

Spectra of Urea and Thiourea in the  $3\mu$  Region\*

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Observations are reported on the polarized infrared spectra of single crystals of urea and thiourea in the  $3\mu$  region. Complex structures accompanying the N—H fundamentals appear, at least in considerable part, to be attributable to combinations and overtones of fundamentals in the neighborhood of  $1650\text{ cm}^{-1}$ .

IN the previous article James E. Stewart presents analyses of the infrared spectra of urea and of thiourea<sup>1</sup> which, except in the  $3\mu$  region, are in essential agreement with the results of a very detailed study of these substances made by one of us<sup>2</sup> a few years ago. In this investigation polarization measurements were made on single crystals of both the ordinary and the deuterium substituted compounds and certain observations were also made at low temperatures to improve resolution. The results obtained were consequently more complete than those of Stewart and permit a somewhat more detailed interpretation in the  $3\mu$  region.

In the  $3300\text{ cm}^{-1}$  region urea and thiourea share an interesting property commonly possessed by amides and polypeptides of exhibiting more bands than can be attributed to N—H valence fundamentals, though the "redundant" bands may be of higher intensity than might be expected of overtones and combinations. (For example the substituted amides and polypeptides exhibit such a band near  $3080\text{ cm}^{-1}$  which has been the subject of much discussion.) Though often misleading this behavior should not be unexpected when a fundamental frequency nearly coincides with one or more overtones or combinations, provided there is a considerable interaction between the vibrations in question.

This situation is realized to an unusual degree in the amides and the fatty acids<sup>3</sup> when in the associated condition. Hydrogen bonding shifts the NH or OH frequency into a region occupied by numerous overtones and combinations and the hydrogen bonded condition very probably results in unusually large interactions between certain vibrations. Owing to the mixing of wave functions the assignment of NH frequencies to definite bands may have limited significance and one may expect the shifts on deuterium substitution to appear slightly anomalous. Though the number, approximate position, and intensity of the "redundant" bands can often be accounted for in a very plausible way, there is generally a lack of the experimental evidence which would make a unique interpretation possible. For example, there is very

commonly the necessity of assuming that certain overtone and combination bands show a *divergence* rather than the more common *convergence*. Furthermore in the spectra of solids there is the possibility that lattice vibrations may be involved in some very complex structures found in the  $3\mu$  region (see Table I).

We have previously shown that in urea, Stewart's bands at  $3333\text{ cm}^{-1}$  and  $3436\text{ cm}^{-1}$  are both close doublets with components oppositely polarized.<sup>4</sup> They presumably contain the major contribution from the four N—H vibrations. Stewart's band at  $3268\text{ cm}^{-1}$  in reality appears to have three components which probably contain  $1689+1630$ ,  $1610+1630$ , and  $2\times 1630$ , and are thus predominantly combinations or overtones of  $\text{NH}_2$  scissors vibrations.

The  $3\mu$  spectrum of thiourea appears to have a complex structure which is incompletely resolved at room temperature. Polarization data can, of course, only distinguish between  $A'$  and  $A''$  absorption, the former containing the bands which would be  $A_1$  and

TABLE I. Bands in the  $3\mu$  spectra of urea and thiourea.\*

	Urea		Thiourea	
	Stewart <sup>b</sup>	Waldron <sup>c</sup>	Stewart <sup>b</sup>	Waldron <sup>c</sup> (spectrum at $-185^\circ\text{C}$ )
3436	$\left\{ \begin{array}{l} 3449 \text{ (vs) } a_1 \\ (2589) \\ 3436 \text{ (vs) } b_2 \\ (2586) \end{array} \right.$	3365	$\left\{ \begin{array}{l} 3390 \text{ (vs) } A' \\ (2551) \\ 3385 \text{ (vs) } A'' \\ (2551) \end{array} \right.$	
3333			$\left\{ \begin{array}{l} 3362 \text{ (vs) } a_1 \\ (2428) \\ 3342 \text{ (vs) } b_2 \\ (2433) \end{array} \right.$	$\left\{ \begin{array}{l} 3349 \text{ (vs) } A' \\ (2381) \\ 3333 \text{ (vs) } A'' \\ (2381) \end{array} \right.$
3268	$\left\{ \begin{array}{l} 3288 \text{ (vw) } B_2(?) \\ 3261 \text{ (m) } B_2 \\ 3226 \text{ (m) } A_1 \end{array} \right.$	3258	$\left\{ \begin{array}{l} 3293 \text{ (w) } A' \\ 3245-95 \text{ (s) } A'' \\ 3199 \text{ (vw) } A' \\ 3177 \text{ (w) } A' \\ 3150-95 \text{ (s) } A'' \\ 3110 \text{ (s) } A'' \end{array} \right.$	
			3156 3097	

\* The band types indicated are supported by polarization measurements though  $B_1$  and  $B_2$  vibrations are not so distinguishable in urea. The frequencies given in parentheses are those of the deuterium shifted bands at  $25^\circ$  and under low dispersion.

<sup>b</sup> See reference 1.

<sup>c</sup> See reference 2.

<sup>4</sup> R. D. Waldron and R. M. Badger, *J. Chem. Phys.* **18**, 566 (1950).

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<sup>1</sup> J. E. Stewart, *J. Chem. Phys.* **25**, 248 (1957).

<sup>2</sup> Robert D. Waldron, Ph. D. thesis, California Institute of Technology (1951).

<sup>3</sup> Bratož, Hadži, and Sheppard, *Bull. sci., Conseil acad. RPF Yougoslav* **1**, 71 (1953).

$B_1$  for the isolated  $C_{2v}$  molecule, and the latter the  $B_2$  bands. The intense band at  $3365\text{ cm}^{-1}$  exhibits some evidence of structure but practically no polarization. Thus it apparently includes bands of both  $A'$  and  $A''$  types and presumably contains at least two NH fundamentals. The bands at  $3258$ ,  $3156$ , and  $3097\text{ cm}^{-1}$  consist predominantly of components which show very strong  $A''$  polarization. Evidence from low temperature measurements must certainly be used with some reservations but at  $-185^\circ$  the  $3365\text{ cm}^{-1}$  band is split

into two components, neither of which shows much intensity change with azimuth of polarization, though both show small frequency shifts.

It therefore seems probable that  $3365\text{ cm}^{-1}$  predominantly contains the four NH fundamentals, and the remainder of the region is to be accounted for by overtones and combinations. Many or all of the frequencies may be shifted by mutual interactions which may well be the cause of the anomalously large shift of the lower NH frequencies on deuterium substitution.

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## Absorption Bands of Rubidium in the Presence of Hydrocarbons\*

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Absorption spectra of rubidium in the presence of fourteen different hydrocarbons (methane, ethane, propane, *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, cyclopropane, butene-2, and benzene) were studied. About one hundred new rubidium-hydrocarbon absorption bands associated with the first four members of the Rb principal series were observed. Some regularities in the occurrence of the bands were found. The positions of the bands are given and the properties of the bands are discussed.

THE absorption lines of some metallic vapors are known to be accompanied by diffuse bands when the absorbing atoms are surrounded by foreign particles. However, the experimental data on this effect are rather fragmentary for theoretical analysis. In the present work a systematic study of the problem was made by employing one absorbing element and a long series of substances of similar structure as perturbing particles. The bands appearing near the first four members of the principal series of rubidium were investigated in the presence of eleven saturated hydrocarbons (methane to *n*-decane, and *n*-dodecane) and for the purpose of comparison, in the presence of cyclopropane, butene-2, and benzene. It is hoped that this article together with one which appeared recently<sup>1</sup> furnish a considerable amount of data for a better understanding of the phenomenon.

### EXPERIMENT

The experimental arrangement and the method of observation was the same as that described previously.<sup>1</sup> The "cold window" absorption tube was used for the work with the gaseous hydrocarbons (lighter than pentane). The "hot window" tube was used with the liquid hydrocarbons. The liquid hydrocarbon was placed in a Pyrex vessel connected to the absorption tube by means of a ball joint (the absorption tube with Rb could be isolated by means of a stop cock when the hydrocarbons

were changed). The hydrocarbon in the vessel was then cooled in a dry ice bath and the air was pumped from the vessel. The hydrocarbon vapor was subsequently admitted into the absorption tube by opening the isolating stopcock and heating the vessel and the connecting tubing by means of a "heating tape" wound on them.

The pressure of the vapor in the absorption tube could not be measured directly when the "hot window" absorption tube was used. The estimated pressures ranged from 15 to 50 cm Hg. In the case of gaseous hydrocarbons the pressure was about one atmosphere as read directly from a pressure gauge connected to the absorption tube.

A rather high temperature (about  $300^\circ\text{C}$ ) was necessary when nonane, decane and dodecane were used. At this temperature the quartz windows of the absorption tube were attacked by Rb vapor and became opaque in the ultraviolet region; thus only the first and the second members of the Rb principal series could be studied with these three hydrocarbons.

The hydrocarbons used were all of research grade (purity 99.0 to 99.9%), except *n*-dodecane which was 95 mol % pure.

### RESULTS

The presence of a hydrocarbon vapor in the absorption tube with rubidium caused two different phenomena: (a) a diffuse absorption band appeared on the long wavelength side of each component of the Rb principal series doublets ("red bands"), (b) diffuse absorption

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<sup>1</sup> Ch'én, Bennett, and Jefimenko, *J. Opt. Soc. Am.* **45**, 182 (1956).