3 crystallographic axes were made.

Experimental

The research equipment was described in a preceding section. Eastman Kodak Co. reagent thiourea was dissolved in H_2O (or D_2O) and crystallized by cooling a drop of warm saturated solution between compressed plates of glass or MgO. Crystals of moderate size (1-5 mm in length) develop in c, b, a, and m faces (Fig. 9) which can be identified microscopically. The crystals are removed from the glass plates while still damp with a small tool consisting essentially of a short segment of a thin razor blade mounted on a pencil shaped holder. The blade is carefully slid under the crystal which is removed with a sliding-lifting motion. The extreme fragility of the thin crystals resulted in most attempts be-

ing unsuccessful, but after a number of trials, a suitable sample could be obtained. For work at shorter wavelengths, crystals grown on MgO were occasionally used. The crystals were not removed from the plates, which permitted the use of thinner crystals than could be manipulated by the previous technique. Thiourea appeared to attack AgCl, although some specimens were made by evaporation of an alcoholic thiourea solution upon sulfided AgCl sheets.

Discussion

X-ray investigation (25) of thiourea yields a space group D_{2h}^{16} P bnm giving a symmetry C_s for the heavy atoms. For reasons explained in some detail in the section on urea, we will assume the symmetry C_s for the entire molecule. (The X-ray parameters indicate a very slightly pyramidal bonding about the central carbon atom. A planar configuration which seems likely from quantum-mechanical and chemical considerations is probably compatible within the experimental error of the X-ray measurements. For the subsequent treatment of the skeletal vibrations, the planar model will be used for simplicity, although if the molecule is actually distorted, no essential difference in the nature of the spectra should occur for small displacements of the carbon atom from the plane of the nitrogen and sulfur atoms.)

From resonance considerations, one would expect thiourea to be entirely planar. This would lead to molecular symmetry C_{2v} as with urea and would cause some vibrations to be infrared inactive if lattice interactions are neglected. In our

treatment we shall consider the more general case C_s. The comparison with C_{2v} can be made by referring to the section on urea.

Figure 9 gives a perspective view of the crystal structure, principal faces, and coordinate axes used in the subsequent description of vibrations. The molecular axes have been chosen to coincide with those of urea.

Thiourea has 18 fundamental frequencies distributed in 2 symmetry species. The following table gives the classification by species of the normal vibrations.

TABLE XI

Species Classification of Components of Transition Moment (M) and Polarizability (α)

Operation	Species	
	A' (M_y, M_z, α_{xx}, α_{yy}, α_{zz}, α_{yz})	A" (M_x, α_{xy}, α_{xz})
σ_{yz}	+	-
Number of vibrations	10	8

The symbol + indicates the component is unchanged, - indicates the component changes sign following the symmetry operation.

The species A' is derived from species A_1 and B_2 of the point group C_{2v}; A" from A_2 and B_1.

The following spectra show the principal bands above 400 cm^{-1} in the infra-red spectrum of thiourea (Fig. 10, 11). For spectra obtained from radiation propagated perpendicular to the c axis, $\vec{R} \perp c$, the polarization $\vec{E} \perp c$ ($\| \sigma_{yz}$) indicates

FIGURE 9

Crystal Structure of Thiourea

Top: Crystal Habit

a = 100 m = 110

b = 010 n = 120

c = 001 r = 101

Center: Unit Cell

Dotted lines represent possible hydrogen bonds with N•••S distances:

I 3.49 Å II 3.52 Å III 3.65 Å

Bottom: Coordinate Axes

σ = symmetry plane

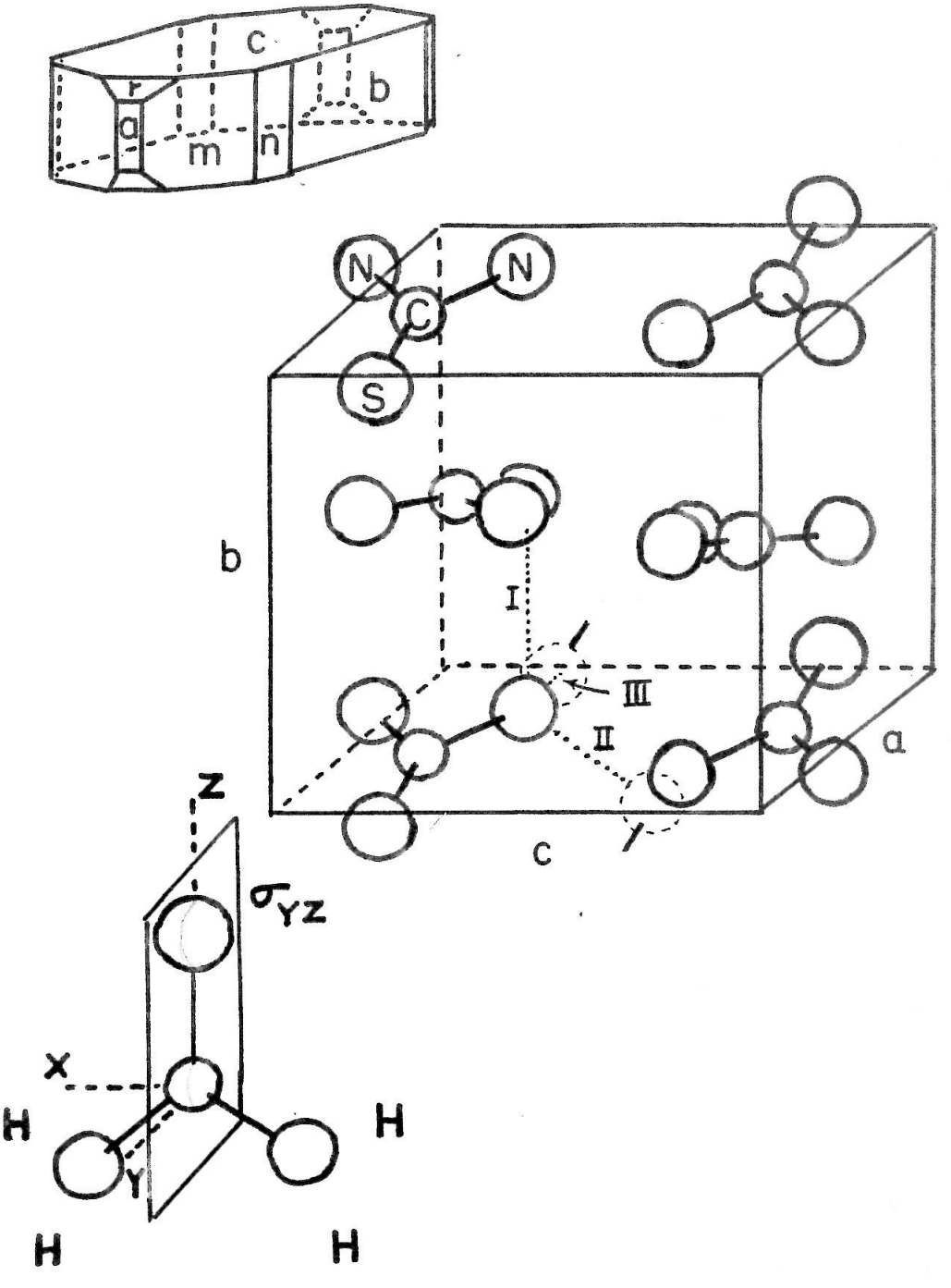

c
r
a
m
n
b
N
N
C
S
b
I
III
II
a
c
Z
σ_{YZ}
X
H
H
Y
H
H

FIGURE 10

Infra-red Spectrum of Thiourea from 700-5000 cm^{-1}

Ordinate: Intensity of transmitted radiation

A. Unpolarized Spectrum

Radiation propagated perpendicular to the c axis

Two different sample thicknesses are shown

B. Polarized -- Thick sample

C. Polarized -- Thin sample

(The direction of propagation for the two samples is not necessarily the same.)

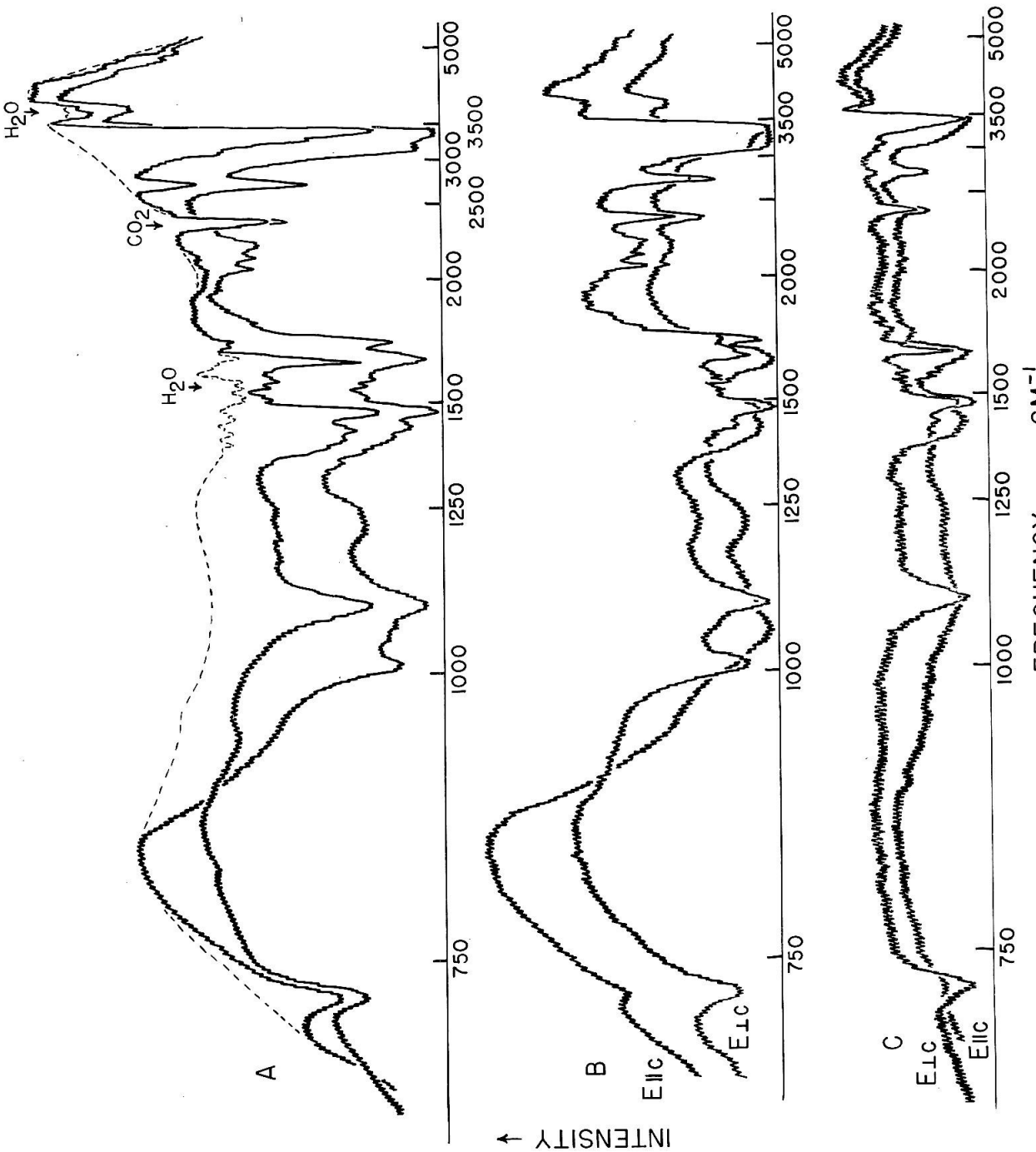

H2O
CO2
H2O
A
B
E∥c
E⊥c
C
E⊥c
E∥c
INTENSITY →
750
1000
1250
1500
2000
2500
3000
3500
5000
FREQUENCY, CM⁻¹

FIGURE 11

Infra-red Spectrum of Thiourea below 700 cm^{-1}

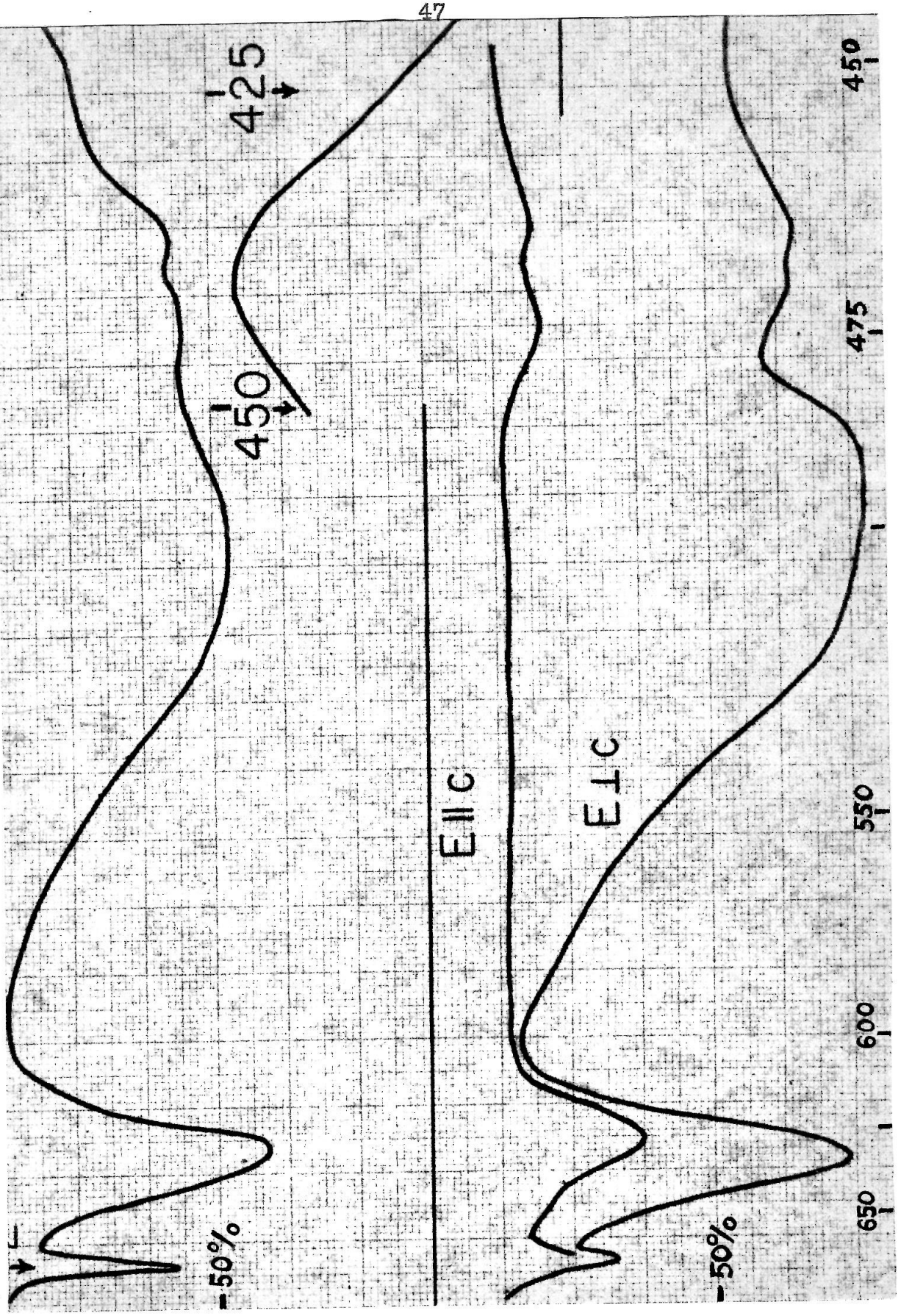
Abscissa: Frequency cm^{-1}

Ordinate: Per cent Transmission

Top. Unpolarized Spectrum

Radiation propagated perpendicular to the c axis

Bottom. Polarized Spectrum


425
450
E ∥ c
E ⊥ c
-50%
-50%
650
600
550
475
450

species A', while polarization $\vec{E} \parallel c$ ($\perp \sigma_{yz}$) indicates species A". Polarization data of spectra for which $\vec{R} \parallel c$ yield information concerning the azimuth of the transition moment in the yz plane for vibrations of species A'.

The following table lists the frequencies, polarization, and comparative densities (for $\vec{R} \perp c$ and incident radiation polarized in the direction of maximum absorption) of the absorption bands for thiourea.

TABLE XII

Infra-red Absorption Bands of Thiourea

Frequency	Polarization	Density	Freq.	Pol.	Dens.
4950-4830 cm^{-1}	mixed	.015	1988	$\vec{E} \perp c$	.01
4460	$\vec{E} \parallel c$	.02	1818	"	.01
3805	$\vec{E} \perp c$	.14	1697	$\vec{E} \parallel c$	.40
3390	"	12	1628	"	2.3
3385	"	15	1620	"	1.7
3349	"	14	1470	"	6.5
3333	"	18	1416	"	7.6
3293	"	3	1224	"	.39
3285-45	"	15	1054	"	1.5
3199	"	.50	1088	"	3
3177	"	2	1009	"	,25
3195-50	"	12	970-20	"	.30
3110	"	8	733	"	2
2700	"	.45	633	"	1.47
2207	"	.13	501	"	30
2114	"	.10	468	"	.42
2037	"	.09	420-400	?	?

As with urea, we may treat the normal vibrations by subdivision into hydrogen and skeletal vibrations. Referring to the change in species in going from urea to thiourea, the following table is immediately derived from Table IV.

TABLE XIII

Species Classification of Hydrogen and Skeletal Vibrations

Species	H stretch.	bend	Skel. stretch.	bend	Designation
A'	2	4	2	2	(10) $\nu_1 - \nu_{10}$
A"	2	4	1	1	(8) $\nu_{11} - \nu_{18}$

Assignment of Frequencies

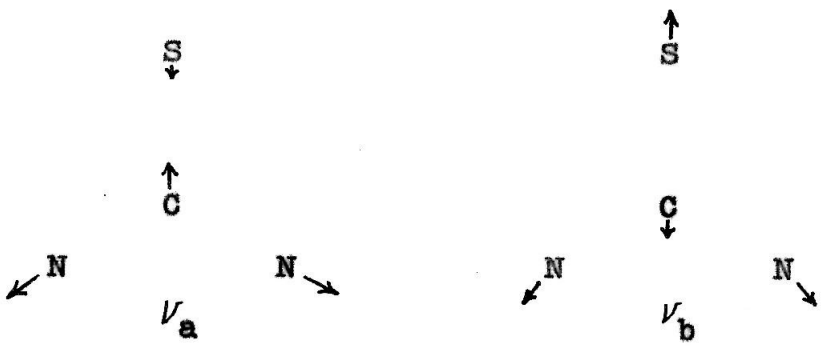
We shall first attempt to identify the fundamentals as was done in treating urea. We again expect the 4 H stretching vibrations in the 3000-3500 cm^{-1} region, and 4 of the 8 H bending vibrations, ν_ε, $\nu_{\varepsilon'}$, ν_ζ, and $\nu_{\zeta'}$ to be of rather low frequency and possibly below 400 cm^{-1}.

The spectrum in the 3000-3500 cm^{-1} is rather complex, but there are at least 4 strong bands which could possibly represent the H stretching fundamentals. In the intermediate and low frequency regions, medium to intense bands of species A' appear at 1628, 1416, 1088, 733, 633, 501, and 468 cm^{-1}.

Intense bands of species A" appear at 1620 and 1470 cm^{-1}. Five fundamental frequencies remain unidentified; 1 A' and 4 A". By analogy with urea, the broad diffuse band at 1054 cm^{-1} is also attributed to a fundamental vibration, $\nu_{\delta'}$.

Skeletal Frequencies

For identification of the skeletal frequencies, we expect a high frequency pair of vibrations near 1500 cm^{-1} corresponding to the stretching vibrations, ν_a and ν_d, a low frequency pair of vibrations near 500 cm^{-1} corresponding to the bending vibrations, ν_c and ν_e, and an intermediate frequency pair of bands corresponding to the remaining vibrations, ν_b and ν_f. The approximate form of the skeletal vibrations, ν_c through ν_f will be practically unchanged from that of urea (Fig. 4 with O replaced by S). ν_a and ν_b will be altered somewhat; the former vibration will involve chiefly C-N stretching and the latter C-S stretching, whereas in urea the vibrations were of mixed character. The approximate form of ν_a and ν_b in thiourea is shown below:



High Frequency Skeletal Vibrations (Schematic)

FIGURE 12

We propose the following assignment of skeletal frequencies. (The value for ν_e is somewhat uncertain.)

TABLE XIV

Assignment of Skeletal Vibrations

	A'				A"	
	ν_a	ν_b	ν_c	ν_f	ν_d	ν_e
Thiourea	1416	733	468	633	1470	(420-400)
Deutero-thiourea	1404	668		617	1512	

ν_c and ν_e were unobserved in deutero-thiourea. The choice of skeletal frequencies is made on the basis of infra-red polarization and intensity, Raman intensity, persistence of bands upon deuterium substitution, and correlation with the spectrum of urea.

ν_a, ν_b, and ν_c, which occur as strong Raman lines, are observed in the infra-red spectrum with proper polarization (A'). Upon deuterium substitution, ν_a and ν_b persist with minor frequency shifts, while ν_c is obscured by a broad absorption band overlapping the region of interest.

ν_d appears as an A" band at 1470 cm^{-1}; nearly identical to the corresponding frequency in urea. This frequency increases upon deuterium substitution in the same manner as in urea.

ν_f must represent either the 633 or 501 cm^{-1} band of species A'. The polarization azimuth (which will be considered later) favors the choice of 501 cm^{-1}, but the former band is preferred for several reasons. 633 cm^{-1} is closer in frequency to the corresponding vibration in urea (790 cm^{-1}). Upon deuteration, a somewhat weaker band occurs at 617 cm^{-1},

which is a reasonable isotope displacement for a skeletal vibration. (However, the possibility cannot be discounted that this is due to a bending vibration associated with residual NHD groups.) The band at 501 cm^{-1} possesses a band width and intensity much greater than that expected for a skeletal bending vibration. Furthermore, upon deuterium substitution a large frequency shift occurs which would be inexplicable if the latter band represented ν_f. 633 cm^{-1} occurs as a very weak line in the Raman spectrum as would be expected for the skeletal vibration. (ν_f was unobserved in the Raman spectrum of urea.)

ν_e is not positively identified. It probably represents one of the weak Raman lines at 418-38 cm^{-1} or 577 cm^{-1}. The latter band was not observed in the infra-red, but a band was observed near 420 cm^{-1} and extending beyond the KBr region. The polarization could not be identified with certainty. We assign this band to ν_e, since it would be expected at a lower frequency than in urea.

Kohlrausch's assignment differs from the foregoing selection for the A" vibrations, ν_d and ν_e. He chooses 1617 and 577 cm^{-1} respectively. The choice for ν_d is untenable considering the isotope shift observed upon deuterium substitution. ν_e is open to some question. The non-appearance of 577 cm^{-1} in the infra-red suggests that the vibration corresponds to an A_2 vibration of C_{2v} which is inactive.

Three of the frequencies reported for the Raman spectrum of crystalline thiourea differ appreciably from our measurements. Kohlrausch reports ν_a at 1374, ν_c at 483, and (ν_e) at

438 cm^{-1}. For an aqueous solution, Edsall reports 1406, 487, and 418 cm^{-1} respectively. The reasons for these discrepancies are not clear. The frequency of the infra-red band at 468 cm^{-1} is subject to some uncertainty since it is partially overlapped by the extremely intense band at 501 cm^{-1}.

Hydrogen Frequencies

A discussion of the H stretching vibrations will be deferred until a later section.

The H scissors bending vibrations, ν_γ and $\nu_{\gamma'}$ are expected in the 1600 cm^{-1} region and are assigned to 1628 and 1620 cm^{-1} respectively. These bands are distinct as shown by the frequency shift and the difference in band widths upon polarization. The rocking vibrations, ν_δ and $\nu_{\delta'}$ appear at 1088 and 1054 cm^{-1} with similar intensities and band shapes as in urea. $\nu_{\delta'}$ appears in a very diffuse band which is probably composed of several components as is the corresponding band in urea. The powerful band at 501 cm^{-1} is logically assigned to ν_ε. The difference in frequency from ν_ε in urea (which must occur below 420 cm^{-1}) is unexpected, although the lower frequencies are somewhat more sensitive than the higher frequencies to the molecular environment in the crystal. $\nu_{\varepsilon'}$, ν_τ, and $\nu_{\tau'}$ should be very weak or inactive in the infra-red, with the latter two vibrations probably occurring below 400 cm^{-1}.

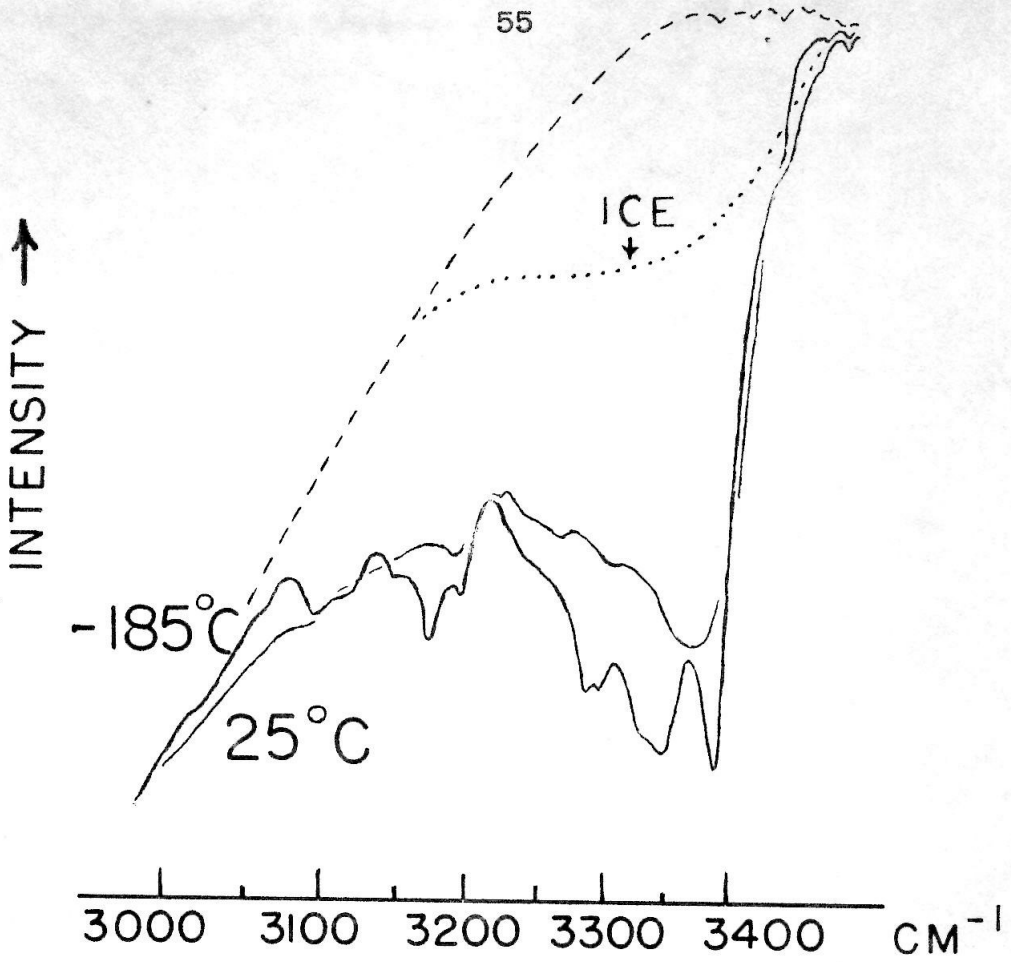
The H valence frequencies are expected in the 3000-3500 cm^{-1} region. The room temperature spectrum of thiourea at these wavelengths is poorly resolved due to overlapping of bands (Fig. 13). Upon polarization, a complex series of

incompletely resolved bands appears for $\vec{E} \parallel c$ (A") extending from about 3100-3400 cm^{-1} (Fig. 14). For $\vec{E} \perp c$ (A'), a single strong band with a low frequency shoulder appears with much weaker absorption at lower frequencies.

When a sample is cooled to liquid air temperatures, a number of striking changes occur. (Fig. 13, 14) The highest frequency in each polarization splits into a well resolved pair of bands; a new A' band appears at 3293 cm^{-1} which appears to be a doublet. The A" bands are narrowed giving better resolution, although the absorption in the 3285-45 cm^{-1} and 3195-50 cm^{-1} regions may consist of several bands each.

We turn our attention first to the polarization $\vec{E} \perp c$. We assign ν_β and ν_α to the 2 strong bands at 3390 and 3349 cm^{-1}. The frequency separation is somewhat lower than for urea or most other XH_2 groups-- possibly due to resonance repulsion by the band at 3293 cm^{-1}. The latter band and the weaker peaks at 3199 and 3177 cm^{-1} must be attributed to combination transitions.

For radiation of polarization $\vec{E} \parallel c$, we assign the 2 high frequency bands at 3385 and 3333 cm^{-1} to $\nu_{\beta'}$ and $\nu_{\alpha'}$ respectively. (The band at 3385 cm^{-1} is definitely distinct from the A' band at 3390 cm^{-1}; the frequency difference is considerably greater than experimental error.) Below these fundamentals, we observe 3 intense bands of which the higher frequency pair appear to have a complex structure. Of the binary combinations of species A", only $\nu_\gamma + \nu_{\delta'}$ and $\nu_\gamma + \nu_d$ would be expected to have frequencies lying in this region. Ternary combinations of ν_δ and $\nu_{\delta'}$ may also be involved.



High Dispersion Spectrum of Thiourea from 3000-3500 cm^{-1}

Unpolarized -- Radiation propagated $\perp$ c axis

FIGURE 13

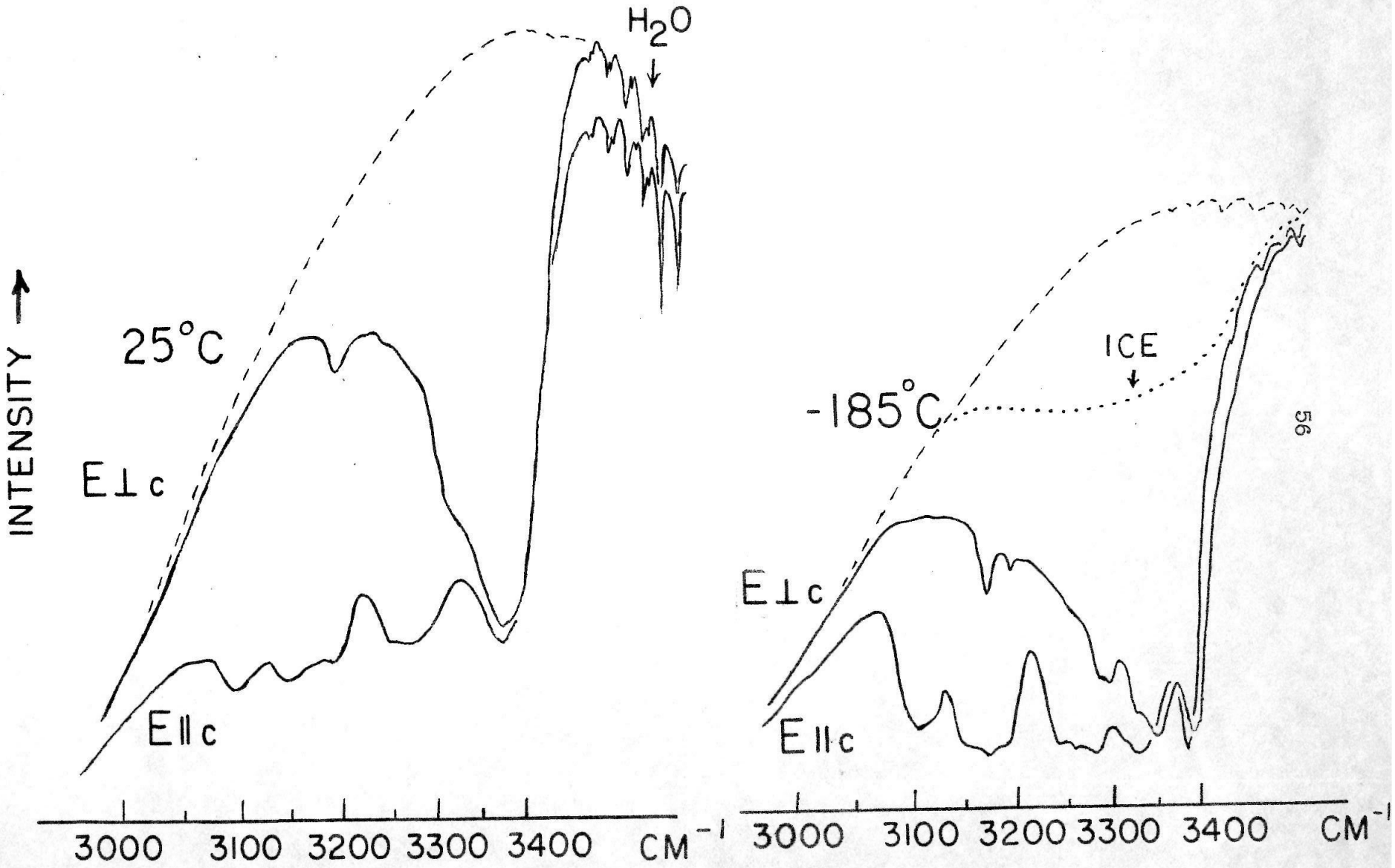
FIGURE 14

High Dispersion Spectrum of Thiourea from 3000-3500 cm^{-1}

Polarized -- Radiation propagated perpendicular to the c axis

Left. 25° C

Right. -185° C


INTENSITY
25°C
H2O
E⊥c
E∥c
3000
3100
3200
3300
3400
CM-1
-185°C
ICE
E⊥c
E∥c
3000
3100
3200
3300
3400
CM-1

It seems improbable that difference bands can play an important role in the absorption since none of the bands were appreciably diminished in intensity upon cooling. At -185° C, a noticeable effect should be observed for levels as low as 50-75 cm^{-1}.

If two or more potential minima existed for configurations of the NH_2 group, multiple sets of fundamentals would be possible, but separations of 100 cm^{-1} and more are quite unlikely especially since no strong hydrogen bonds are possible.

The following table summarizes the previous assignments and presents tentative assignments for certain overtone and combination transitions which are compatible with polarization.

TABLE XV

Vibrational Assignment

Fundamentals

A'		A"	
3390 = $\nu_1 = \nu_\beta$	733 = $\nu_6 = \nu_b$	3385 = $\nu_{11} = \nu_{\beta'}$	420-400 = $\nu_{17} = \nu_e$
3349 = $\nu_2 = \nu_\alpha$	633 = $\nu_7 = \nu_f$	3333 = $\nu_{12} = \nu_{\alpha'}$	Unobserved
1628 = $\nu_3 = \nu_\gamma$	501 = $\nu_8 = \nu_\epsilon$	1620 = $\nu_{13} = \nu_{\gamma'}$	(ν_{16}, ν_{18})
1416 = $\nu_4 = \nu_a$	468 = $\nu_9 = \nu_c$	1470 = $\nu_{14} = \nu_d$	
1088 = $\nu_5 = \nu_\delta$	Unobserved (ν_{10})	1054 = $\nu_{15} = \nu_{\delta'}$	

TABLE XV (CONTINUED)

Combinations and Overtones

4950-4830	$\vec{E} \perp, \parallel c$	$\nu_{1,2,11,12} + \nu_{3,13}$	2207	$\vec{E} \parallel c$	$\nu_6 + \nu_{14}$
4460	$\vec{E} \parallel c$	$\nu_5 + \nu_{11}$	2114	"	$\nu_8 + \nu_{13}$, $\nu_5 + \nu_{15}$
3805	$\vec{E} \perp c$	$\nu_2 + \nu_9$	2037	"	$\nu_3 + \nu_{17}$
3293	"	$3\nu_5$	1988	$\vec{E} \perp c$	$4\nu_8$
3285-45	"	$2\nu_5 + \nu_{15}$	1818	"	$\nu_5 + \nu_6$
3199	"	$2\nu_3$	1697	"	$\nu_7 + \nu_{15}$
3177	"	$2\nu_{13}$	1224	"	?
3195-50	"	$\nu_3 + \nu_{13}$	1009	"	$2\nu_8$
3110	"	$\nu_3 + \nu_{14}$	970-20	"	$\nu_8 + \nu_{17}$
2700	"	$\nu_5 + \nu_{13}$			

The band at 1224 cm^{-1} probably represents a combination involving one of the unobserved low frequency fundamentals.

DEUTERIUM SUBSTITUTED THIOUREA

The changes in frequency observed in deuterium substitution in urea are closely paralleled in the case of thiourea. The spectrum of deutero-thiourea from 400-5000 cm^{-1} is shown in Figures 15 and 16.

The following table lists the frequencies, polarization, and relative densities of the infra-red bands attributed to $(ND_2)_2CS$. Less prominent bands considered to be due to molecules with residual NHD groups will be discussed in the text.

FIGURE 15

Infra-red Spectrum of Deutero-thiourea from 700-5000 cm^{-1}

Ordinate: Intensity of transmitted radiation

Radiation propagated perpendicular to the c axis

A. Unpolarized Spectrum

B. Polarized Spectrum

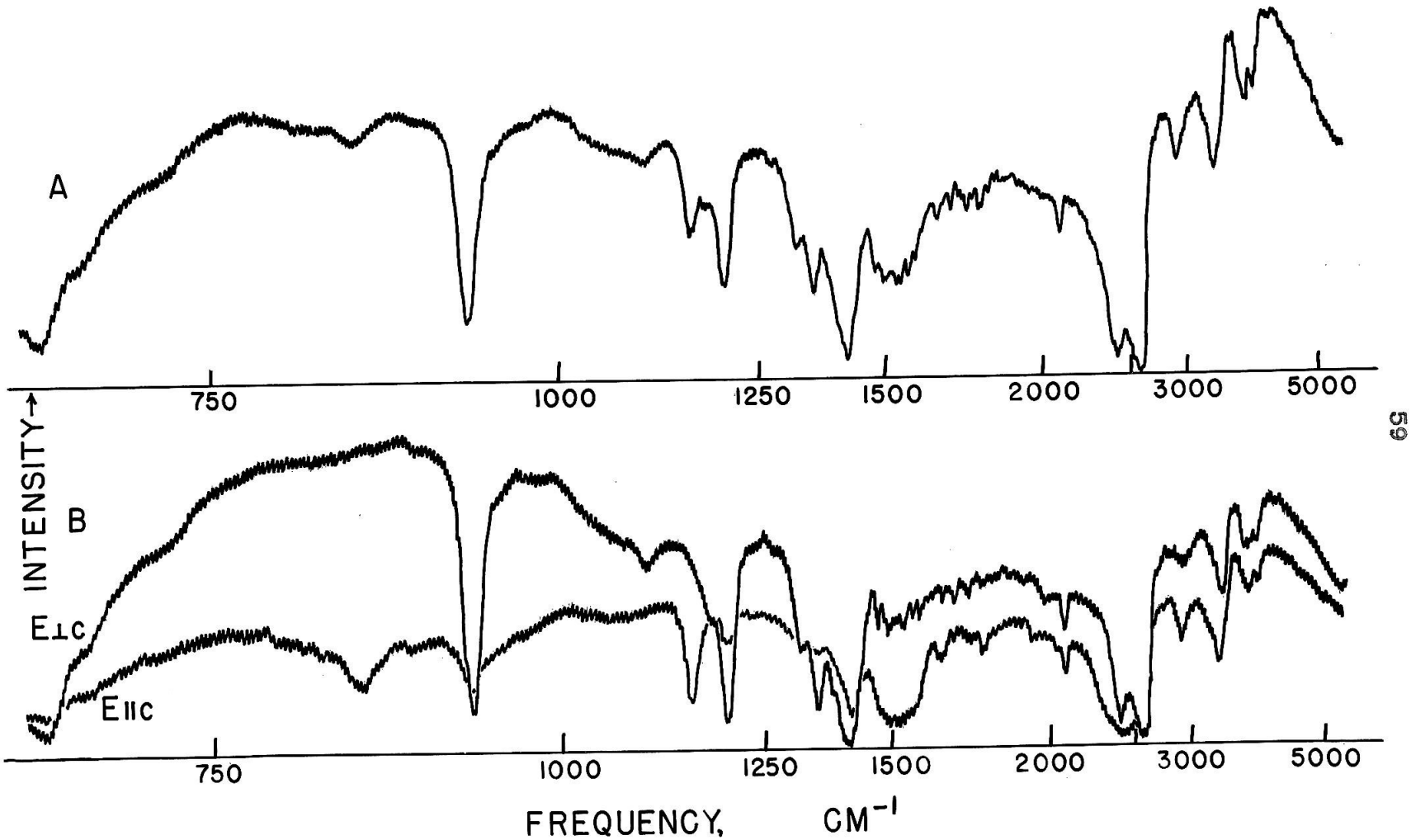

A
750
1000
1250
1500
2000
3000
5000
INTENSITY→
B
E⊥c
E∥c
750
1000
1250
1500
2000
3000
5000
FREQUENCY, CM⁻¹

FIGURE 16

Infra-red Spectrum of Deutero-thiourea below 700 cm^{-1}

Abscissa: Frequency cm^{-1}

Ordinate: Percent Transmission

Top. Unpolarized Spectrum

Radiation propagated perpendicular to the c axis

Bottom. Polarized Spectrum

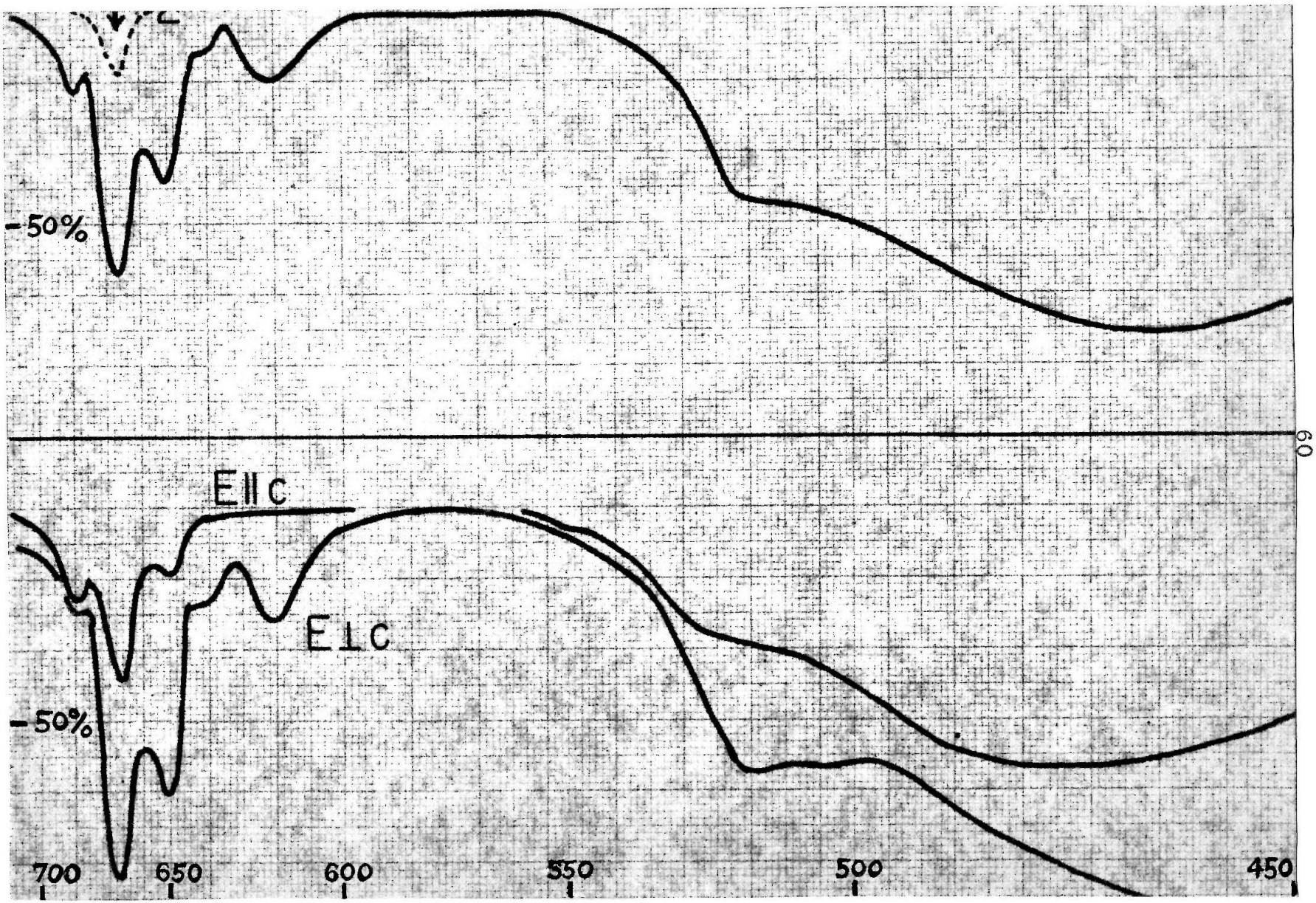

-50%
E∥c
E⊥c
-50%
700
650
600
550
500
450

TABLE XVI

Infra-red Absorption Bands of Deutero-thiourea

Frequency	Polarization	Density	Freq.	Pol.	Dens.
2890	$\vec{E} \parallel c$	.22	1196	$\vec{E} \perp c$	2
2551	$\vec{E} \perp c$, "	15-20	1150	$\vec{E} \parallel c$	.80
2381	" , "	10-15	921	"	7
2079	" "	.08	839	"	.18
1754	"	.16	668	"	.90
1512	"	.90	652	"	.52
1404	"	10	617	"	.17
1340	"	.60	450-400	"	30
1311	"	.26			

Assignment of Frequencies

We shall proceed to identify the absorption bands associated with the fundamental vibrations. In the absence of high dispersion spectra in the 2500 cm^{-1} region, we shall assume the 4 D stretching vibrations occur in this region. At lower frequencies, strong bands of species A' appear at 1404, 1196, 921, and 668 cm^{-1} which are considered to be fundamentals. The intense band below 450 cm^{-1} probably represents the high frequency shoulder of ν_5 overlapped by bands associated with the same vibration in NHD groups.

Intense bands of symmetry species A" occur at 1512 and 1150 cm^{-1}. Seven fundamentals remain unidentified; 3 A' and 4 A". The weaker band at 617 cm^{-1} has previously been identified with the skeletal vibration ν_f.

Skeletal Frequencies

The skeletal frequencies were treated in conjunction with the corresponding vibrations of thiourea (p. 50). An approximate value for the unobserved frequencies, ν_c and ν_e is calculated from the isotope product theorem in a later section.

Hydrogen Frequencies

The hydrogen frequencies undergo shifts comparable with those of urea upon deuterium substitution. In the D valence region, only low dispersion spectra are available. As with urea, the unpolarized spectrum appears to consist of a doubled envelope of bands. Each envelope consists of more than one component as shown by the failure of the bands to polarize satisfactorily, and by a difference in band width for the low frequency envelope. We consider the reciprocating vibrations, ν_β and $\nu_{\beta'}$ correspond to the high frequency envelope at 2551 cm^{-1}. The low frequency envelope is then assigned to the synchronous vibrations, ν_α and $\nu_{\alpha'}$. The frequency separation between the two envelopes is nearly the same as for urea.

The low frequency band for $\vec{E} \parallel c$ extends about 200 cm^{-1} to lower frequencies. High dispersion investigations would undoubtedly reveal a complex series of bands similar to those observed for normal thiourea.

The scissors bending vibrations, ν_γ and $\nu_{\gamma'}$ appear at 1196 and 1150 cm^{-1} respectively. The corresponding isotopic frequency ratios are $\nu_\gamma(H)/\nu_\gamma(D) = 1.36$ and $\nu_{\gamma'}(H)/\nu_{\gamma'}(D) = 1.41$ respectively. The rocking vibration, ν_δ is assigned to the

A' band at 921 cm^{-1}. The corresponding A" vibration, $\nu_{\delta'}$ is assigned to the weak band at 839 cm^{-1}. The isotopic frequency ratios; $\nu_{\delta}(H)/\nu_{\delta}(D) = 1.18$ and $\nu_{\delta'}(H)/\nu_{\delta'}(D) = 1.26$ are somewhat smaller than expected. It is probable that ν_{δ} interacts considerably with ν_b. This is in accord with the rather large isotope shift observed for the latter band. ν_{ϵ} which appears as an intense broad band in normal thiourea is shifted to lower frequencies and probably accounts for most of the A' absorption below 450 cm^{-1}.

The following table reviews the assignments postulated in the previous discussion and lists tentative assignments for some of the combination and overtone bands.

TABLE XVII

Vibrational Assignment

Fundamentals

A'		A"	
$2551 = \nu_1 = \nu_{\beta}$	$921 = \nu_5 = \nu_{\delta}$	$2551 = \nu_{11} = \nu_{\beta'}$	$839 = \nu_{15} = \nu_{\delta'}$
$2381 = \nu_2 = \nu_{\alpha}$	$668 = \nu_6 = \nu_b$	$2381 = \nu_{12} = \nu_{\alpha'}$	Unobserved
$1404 = \nu_3 = \nu_a$	$617 = \nu_7 = \nu_f$	$1512 = \nu_{13} = \nu_d$	$(\nu_{16} - \nu_{18})$
$1196 = \nu_4 = \nu_{\gamma}$	Unobserved $(\nu_8 - \nu_{10})$	$1150 = \nu_{14} = \nu_{\gamma'}$	

Combinations and Overtones

2890	$\vec{E} \parallel c$	$\nu_3 + \nu_{13}$	1340	$\vec{E} \perp c$	$2\nu_6$
2079	?	?	1311	"	2(652)
1754	"	$\nu_5 + \nu_{16}$	652	"	?

The band at 652 cm^{-1} probably represents an overtone or

combination of lower frequencies which gains intensity by Fermi resonance with ν_b. The band at 2079 cm^{-1} does not polarize well, and an assignment is not attempted.

The absorption near 3400 cm^{-1} is due principally to residual NH stretching vibrations. The weak band at 1093 cm^{-1} represents an NHD rocking vibration corresponding to ν_5 of normal thiourea. The small shoulder at 686 cm^{-1} may correspond to the C=S stretching of incompletely substituted molecules, although the intensity appears slightly greater for $\vec{E} \parallel c$. There appears to be a broad background absorption for $\vec{E} \parallel c$ in the 700-1000 cm^{-1} region similar to that at 900-1200 cm^{-1} in urea and thiourea. It seems likely that low temperature measurements would reveal some structure, probably associated with binary combinations of fundamentals in the 400 cm^{-1} region.

Theoretical Treatment

A. Evaluation of Force Constants

The solution of the secular equation for molecular force constants under an assumed valence force potential is subject to the same limitations discussed for urea.

Using the equations presented in the treatment of urea, (p. 34) the solution of equations 1 to 3 gives imaginary force constants. An approximate real solution derived as for urea gives:

$k_1 = f_{C-S} = 6.05 \times 10^5$ dynes/ cm

$k_2 = f_{C-N} = 5.22$ " " "

$Rk_3 = 1.46$ " " "

The solution of the B_1 equations (4 and 5) gives:

$$k_2 = 7.20 \times 10^5 \text{ dynes/ cm}$$
$$k_4 = .29 \quad " \quad " \quad "$$

Equation 6 yields:

	Thiourea	Deutero-thiourea
$k_5 =$	$.312 \times 10^5$ dynes/ cm ,	$.301 \times 10^5$ dynes/ cm

Similar calculations for the A_1 and B_1 frequencies were not made since the low frequency fundamentals were not observed.

The interpretation of the force constants in terms of resonance energy is somewhat arbitrary since the force constant for a "normal" C=S double bond is difficult to define. The force constant for the C-N bond appears to have a value nearly equal to that in urea. The near equality of the B_1 frequency, ν_d in urea and thiourea for both the hydrogen and deuterium compounds serves to confirm this view. The C-N distance calculated from X-ray data is 1.33 Å, the same as for urea. The C-S distance is .05 Å greater than the sum of double bond radii for carbon and sulfur as given by Pauling (5). The data above are in accord with the values predicted for a resonating molecule.

B. <u>The Isotope Product Rule</u>

The isotope product theorem cannot be applied to thiourea considered as a molecule of symmetry C_s with the available data due to our lack of knowledge of some of the low

frequency fundamentals. However, the formula may be applied to calculate ν_c and ν_e for deutero-thiourea if the molecule is considered to be of symmetry C_{2v}.

From the general formula given on p. 38, we obtain for the right hand side; for species A_1 .2569, for species B_1 .2736. Assuming the same percentage deviation as in urea (2.5%) when the fundamentals are used to approximate the zero order frequencies, we calculate ν_c = 410 cm^{-1} and ν_e = 376 cm^{-1}.

C. Structural Information

Although the gross structural features are known from X-ray work, it is of interest to ask what additional information concerning the structural details, particularly the configuration of the hydrogen atoms, can be proved or even implied from the spectroscopic data.

Information concerning the azimuth of the A' transition moments is provided by polarization measurements in the yz plane. By measuring the absorption coefficient of polarized radiation for $\vec{E} \parallel a$ and $\vec{E} \parallel b$, the ratio of components $|\vec{M}_a / \vec{M}_b|$ of the transition moment of various fundamentals can be determined apart from sign.

The transition moment $\vec{M} = \vec{M}_a + \vec{M}_b$ associated with an A' vibration of one molecule is transformed by the symmetry planes into 4 vectors, $\pm\vec{M}_a \pm\vec{M}_b$. From radiation theory, the transition probability or absorption coefficient for plane polarized radiation with $\vec{E} \parallel a$ will be proportional to $|\vec{M}_a|^2$, while for $\vec{E} \parallel b$, it will be proportional to $|\vec{M}_b|^2$.

(Two additional complications arise in the proposed treatment: first, the anisotropy of polarizability will affect the electric field strength and consequently the absorption coefficient; second, the transition probabilities for combination and difference bands involving lattice vibrations which constitute the natural band width of absorption may be different for the two directions. Both effects will be neglected although it may be mentioned that the first effect should tend to depolarize the absorption, and the second effect, if present, in no way affected the band widths as observed for the two polarizations.)

The molecules are arranged in the crystal lattice in planes making angles $\phi = \pm 25\text{-}26^{\circ}$ with the a axis. If the molecules were entirely planar (symmetry C_{2v}) the vibrations of species A_1 and B_2 would be distinguishable from polarization intensities; the A_1 bands would absorb more strongly along the a axis, while the B_2 bands would appear with greater intensity parallel to b.

All of the A' fundamentals except ν_8 are more intense for $\vec{E} \parallel a$. The table below lists the optical densities at the band maxima for the indicated polarization corrected for the effedt of finite slit width as developed in Appendix I.

TABLE XVIII

Polarization Intensity Ratios and Transition Moment Azimuths of the A' Fundamentals

Sample	Band	Corrected Optical Density $\vec{E} \parallel a$	$\vec{E} \parallel b$	$\theta = \cot^{-1} \lvert \vec{M}_a / \vec{M}_b \rvert$ $\lvert \vec{M}_a / \vec{M}_b \rvert^2$	$\lvert \vec{M}_a / \vec{M}_b \rvert$	θ
1	ν_β = 3390			>1.3	>1.14	<42°
1	ν_α = 3349			"	"	"
1	ν_γ = 1628	.218 ±.01	.133 ±.01	1.64	1.28	38° ± 2°
2	ν_γ = "	.616 .02	.325 .01	1.89	1.37	36 "
1	ν_a = 1416	.70 .02	.46 .01	1.52	1.23	39 "
1	ν_δ = 1088	.279 .02	.172 .01	1.62	1.27	38 "
3	ν_b = 733	1.15 .05	.80 .04	1.44	1.20	40 3°
3	ν_f = 633			>1.25	>1.1	<43
3	ν_ε = 501			$\ll 1$		$\gg 45$

Density measurements were impossible for ν_ε due to the high intensity of the band. ν_f is partially overlapped by this absorption at 501 cm^{-1} making a quantitative measurement unsatisfactory. The polarization of the A' H stretching fundamentals is shown in Figure 17. The effect of instrumental polarization tends to conceal the polarization of the bands, but the fundamentals are definitely polarized more intensely parallel to the a axis. Quantitative measurements were not attempted due to the uncertainty of the ice level in the low temperature spectra.

The angle Ψ between the transition moment and the plane of the molecule is given by: $\Psi = \theta - \phi$. For the skeletal

FIGURE 17

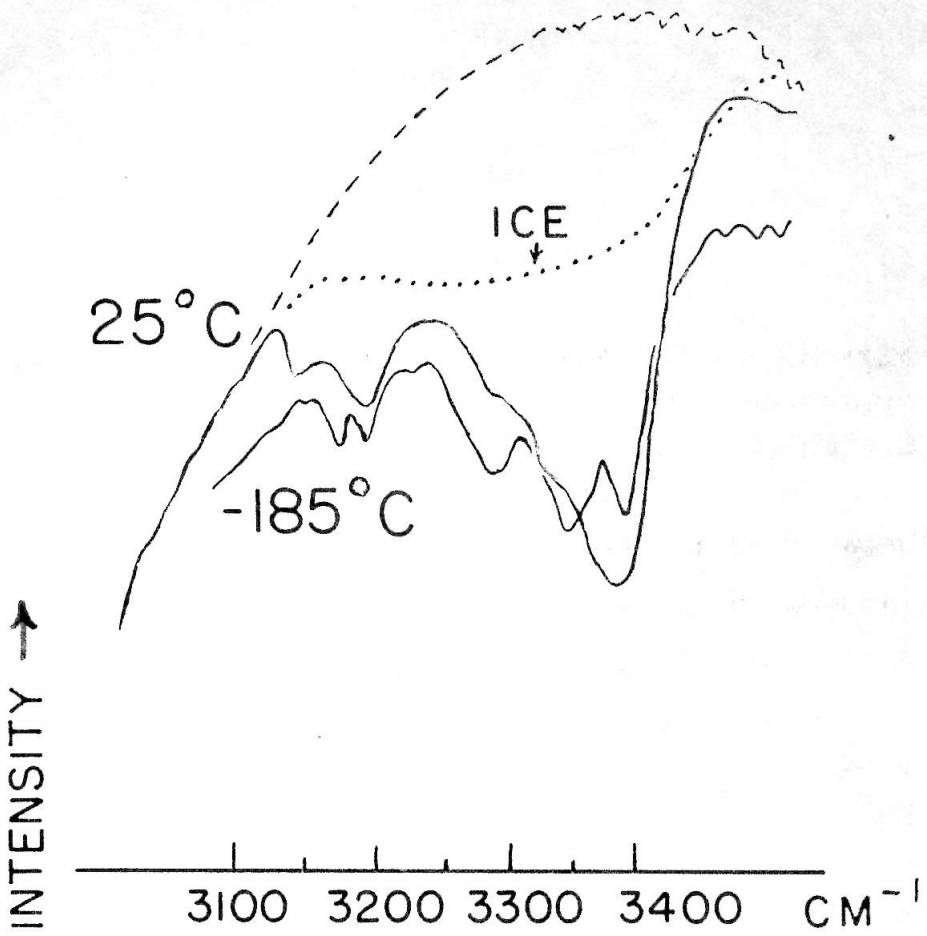
High Dispersion Spectrum of Thiourea from 3000-3500 cm^{-1}

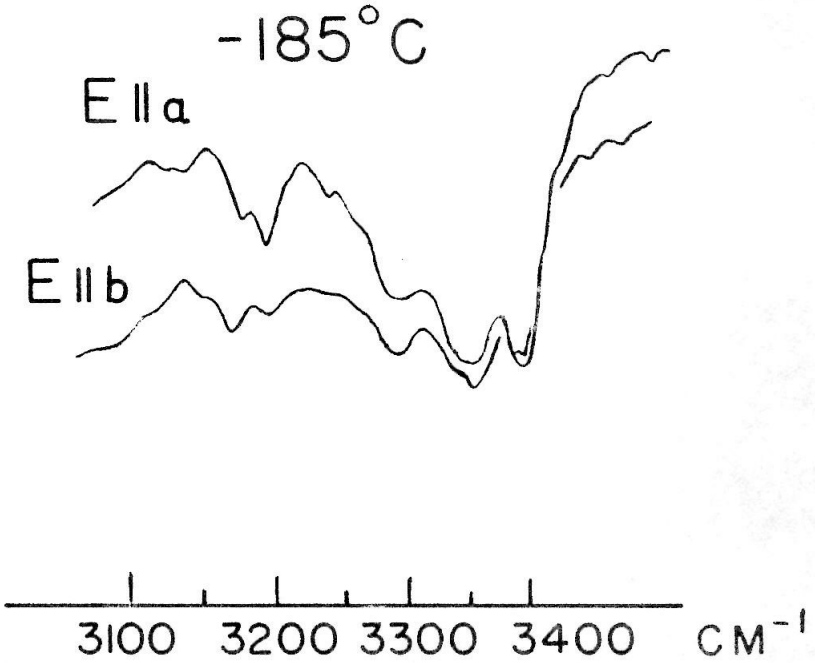
Radiation propagated parallel to the c axis

Top. Unpolarized Spectrum at 25° C and -185° C

Bottom. Polarized Spectrum at -185° C

(The difference in background intensity for the two polarizations is caused by instrumental polarization.)


ICE
25°C
-185°C
INTENSITY
3100 3200 3300 3400 CM⁻¹


-185°C
E ll a
E ll b
3100 3200 3300 3400 CM⁻¹

vibrations, ν_a and ν_b, the transition moment is expected to lie in the plane of the molecule, so for these bands: $\Psi = \theta - 26^\circ = 13$ and 14° respectively. The near equality of θ for all of the A' fundamentals above 700 cm^{-1} suggests that all of these bands are actually polarized in the plane of the molecule, and the slight depolarization (10 - 14°) is due to crystal anisotropy. ν_ε at 501 cm^{-1} clearly corresponds to a B_2 vibration since it is quite strongly polarized $\parallel$ b. ν_f at 633 cm^{-1} may be said to have anomalous polarization. The vibration should give rise to a B_2 band, but the transition moment can at most lie at 69° ($\theta + |\phi|$) from the plane of the molecule. No suitable alternative assignment for this band is obvious to the author.

The ambiguity in Ψ makes it difficult to draw definite conclusions regarding the configuration of the NH_2 group. Three of the N...S distances are less than the sum of the N-H interatomic distance and the van der Waals radii of H and S. The calculated distances and angles are: (Fig. 9)

I	(N•••S)	3.49 Å	(C-N•••S angle)	100°
II	"	3.52 Å	"	119°
III	"	3.65 Å	"	102°

Hydrogen bonds directed along I and III are improbable since ν_β would then be expected to polarize predominantly parallel to the b axis. Bonding to II and III is also unlikely since ν_β would polarize almost completely along the a axis, while ν_α and ν_γ would be essentially depolarized. It seems probable that hydrogen bonds directed roughly along I and II

are actually present in the crystal. The N•••S distances are about .5 Å greater than the N•••O distances in urea; approximately equal to the difference in van der Waals radii of S and O. The sulfur atoms corresponding to bonds I and II are situated 1.6 and .6 Å respectively from the plane of the molecule. The N•••S separations correspond to relatively weak hydrogen bonds, and they would not be expected to distort the NH_2 group appreciably from the planar configuration.

The NH stretching frequencies in thiourea are very nearly the same as for urea showing an average displacement of 33 cm^{-1} toward lower frequencies. The physical properties of thiourea indicate nearly the same hydrogen bond strength as for urea, the melting points of the compounds being 182 and 132° C respectively. The formation of hydrogen bonds to sulfur is unusual, and probably only occurs when the negativity of the sulfur atom is enhanced through resonance or formal charge.

PART III

THE VIBRATIONAL SPECTRUM OF GLYCINE

THE VIBRATIONAL SPECTRUM OF GLYCINE

Introduction

For the application of molecular spectroscopy to the study of proteins, polypeptides, and related natural products, a basic knowledge of the spectra of amino acids is valuable for providing empirical information concerning characteristic frequencies as well as furnishing information pertaining to intermolecular forces, hydrogen bonding, etc.. The study of glycine is of fundamental importance since it represents the simplest compound of the class, and its structure has been determined by X-ray diffraction.

The spectrum of glycine has been investigated previously by a number of workers in the Raman and infra-red fields. Raman spectra of solutions of glycine have been reported by Wright and Lee (26), Edsall (27), Kahovec and Kohlrausch (28), Goubeau and Luning (29), and Sannie and Poremski (30). The Raman spectrum of crystalline glycine was investigated by Kahovec and Kohlrausch (28) and by Ananthakrishnan (11). Infra-red spectra of solutions of glycine in H_2O and D_2O have been given by Barnes, Gore, and Petersen (31), and the crystal was investigated by Wright (32), Duval and Lecomte (33), Lenormant (34), Klotz and Gruen (35), and Kellner (36).

In the present investigation, the infra-red spectrum of single crystals of glycine and deuterium-substituted glycine were examined in the 400-5000 cm^{-1} region with plane polarized radiation.

Experimental

The crystals were grown by cooling a warm saturated solution between compressed glass or AgCl plates. Subsequent evaporation accounted for most of the crystal growth. The crystals on glass plates were removed in the manner described on p. 42. The samples prepared on AgCl were not removed. Deuterium substitution was accomplished by repeated solution and vacuum evaporation of glycine in D_2O. (The CH hydrogen should not exchange appreciably in neutral solution. The samples were actually in solution only a few minutes except for the final evaporation.) Some difficulty was experienced in achieving complete substitution, and the best obtainable sample appeared to retain about 5 % residual replaceable hydrogen.

Crystal orientations were established from interference figures under the polarizing microscope and goniometric measurements. Spectra were obtained for radiation propagated parallel to the b axis and perpendicular to the ab plane.

Discussion

For a discussion of the spectra and interpretation of the polarization of the absorption bands in relation to the electric transition moment associated with the various vibrations, we shall review briefly the crystal structure of α-glycine.

X-ray determinations (37) give the space group C_{2h}^5 P $2_1/n$. Figure 18 shows a perspective view of a crystal and the projection of part of a unit cell upon the ac plane (010).

FIGURE 18

Crystal Structure of Glycine

Top: Crystal Habit

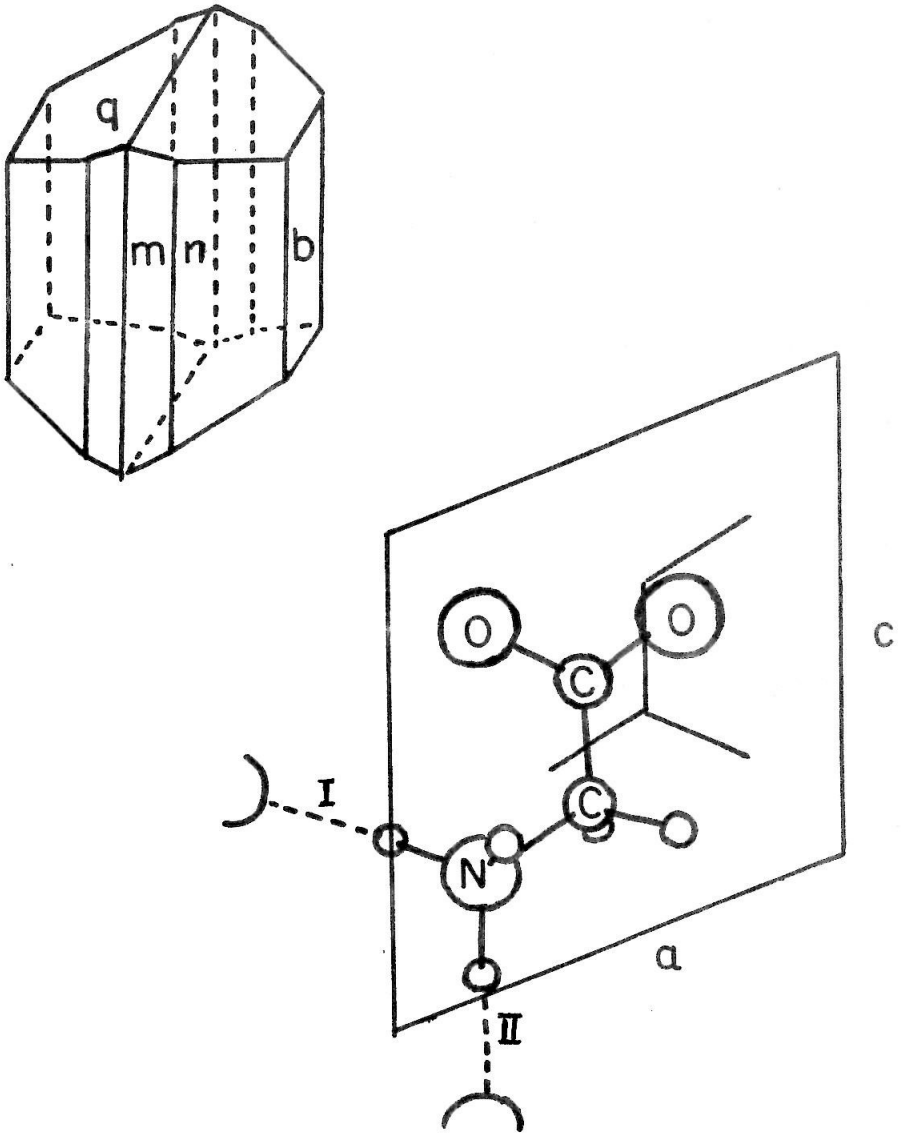
b = 010

m = 110

n = 120

q = 011

Bottom: Projection of Two Molecules on the 010 Plane
There are 4 molecules per unit cell; the remaining pair are related to those given by the n glide plane.
Dotted lines represent hydrogen bonds with N•••O distances:
I 2.88 Å II 2.76 Å


q
m
n
b
O
O
C
C
N
I
II
c
a

An arbitrary vector associated with one molecule is carried by the symmetry operations of the point group into 4 vectors lying in a plane containing the b axis. Thus the spectrum of the crystal viewed along the two-fold axis will show complete polarization, while the spectrum for radiation propagated perpendicular to the b axis will possess a dichroic ratio depending upon the components of the given vector parallel and perpendicular to b in a plane normal to the direction of propagation.

Glycine with 10 atoms has 24 fundamental vibrations without symmetry restrictions. The following spectra show the principal bands in the infra-red above 700 cm^{-1} (Fig. 19).

In first approximation, we may classify the normal vibrations as hydrogen vibrations or skeletal vibrations. The 5 hydrogen atoms contribute 15 degrees of freedom giving 5 stretching and 10 bending frequencies. The heavy atom skeleton may be treated as a 5 particle system with 9 fundamental frequencies.

Hydrogen Vibrations

In the discussion of the hydrogen vibrations we must consider the configuration of the molecule. Substantially conclusive evidence exists in verification of the inner salt or "zwitterion" formula $^{+}NH_3CH_2CO_2^{-}$.(38) Assuming this model, the consideration of the hydrogen vibrations reduces to the motions characteristic of the methylene group, CH_2, and the ammonium group, NH_3^{+}. The 5 H stretching vibrations will be expected to occur in the 2500-3500 cm^{-1} region as in nearly all compounds containing CH and NH bonds.

FIGURE 19

Infra-red Spectrum of Glycine from 700-5000 cm^{-1}

Ordinate: Intensity of transmitted radiation

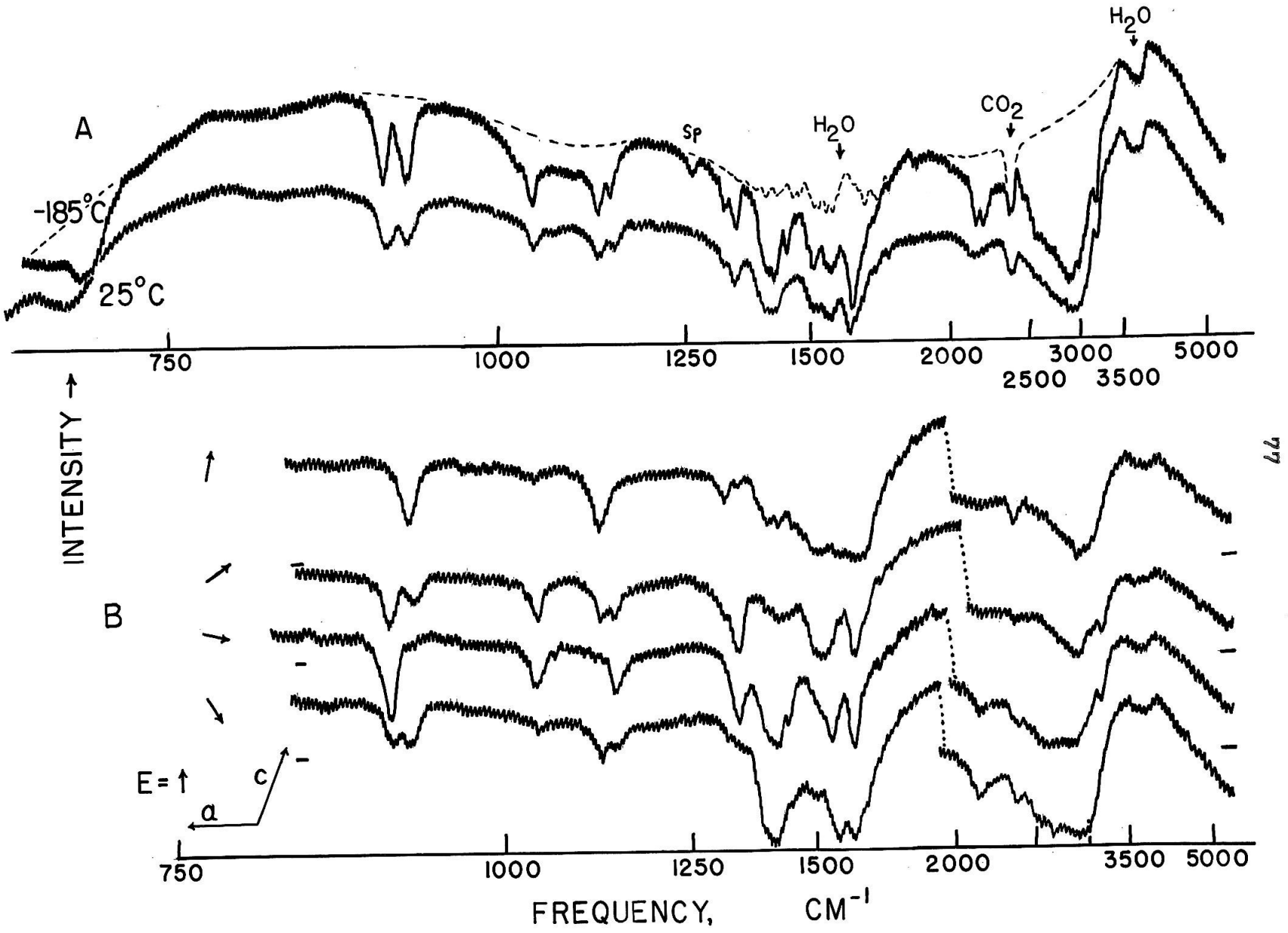
A. Unpolarized Spectrum at 25° C and -185° C

Radiation propagated parallel to the b axis

Sp indicates a spurious band

B. Polarized Spectrum at 25° C

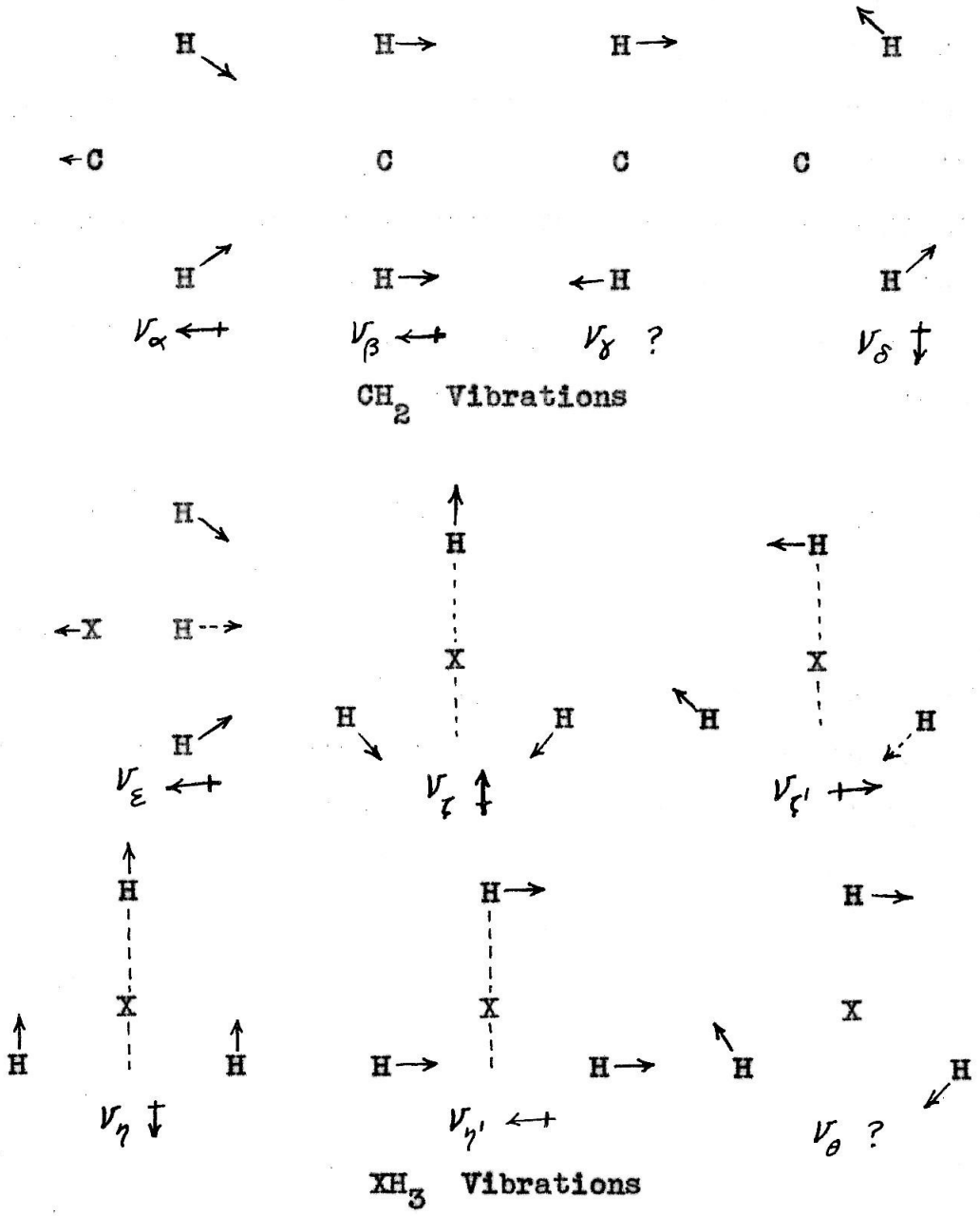
The arrow indicates the direction of the electric vector with respect to the crystallographic axes shown at the bottom of the figure.


A
-185°C
25°C
SP
H_2O
CO_2
H_2O
750
1000
1250
1500
2000
3000
5000
2500
3500
INTENSITY →
B
E = ↑
c
a
750
1000
1250
1500
2000
3500
5000
FREQUENCY, CM^{-1}

The assignment of intermediate frequencies is subject to several limitations: first, the complexity of the spectra with 19 fundamentals below the H stretching frequencies makes a completely unambiguous assignment virtually impossible; second, since no symmetry is present, interaction of all vibrations is allowed and the actual form of the normal vibrations may be poorly approximated by proposed motions of subgroups of atoms within the molecule. Nevertheless, certain statements concerning the vibrations may be made; in particular, characterization of the vibrations in terms of principal contributing motion is possible for certain frequencies.

In the usual approximation of separation of skeletal and hydrogen vibrations, one may predict roughly the frequencies corresponding to bending motions of the CH_2 and NH_3^+ groups from empirical correlations with spectra of hydrocarbons, alkylammonium ions, hydrazinium ions, etc.. The information concerning the NH_3^+ group is less firmly established, but the vibrations should approximate in form those of the CH_3 group whose frequencies are better known.

For the bending vibrations of the CH_2 group, the spectra of propane, long n-paraffins, and polyethylene yield bands which are identifiable with deformations of CH_2 groups. Rasmussen (39) has discussed the assignments of a number of hydrocarbons and considered the problem of characterization of various hydrogen bending frequencies. The approximate form and transition moment of the normal vibrations is illustrated in Figure 20. The scissors vibration, ν_α occurs at about 1460 cm^{-1}, the wagging mode, ν_β near 1350 cm^{-1}, the twisting



Hydrogen Bending Vibrations

FIGURE 20

vibration, ν_γ (weak or absent in the infra-red) near 1300 cm^{-1}, and a rocking mode, ν_δ near 750 cm^{-1}. The last vibration, lying close to the frequencies associated with skeletal

stretching vibrations, appears to be less clearly characterized, and may couple with the latter motions appreciably. There is evidence to indicate that the rocking vibrations may occur at somewhat higher frequencies than the figure cited. (40)

For the prediction of the bending frequencies of the NH_3^+ group, we shall first examine the characteristic frequencies of the CH_3 group. The form of the 6 bending modes and the probable direction of the transition moments are illustrated in Figure 20. In methyl groups, the symmetric bending vibration, ν_ξ occurs commonly near 1380 cm^{-1}, the asymmetric pair, ν_ζ and $\nu_{\zeta'}$ appear near 1460 cm^{-1}. (The latter pair are degenerate in molecules with 3-fold symmetry axes such as the methyl halides.) The rocking frequencies, ν_η and $\nu_{\eta'}$ are somewhat variable in frequency, occurring near 1050 cm^{-1} in unhindered molecules such as methyl acetylene and methyl chloride, but appearing as high as 1150-1200 cm^{-1} and as low as 800 cm^{-1} in certain cases. The torsional motion, ν_θ occurs at about 290 cm^{-1} in ethane. Upon deuterium substitution, shifts occur to the regions indicated below. The results are summarized in the following table (41).

TABLE XIX

Characteristic Frequencies of CH_3 Bending Vibrations

Molecule	ν_ε H	ν_ε D	$\nu_{\zeta,\zeta'}$ H	$\nu_{\zeta,\zeta'}$ D	$\nu_{\eta,\eta'}$ H	$\nu_{\eta,\eta'}$ D	ν_θ H
CH_3Cl	1354.9	1029	1454.6	1058	1015	775	
CH_3Br	1305.1	987	1445.3	1053	952	717	
C_2H_6	1375 1379.1	1158 1072	1472 1460	1102 1055	1190 821.5	970 601	290

For NH_3^+, we expect certain frequency shifts to appear -- presumably to higher frequencies. (Thus the NH_4^+ ion gives frequencies shifted to higher values than in CH_4.) Hydrogen bonding may be expected to raise the bending frequencies also. An examination of the Raman spectra of substituted ammonium ions in solution reveals a high frequency band near 1600 cm^{-1}: $CH_3NH_3^+$ (1620 cm^{-1}), $N_2H_6^{++}$ (1645 cm^{-1}) (42). (These occur in the region of liquid water bands but with considerably greater intensity than the latter.) Upon deuteration, shifts to about 1200 cm^{-1} are observed: $CH_3ND_3^+$ (1190 cm^{-1}), $N_2D_6^{++}$ (1199 cm^{-1}). The Raman spectrum of crystalline $N_2H_6Cl_2$ reveals bands at 1594 and 1519 cm^{-1}. These lines, except 1519 cm^{-1}, probably correspond to ν_ζ and $\nu_{\zeta'}$ since ν_ε appears only weakly in the Raman spectrum. 1519 cm^{-1} may correspond to ν_ε.

For the rocking vibrations, ν_η and $\nu_{\eta'}$, the spectra of $CH_3NH_3^+$, $C_2H_5NH_3^+$, and $N_2H_6^{++}$ reveal bands at 1271, 1205, and a pair at 968 and 1110 cm^{-1} respectively. For the first two cases, there may be considerable interaction with the CH_3

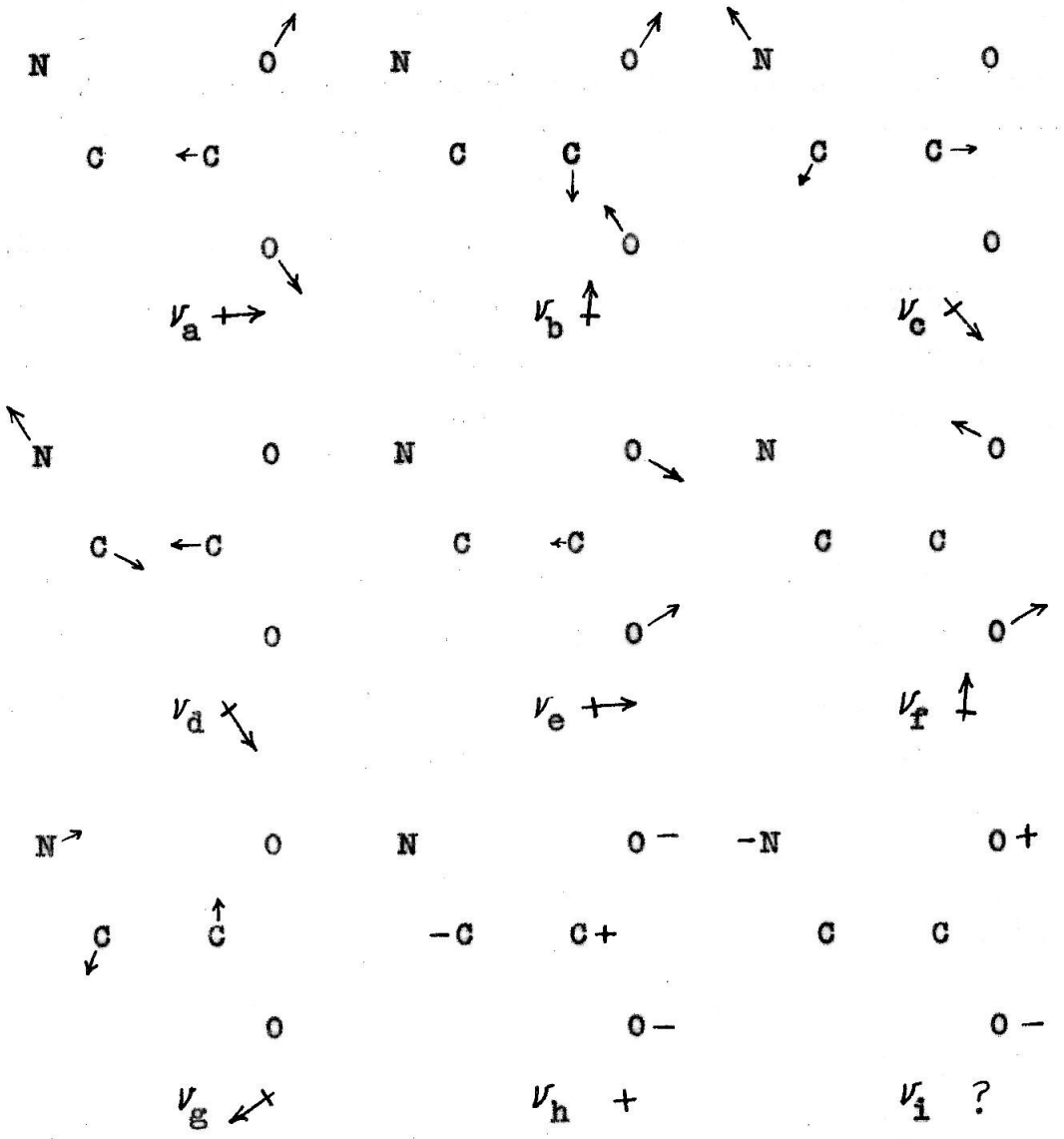
group. The bands corresponding to ν_η and $\nu_{\eta'}$ should occur only weakly in the Raman spectrum, and may easily escape detection. The results of deuterium substitution are not clear. For $CH_3ND_3^+$, no band was reported below the C-N stretching band at 947 cm^{-1}. In $N_2D_6^{++}$, a weak band at 828 or a second at 945 cm^{-1} may be associated with rocking motions. No data are available for torsion.

Skeletal Frequencies

The skeletal vibrations may be discussed in relation to an idealized planar 5-particle system. (X-ray data indicate that the nitrogen atom lies at .27 Å from the plane of the carbon and oxygen atoms.)

There are 9 skeletal vibrations of which 2 involve essentially out-of-plane bending motions. The 7 planar vibrations may be further subdivided into 4 stretching and 3 bending vibrations. A schematic representation of proposed skeletal vibrations is given in Figure 21. Two of the stretching modes will involve synchronous and reciprocating motions of the CO_2^- group corresponding to the degenerate vibration at 1415 cm^{-1} in $CO_3^=$. The 2 remaining skeletal stretching vibrations, ν_c and ν_d involve the elongation of single bonds and are expected to occur in the 1000 cm^{-1} region similar to the corresponding bands in propane.

The bending vibrations are expected to occur near or below 500 cm^{-1}. The vibrations may be described as a scissors bending of the CO_2^- group, ν_e; CO_2^- rocking, ν_f; N-C-C bending, ν_g; and 2 out-of-plane modes, CO_2^- wagging, ν_h; and skeletal



Skeletal Vibrations (Schematic)

FIGURE 21

torsion, ν_i. The low frequencies may not be well characterized by the foregoing descriptions, and probably involve combinations of the group motions.

Before attempting to assign the observed frequencies, we shall examine some empirical data concerning the skeletal

frequencies of related compounds.

Investigations of the infra-red and Raman spectra of carboxylic acids and salts in solutions of H_2O and D_2O have established with some certainty the identification of frequencies near 1410 cm^{-1} and 1560-1620 cm^{-1} with vibrations of the CO_2^- group. (27)(31). Bands appearing at these frequencies undergo modification in acid solution; the band near 1600 cm^{-1} disappearing and a new band appearing near 1730 cm^{-1} characteristic of the C=O group, and the band at 1410 cm^{-1} changing intensity and shifting slightly. These changes are interpreted as arising from conversion of the CO_2^- groups into CO_2H at lower pH.

The two remaining skeletal stretching frequencies are expected in the 1000 cm^{-1} region from empirical and valence force considerations. The Raman spectra of C_2H_6 and $CH_3NH_3^+$ give intense polarized lines at 993 and 998 cm^{-1} respectively (27)(41). The skeletal frequencies in C_3H_8 and $C_2H_5NH_3^+$ occur at 870 and 1053 cm^{-1}, and 873 and 1047 cm^{-1} respectively (27)(39). The almost exact identity of frequencies in the illustrative cases indicates the C-N force constant exceeds the C-C force constant by an amount which virtually compensates for the mass increase in going from a CH_3 to an NH_3^+ group. The frequencies in glycine are thus expected to coincide closely with those of the propionate ion, $C_2H_5CO_2^-$ in which the NH_3^+ is replaced by CH_3.

The bending frequencies of the CO_2^- group would be expected near those in the acetate ion where no other low frequency lines other than a CH_3 torsion would be possible.

Three weak to moderate lines appear in the Raman spectrum at 475, 613, and 652 cm^{-1} (27).

The N-C-C bending vibration, ν_g is expected near that for propane or $C_2H_5NH_3^+$ which occur at 374 and 411 cm^{-1} respectively.

The proposed directions of transition moments are based on simple fixed charge models with dipole moment a linear function of interatomic distance. For vibrations in which the chief contributing motion consists of the movement of nearly neutral groups, the effect of small motions of charged groups may be expected to alter markedly the direction of the change in dipole moment.

Interpretation of the Observed Spectrum

The following table lists the frequencies, azimuths and relative intensities of the infra-red bands.

TABLE XX

Infra-red Absorption Bands of Glycine

Frequency	Azimuth		Density	Frequency	Azimuth		Density
3221	$85^\circ \pm 10^\circ$		.50	1406	$125^\circ \pm 7$		1.3
3120				1391	18	10	.4
2950	22	15	2-5	1337	70	5	.85
2899				1309	19	7	.20
2732				1138	87	7	.30
2633	139	15	.5-1	1116	13	5	.41
2577				1038	74	5	.25
2460	67	15	.1	915	18	5	.35

TABLE XX (CONTINUED)

Frequency	Azimuth	Density	Frequency	Azimuth	Density
2155	130° ± 10°	.3	895	86° ± 7°	.50
1618	14 15	1.4	693	156 7	.75
1562	147 15	1.1	607	113 7	.27
1524	41 7	1.35	521	137 10	.20
1445	117 15	.5	502	91 7	.72

The azimuth is the position of maximum absorption measured clockwise from the vertical in Figure 19. (This corresponds to the clockwise angle from a line perpendicular to the a axis in Figure 18; e.g. the azimuth of the c axis is 22°) The density represents the optical density of a reference thickness for polarizer set at band azimuth.

Examination of the spectrum reveals a broad region of absorption of irregular outline in the hydrogen valence region extending from about 3200-2500 cm^{-1}. This region should contain the 5 H-stretching fundamentals and will be discussed later.

In the 1300-1700 cm^{-1} region, 5 strong bands are observed with at least 3 weaker bands present. In accord with the previous discussion, we assign the bands at 1618 and 1406 cm^{-1} to ν_a and ν_b respectively. The band at 1562 cm^{-1}, although lying closer to ν_a for acetate or propionate ion, is incompatible with polarization measurements. The corresponding frequency in deutero-glycine occurs at 1642 cm^{-1} which supports the above assignment.

The bands at 1562 and 1524 cm^{-1} occurring at higher fre-

quencies than commonly attributed to CH bending vibrations are then assigned to the bending vibrations of the NH_3^+ group, ν_ζ, $\nu_{\zeta'}$, and ν_ε. The polarization of 1524 cm^{-1} does not lie along the C-N axis as expected for ν_ε, but the difference in hydrogen bond strength between the individual H atoms introduces some asymmetry into the group. Some interaction with the skeletal vibrations may also occur. The band at 1562 cm^{-1} corresponds to the asymmetric pair of vibrations, ν_ζ and $\nu_{\zeta'}$ which are degenerate in the symmetric top molecules. The incomplete polarization of this band indicates a superposition of frequencies. The remaining strong band at 1337 cm^{-1} is then assigned to ν_β in agreement with its polarization azimuth.

In the region between 800 and 1300 cm^{-1}, there are observed 5 bands of medium to high intensity. The Raman spectrum gives an intense line at 895 cm^{-1} and a medium strength line near 1040 cm^{-1} at nearly the same frequencies as the skeletal vibrations previously stated for C_3H_8 and $C_2H_5NH_3^+$. The Raman spectrum of sodium propionate yields strong lines at 886 and 1078 cm^{-1} which may be attributed to skeletal stretching vibrations (27). The infra-red spectrum was recorded in this laboratory yielding lines at 884 and 1080 cm^{-1}.

The bands at 895 and 1038 cm^{-1} in glycine are accordingly assigned to the skeletal vibrations, ν_c and ν_d respectively. The polarization of both bands is essentially along the C-N axis as expected since the NH_3^+ group is the most highly charged unit involved in the motions.

Two of the remaining bands must be assigned to the NH_3^+

rocking vibrations, ν_η and $\nu_{\eta'}$. The spectrum of sodium propionate reveals CH_3 rocking bands at 817 and 1008 cm^{-1}. We expect the NH_3^+ bands at slightly higher frequencies and assign the bands at 915 and 1116 cm^{-1} to the rocking vibrations, ν_η and $\nu_{\eta'}$. The higher frequency line at 1138 cm^{-1} probably represents a combination band gaining intensity by Fermi resonance with 1116 cm^{-1}. The isotope shift of the band at 915 cm^{-1} upon deuterium substitution is rather low (frequency ratio = 915/ 766 = 1.19) indicating some interaction with skeletal or CH vibrations.

Below 800 cm^{-1}, 4 bands are observed at 693, 607, 521, and 502 cm^{-1}. The polarization of the band at 693 cm^{-1} suggests its assignment as ν_δ. The frequency is lower than that usually ascribed to CH_2 rocking motions. The band at 607 cm^{-1} has a large component of the transition moment along the b axis and is assigned to the out-of-plane vibration, ν_h. The remaining bands at 521 and 502 cm^{-1} must correspond to bending vibrations involving combinations of ν_e and ν_f. Since none of the low frequency bands are polarized along the C-C axis, it is probable that no pure symmetric CO_2^- bending mode, ν_e exists. ν_g, ν_i, and ν_θ probably occur below 400 cm^{-1}. Kahovec and Kohlrausch reported a weak line in the Raman spectrum at 236 cm^{-1} which may correspond to either ν_i or ν_θ.

Among the weaker bands observed, the absorption at 1445 cm^{-1} is logically assigned to the CH_2 scissors bending vibration, ν_α. A very weak band observed at 1210 cm^{-1} may possibly correspond to the CH_2 twisting vibration, ν_β. This band was also reported by Kahovec and Kohlrausch.

The band at 2155 cm^{-1} probably represents a combination band of vibrations from the 1500 and 600 cm^{-1} regions.

The Hydrogen Valence Region

In the H valence region, the broad area of absorption separates into a number of bands upon cooling the sample to liquid N_2 temperatures. The use of extremely thin samples (Fig. 22) revealed two broad absorption bands near 2950 and 2600 cm^{-1} which contribute most of the intensity to the region. The high frequency band does not polarize completely, and appears to consist of an overlapping of several bands. The low frequency band polarizes essentially along the NH bond I (Fig. 18). The N•••O distance along I is 2.88 Å as determined from X-ray parameters. No distinct band polarized along the short hydrogen bond II (2.76 Å) is observed. The spectral absorption corresponding to such a short interatomic distance generally appears as a greatly broadened band, which may escape detection in thin sections. There appears to be a general background absorption extending past 2000 cm^{-1}, which may correspond to such a band.

We consider the band at 2950 cm^{-1} to correspond to the 2 CH stretching vibrations superimposed upon the NH stretching vibration directed along the long hydrogen bond (3.05 Å) perpendicular to the ac plane. The band at 2633 cm^{-1} is assigned to the stretching of the NH bond I . The absorption due to NH stretching along II is probably very diffuse and should occur at 2500 cm^{-1} or lower. The form of the normal vibrations corresponding to the bands near 2950 cm^{-1} probably

FIGURE 22

Low Dispersion Spectrum of Glycine and 10% D-Glycine

Top: Spectrum of glycine from 2400-3200 cm^{-1}

A. Unpolarized spectrum at 25° C and -185° C

B. Polarized spectrum at -185° C

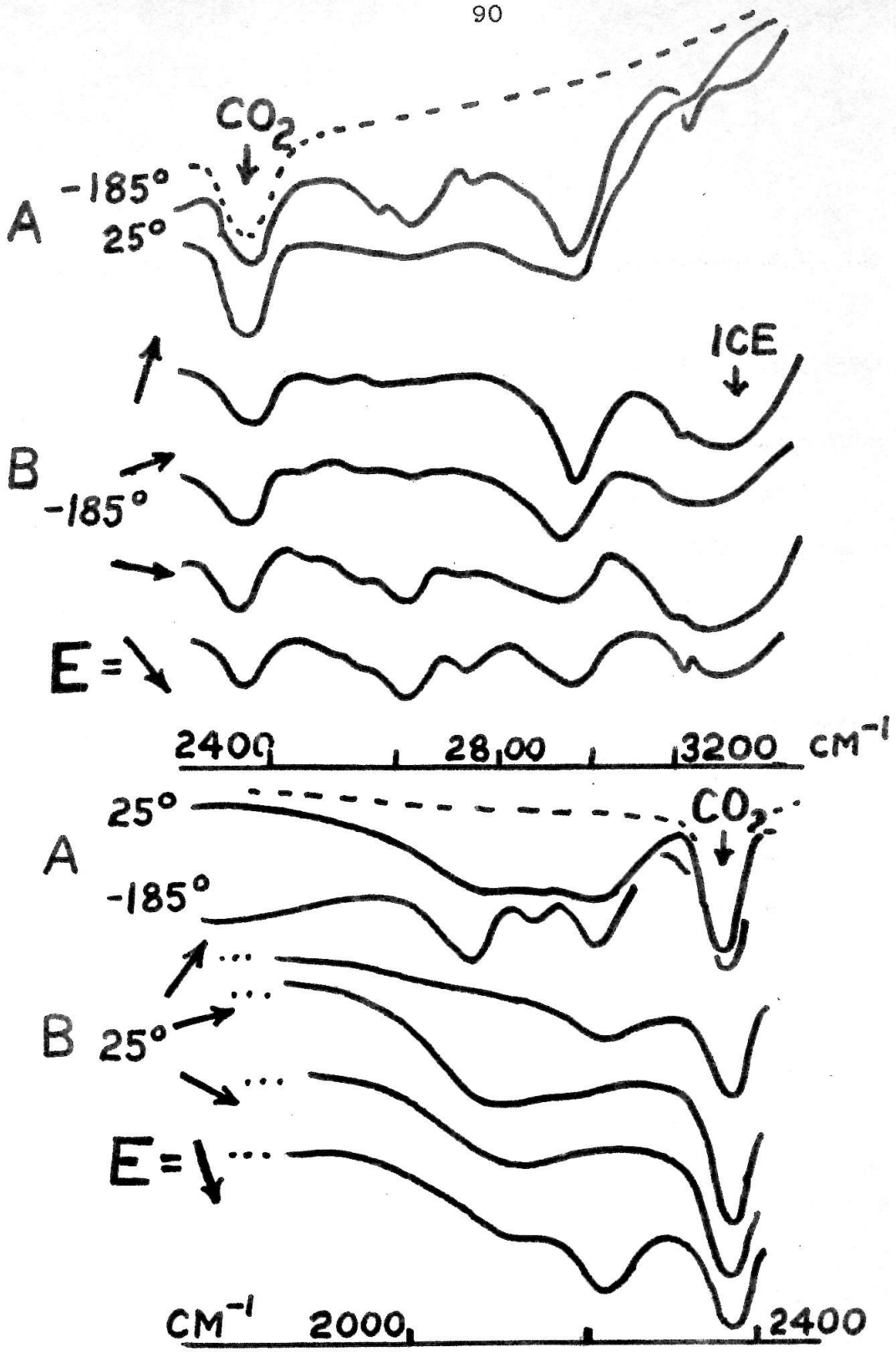
The arrow indicates the direction of the electric vector: a axis horizontal, c axis 22° clockwise from vertical.

Bottom: Spectrum of 10% Deutero-Glycine from 2000-2400 cm^{-1}

A. Unpolarized spectrum at 25° C and -185° C

B. Polarized spectrum at 25° C

(See B above)


CO2
A
-185°
25°
ICE
B
-185°
E =
2400
2800
3200
cm-1
25°
CO2
A
-185°
B
25°
E =
cm-1
2000
2400

involves combinations of CH and NH stretching motions. There is probably some interaction of the other NH vibrations also. A considerable simplification of the NH stretching vibrations is possible for the case of partially deuterated glycine which is discussed later.

The frequencies attributed to NH stretching vibrations are considerably lower than those occurring in most ammonia derivatives. The frequency shifts are not abnormal, however, when compared with the NH stretching frequencies of tetracoordinate nitrogen. The NH stretching frequencies in crystalline NH_4Cl and NH_4Br occur near 3040 cm^{-1} (symmetric), and 3130 cm^{-1} (degenerate).(43) The additional shifts are attributed to hydrogen bonding.

DEUTERIUM SUBSTITUTED GLYCINE

The spectrum of deuterium substituted glycine was investigated to aid in the assignment of the glycine frequencies and to obtain additional information concerning the hydrogen bonds.

The spectrum of deutero-glycine is reproduced in Figure 23, which gives the polarization spectra for radiation propagated parallel to the b axis in the 700-5000 cm^{-1} region.

The table below lists the frequencies, azimuths and approximate densities of the absorption bands.

FIGURE 23

Infra-red Spectrum of Deutero-glycine from 700-5000 cm^{-1}

Ordinate: Intensity of transmitted radiation

A. Unpolarized Spectrum

Radiation propagated parallel to the b axis

B. Polarized Spectrum

The arrow indicates the direction of the electric vector with respect to the crystallographic axes shown at the bottom of the figure.

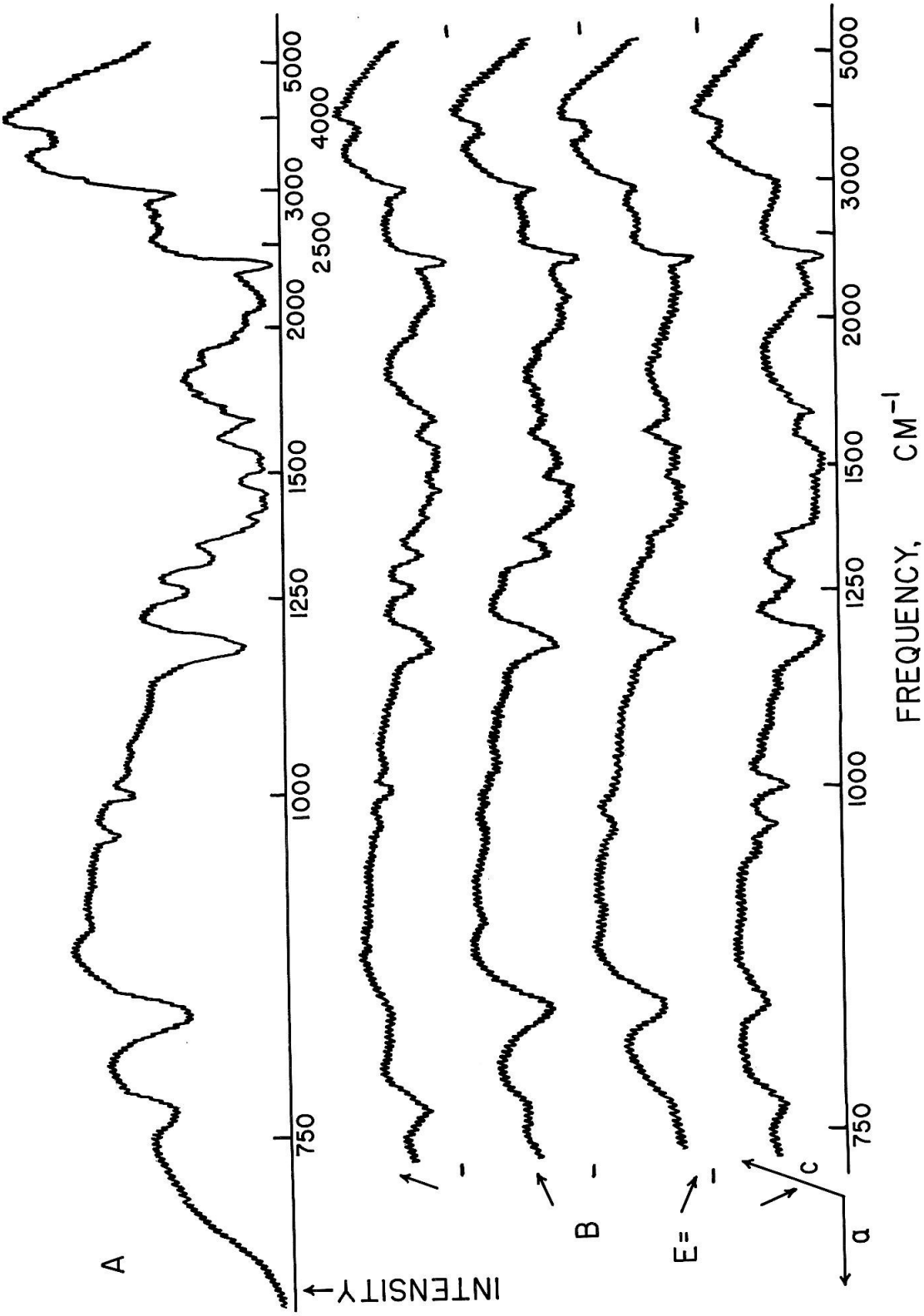

A
INTENSITY
B
E=
c
a
750
1000
1250
1500
2000
2500
3000
4000
5000
FREQUENCY, CM⁻¹

TABLE XXI

Infra-red Absorption Bands of Deutero-glycine

Frequency	Azimuth	Density	Frequency	Azimuth	Density
3040		.4	1271	$174^\circ \pm 10^\circ$	.38
2155			1185		.75
2041		2-4	1003	165 10	.29
1972			966	157 15	.15
1642	$44^\circ \pm 20^\circ$	1	828	97 10	.50
1529	172 20	1.5	766	17 10	.36
1451	92 25	1.5-2	670	122 15	.16
1403	137 20	1	600	22 20	.16
1328	49 10	.4	503	54 15	.22

As before, the azimuth represents the position of maximum absorption measured clockwise from the vertical in Figure 23. The density refers to the optical density at band azimuth.

The presence of residual hydrogen complicates the spectrum above 1400 cm^{-1}, due to vibrations of NHD_2^+ groups. The band envelopes in the 2000 cm^{-1} and 3000 cm^{-1} regions are poorly resolved as a consequence. The narrow band near 3040 cm^{-1} appears to be due mainly to CH vibrations, since its intensity remains roughly constant in later stages of deuteration. The weak bands near 2800 cm^{-1} are undoubtedly due to the stretching vibrations of residual NH bonds.

Interpretation of the Observed Spectrum

The 2 CH stretching vibrations are assigned to the band at 3040 cm^{-1}. In the ND valence region, a broad irregular

band envelope is observed with slight intensity maxima near 2155, 2041, and 1972 cm^{-1}. The polarization in this region is obscured, due in part to overlapping of the fundamentals, and in part to ND vibrations associated with NHD_2^+ groups.

In the 1500 cm^{-1} region, 4 strong bands are observed at 1642, 1529, 1451, and 1403 cm^{-1}. We attribute the bands at 1642 and 1403 cm^{-1} to ν_a and ν_b, the synchronous and reciprocating vibrations of the CO_2^- group. The polarizations are roughly in agreement with prediction, but the precision is low due to the high density of the bands and overlapping NH bending frequencies. The bands at 1529 and 1451 cm^{-1} are probably largely due to residual NH bending vibrations, although the latter band occurs where ν_α is expected.

Between 1100 and 1400 cm^{-1}, there are observed 3 strong bands. The absorption at 1328 cm^{-1} corresponds in polarization to the band at 1337 cm^{-1} in normal glycine (G-1337), and is assigned to the CH_2 wagging vibration, ν_β. The remaining bands at 1271 and 1185 cm^{-1} are assigned to the bending vibrations of ND_3^+ groups, ν_ζ, $\nu_{\zeta'}$, and ν_ε. The polarization of 1271 cm^{-1} is shifted slightly from that of G-1562, while the band at 1185 cm^{-1} does not polarize appreciably. The latter band probably represents a superposition of $\nu_{\zeta'}$ and ν_ε. The isotope shifts give frequency ratios ranging from 1.23 to 1.32 which are somewhat smaller than would correspond to pure NH (or D) bending modes.

The spectrum from 700-1100 cm^{-1} reveals strong bands at 766 and 828 cm^{-1} with weaker bands at 1003 and 966 cm^{-1}. A slight residual absorption occurs near 900 cm^{-1} as well as

weak absorption near 1050 cm^{-1} due to partially substituted molecules.

The substitution of deuterium for hydrogen will probably alter the form of the skeletal stretching vibrations, ν_c and ν_d, since the characteristic frequencies for C-C and C-N stretching will no longer coincide. The polarization of the skeletal frequencies supports this premise; only one band in the region being polarized along the C-N axis. This band at 828 cm^{-1} is assigned to a C-N stretching vibration. The C-C stretching vibration must correspond to either 1003 or 966 cm^{-1} which polarize at practically the same azimuth. One cannot confidently predict the direction of polarization for a C-C stretching vibration, since even slight coupling with hydrogen motions would introduce a significant component to the transition moment.

The band at 766 cm^{-1} is polarized the same as G-915 and is assigned to an ND_3^+ rocking vibration, ν_η. The isotopic ratio: 915/ 766 = 1.19 is again abnormally low indicating interaction with other vibrational modes. The remaining ND_3^+ rocking frequency was not observed.

Below 700 cm^{-1}, bands are observed at 670, 600, and 503 cm^{-1}. The low frequency line is appreciably broadened, and may consist of more than one component.

The band at 670 cm^{-1} is assigned to the CH_2 rocking vibration, ν_δ corresponding to G-693. The polarization has shifted somewhat; the agreement with prediction being better than for normal glycine. The band at 600 cm^{-1} is assigned to ν_h; the corresponding band is G-607. The polarization azi-

muth has rotated 90° from that of G-607, but the chief component is probably parallel to the b axis. The band at 503 cm^{-1} probably represents a planar bending vibration corresponding to G-502.

The following table summarizes the assignment of fundamental vibrations for glycine and deutero-glycine.

TABLE XXII

Vibrational Assignment

Glycine		Vibration	D-Glycine
2950		NH (D) stretching	2155
2633			2041
(2400-2500)?			(1850-2000)?
2950 (2)		CH stretching	3040 (2)
1618	ν_a =	CO_2^- synch. stretching	1642
1406	ν_b =	" recip. stretching	1403
607	ν_h =	" wagging	600
1524	ν_ε =	NH_3^+ (D) sym. bending	1185
1562 (2)	$\nu_{\zeta,\zeta'}$ =	" asym. bending	1185, 1271
1445	ν_α =	CH_2 scissors bending	(1450)?
1337	ν_β =	" wagging	1328
(1210)?	ν_γ =	" twisting	
693	ν_δ =	" rocking	670
1116, 915	$\nu_{\eta',\eta}$ =	NH_3^+ (D) rocking	? , 766
895	ν_c =	N-C-C sym. stretching	828 (C-N)
1038	ν_d =	" asym. stretching	1003 or 966
521, 502		skeletal bending	503

Partially Deuterated Glycine

In order to gain more specific information on the relation between hydrogen bond strength and vibrational frequency of the NH linkage, a partially deuterated sample was prepared containing deuterium substituted for about 10 % of the replaceable hydrogen. It was reasoned that whereas the NH vibrations in an NH_3^+ group probably interact considerably with one another as well as with CH bonds, the ND stretching vibration in an NH_2D^+ group would be expected to oscillate nearly independently of the other atoms. In the crystal lattice, the ND bond should be distributed practically at random between the various hydrogen bond positions, and the spectrum should consist of bands polarized essentially along the ND bonds with frequency shifts characteristic of the particular hydrogen bond involved.

This expectation is confirmed in part by the observed spectrum. The spectrum at room temperature and at -185° C reveals two bands in the 2000 cm^{-1} region in addition to the glycine combination band at 2155 cm^{-1}. The low frequency line at 2066 cm^{-1} (Fig. 22) occurs at an azimuth of 99° ± 15° and must correspond to an ND stretching vibration along the hydrogen bond I (Fig. 18). A high frequency line occurs at 2203 cm^{-1} and azimuth 0° ± 15° which probably corresponds to ND bonds directed along the weak hydrogen bond perpendicular to the ac plane (010). This bond has been reported to be of the bifurcated type (37), with N···O distances of 3.05 and 2.93 Å. The bond angle favors the direc-

tion of the hydrogen atom toward the oxygen atom at 3.05 Å from the nitrogen atom.

A third band corresponding to the short hydrogen bond II was not observed. Presumably it would occur at lower frequencies and probably becomes extremely broadened so as to be undiscernible. The N•••O distance for this bond (2.76 Å) is one of the shortest known for an NH•••O hydrogen bond, and the NH stretching frequency would be expected to be extremely diffuse. The frequencies above may be compared with the "normal" frequencies for ND stretching in the deutero-ammonium halides:(45)

ND_4Cl	$\nu_1 = 2214\ cm^{-1}$,	$\nu_3 = 2350\ cm^{-1}$
ND_4Br		$\nu_3 = 2358$ "

Applications

The use of polarization data would seem to be of general applicability in the determination of group orientations in solid phases. The polarization seems to agree within 15 or 20 degrees with that predicted for the vibrations of polar constituents. The technique of partial deuteration may be of value in the study of amines, complex ions, and hydrates. The frequency of the ND stretching seems to be a sensitive function of the hydrogen bond distance, but quantitative treatment must await the compilation of data from several compounds.

CONCERNING THE STRUCTURE OF l-LEUCINE

Certain empirical information derived from the spectrum of glycine can be used to advantage in the interpretation of the spectrum of l-leucine, 2-amino-4-methylpentanoic acid. The polarization studies may then be used to ascertain the lattice orientation of certain molecular substituents.

A search of the literature failed to reveal any X-ray diffraction studies on l-leucine. The macroscopic crystallography was studied by Takahashi, Yaginuma, and Hayakawa (44), who reported the compound as crystallizing in the orthorhombic system with axial ratio a:b:c = 1.5155:1:1.0035. The refractive indices and optic axes were also reported.

Experimental

Leucine crystallizes in thin sheets parallel to 101. Single crystals were obtained in ribbons elongated parallel to the b axis. The a and c axes were probably correctly identified with a polarizing microscope, although the interference figures were not well formed. The crystals were mounted in the reflecting microscope, and polarization spectra for $\vec{E} \parallel$ and $\perp$ b were taken. In addition, studies were made by rotating the sample about the b axis $\pm 45^{\circ}$ with polarization $\vec{E} \perp$ b. This gave essentially the polarization along the a and c axes.

Discussion

Since no symmetry elements of the second kind are permitted, the only point group consistent with orthorhombic symmetry is D_2. The general position is 4-fold. The presence of at least a half dozen infra-red bands polarized almost completely along the crystallographic axes makes it very probable that only 4 molecules are present per lattice point.

The infra-red spectrum of l-leucine is extraordinarily rich in lines as expected from the complexity of the molecule. The 22 atoms would give rise to 60 fundamental modes of vibration. The identification of characteristic frequencies is consequently subject to some uncertainty, since a complete assignment is out of the question.

The absorption bands in the 3000 cm^{-1} region give an appearance similar to glycine. This fact plus the absence of characteristic C=O stretching vibrations near 1700 cm^{-1} leads to the conclusion that leucine, like glycine, is a "zwitterion". Two of the hydrogen bond distances are probably nearly the same as the longer bonds in glycine (2.88 and 3.05 Å) judging from the observed frequencies. The shorter bond of the pair lies approximately in the 010 plane.

At lower frequencies, strong bands are observed at 1618 and 1411 cm^{-1} which we consider to be due to the synchronous and reciprocating vibrations of the CO_2^- group. The 1618 cm^{-1} band is polarized largely along the b axis, and slightly stronger in the 001 plane. The band at 1411 cm^{-1} is polarized almost completely in the 010 plane slightly stronger

parallel to the c axis. This suggests that the CO_2^- group is oriented with the O-O axis in the 010 plane and the bisector of the O-C-O angle directed about 20° from the b axis and lying not too far from the 001 plane.

At 849 cm^{-1}, an intense band occurs which we consider as due to the C-N stretching vibration. This band is polarized roughly in the 010 plane and predominantly along the a axis. We accordingly consider the C-N bond to lie in this direction. A strong band at 1366 cm^{-1} is assigned to the group of symmetric CH_3 bending vibrations. The absorption is polarized almost completely in the 010 plane with no indicated azimuth. This would tend to indicate the isopropyl group lies in the 010 plane.

A band at 775 cm^{-1} is assigned to the CH_2 rocking vibration. This band is polarized nearly completely in the 001 plane and largely along the a axis. This direction is considered to correspond to the H-H axis of the CH_2 group.

The previous group orientations can be assembled into several molecular models. A choice could probably be made with a knowledge of the space group and unit cell dimensions.

The foregoing data would be useful in setting up a trial structure if an X-ray study were undertaken. A spectrum of deutero-leucine would be helpful in verifying the orientation of the C-N bond.

APPENDIX I

Correction of observed optical densities for the effect of finite slit width:

The intensity I of transmitted radiation may be expressed as a function of wavelength

$I(\lambda) = I_o(\lambda) \exp -d(\lambda)$ where I_o is the incident intensity and d is the absorption coefficient.

The observed density is given by

$-d' = \ln \bar{I} / \bar{I}_o$ where $\bar{I}$ is the weighted average intensity; $\bar{I} = \int I(\lambda)\, g(\lambda)\, d\lambda$ where $g(\lambda)$ is the transmission function of the instrument.

Assume $g(\lambda) = |s - \Lambda|$, $\Lambda \leq s$

$= 0$, $\Lambda > s$ where $\Lambda = \lambda - \lambda_o$

Then $d' = \ln \int_{-s}^{s} |s - \Lambda|\, I_o(\lambda)\, d\Lambda - \ln \int_{-s}^{s} |s - \Lambda|\, I(\lambda)\, d\Lambda$

Assuming the band and background are symmetrical about the band center λ_o, we have

$$d' = \ln 2 \int_o^s (s - \Lambda) I_o(\lambda)\, d\Lambda - \ln 2 \int_o^s (s - \Lambda)\, I(\lambda)\, d\lambda$$

Substituting and assuming $I_o(\lambda)$ is a constant

$$d' = - \ln 2 / s^2 \int_o^s (s - \Lambda) \exp(-d(\lambda))\, d\Lambda$$

Two expressions for $d(\lambda)$ will be treated: I, $d(\lambda) = d_m \exp(-\frac{1}{2}(\Lambda / L)^2)$; II, $d(\lambda) = d_m / (1 + (\Lambda / L)^2)$

where d_m is the density at band maximum, L is a band width parameter -- standard deviation and half width respectively.

Case I

$$\int_o^s (s - \Lambda) e^{-d_m} \exp(-\tfrac{1}{2}(\Lambda/L)^2)\, d\Lambda = L^2 \int_o^n (n - x) e^{-a} \exp -\tfrac{1}{2}x^2\, dx$$

The integrand is expanded in a power series:

This wave form for a square slit function has been treated previously (45). (A typographical error was determined in this reference.)

$$e^{-a} \exp -\tfrac{1}{2}x^2 = e^{-a}\left[1 + ax^2/2 + (a^2 - a)x^4/8 + (a^3 - 3a^2 + a)x^6/48 + (a^4 - 6a^3 + 7a^2 - a)x^8/384 + \ldots\right]$$

Substituting and integrating:

$$d' = d_m - \ln\left[1 + an^2/12 + (a^2 - a)n^4/120 + (a^3 - 3a^2 + a)n^6/1344 + (a^4 - 6a^3 + 7a^2 - a)n^8/17280 + \ldots\right] \quad \text{where } a = d_m$$

Case II

$$\int_o^S (s - \Lambda) \exp(-d_m/1 + (\Lambda/L)^2)\, d\Lambda = L^2 \int_o^n (n - x) \exp(-a/1 + x^2) dx$$

$$= e^{-a} \int_o^r e^{au^2} \left[n(1 - u^2)^{-3/2} - u(1 - u^2)^{-2}\right] du \quad \text{where } r = n/\sqrt{n^2 + 1}$$

The integrand is expanded in power series:

$$\int f(n,u)\, du = \int \left[n - u + (3/2 + a)nu^2 - (2 + a)u^3 + (15/8 + 3a/2 + a^2/2)nu^4 - (3 + 2a + a^2/2)u^5 + (35/16 + a15/8 + 3a^2/4 + a^3/6)nu^6 - \ldots\right] du$$

We obtain

$$d' = d_m - \ln q\left[2 - q + (1 + 2a/3 - q - aq/2)r^2 + (3/4 + 3a/5 + a^2/5 - q - 2aq/3 - a^2q/6)r^4 + (5/8 + 15a/56 + 3a^2/14 + a^3/21 - q - 3aq/4 - a^2q/4 - a^3q/24)r^6 + (35/64 + 35a/72 + 5a^2/24 + a^3/18 + a^4/108 - q - 4aq/5 - 3a^2q/10 - a^3q/15 - a^4q/120)r^8 + \ldots\right] \quad \text{where } a = d_m \text{ and } q = 1/\sqrt{n^2 + 1}$$

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Propositions presented by Robert D. Waldron

1. The formula of cyanamide is generally given as NH_2CN. I propose that the most stable structure for cyanamide vapor is the diimide form; HNCNH.

2. The overtone of the hydrogen stretching vibration of strongly hydrogen bonded substances is missing from the 5500-7000 cm^{-1} region or at least very weak. I propose that the second or third vibrational levels are broadened due, in part, to passage of the hydrogen atom through a potential barrier to the acceptor atom (quantum-mechanical "tunneling"). A study of the fundamentals and possibly overtones of deuterium and tritium derivatives would be useful in providing information concerning the potential energy of hydrogen bond formation.

3. The crystal structure of l-leucine could be determined from the space group and unit cell dimensions, together with infra-red polarization data (Thesis, p. 99).

4. The fractional change in frequency for diatomic hydrides, XH, with change in ionization follows the approximate relation:

$$\frac{\Delta\nu/\nu}{\Delta E} = c\,\Delta q$$

where ΔE is the electronegativity difference of X and H, Δq is the change in charge.

This relation is of general applicability and may be used to predict the stretching frequencies of polyhydrides and ions; H_3O^+, OH^-, CH_3^+, CH_3^-, NH_2^-, PH_4^+, etc..

5. The existence (1) of optically active carbanions suggests that active forms of cyclic imines should be capable of existence. I propose that attempts be made to resolve cyclic imines

with added stabilization of intramolecular hydrogen bonds; e.g., hydroxylamine or alkanolamine derivatives and fluorocarbons, or N-fluoroalkyl derivatives and alkanols.

6. A variation-perturbation theory for potential functions with more than one pole. Assume the perturbation function H' expressible as a power series with a finite number of negative exponents in r as perturbing H°, an entire function whose wave equation solution is known. (ψ°) If the value of the unperturbed wave function at the pole is B, choose as the variation function $\phi = \psi^{\circ} - B\,g(r)$ where $g(r) = \exp -\lambda r$ or some other suitable function. Now evaluate the integrals: $(\psi^{\circ})^2 H^{\circ}$, $\phi^2 H^{\circ}$, and $\phi^2 H'$. Integrals 2 plus 3 constitute an upper limit to the energy of the system and thus integrals 2 plus 3 minus 1 constitute an upper limit to the perturbation energy.

7. The use of molecular spectroscopy in the constitution of reaction intermediates should be pressed. Relatively simple cases for study might include addition compounds of formaldehyde; hydrate, cyanhydrin, or bi-sulfite. Studies in the Walden inversion of CH_3I by NaI in solution may also be profitable.

8. The advent of recording spectrometers makes the conventional order of parts; source, sample, monochromator unnecessary. I propose that there would be several important advantages in placing the sample after the monochromator.

9. Experimental studies in the infra-red could easily be made with the circular polarization. This technique would have application in the determination of the absolute configuration

of optically active compounds.

10. The frequency of a molecular vibration may be expressed as: $\nu = \sqrt{k/\mu}\ (1/2\pi)$ where k is an effective force constant, and μ is an effective reduced mass. The classical amplitude of vibration is given by $x = \sqrt{h(n + \frac{1}{2})/\pi\sqrt{k\mu}}$. I propose that a simple collision theory broadening of spectral lines will allow the determination of x and consequently μ. This would offer a means of verifying the assignments of vibrations for molecules in the condensed states.

11. The study of the configuration of the methyl free radical could be attacked most profitably by the molecular beam magnetic resonance method.

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