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Low Frequency Vibrations of Molecular Crystals, XIV Raman and Far-infrared Spectra of HNCS and DNCS

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Low Frequency Vibrations of Molecular Crystals, XIV† Raman and Far-infrared Spectra of HNCS and DNCS

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Abstract—The infrared and Raman spectra of polycrystalline HNCS and DNCS have been recorded from 33 to 4000 cm^{-1}. The data have been treated in detail and a vibrational assignment of the six internal fundamentals is suggested. The vibrational data imply a very short N—H———N distance of 2.9 Å. The subsequent structural implications of such a strong H-bond are considered. Evidence was found that HNCS has two distinct crystalline phases and spectra have been recorded for each form. Factor group splitting of the N—H bending fundamental suggests that the crystal has at least four or possibly eight molecules per unit cell depending upon whether or not the crystal is centrosymmetric. Suggested assignments are given for some of the lattice modes.

Introduction

In an earlier publication[1] we reported the mid infrared spectra of gaseous and solid HNCS and DNCS. The assignment of the out-of-plane skeletal bending mode, ν_6, was stated to be quite uncertain since the only apparent choice gave an extremely high frequency when compared to the similar motions of the HN_3 and HNCO molecules. At the time of our initial investigation, it was not possible for us to obtain the Raman spectrum of this slightly colored material. It was expected that this N=C=S out-of-plane mode might have a

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reasonable polarizability change and thus be detected in the Raman effect. Therefore, we have investigated the Raman spectra of solid HNCS and DNCS.

Also, in the earlier investigation three definite bands were observed in the spectra of the solids in the vicinity of ν_5, the N—H bending mode. No satisfactory explanation could be given for their origin, although a tentative suggestion of lattice modes was given. We have now investigated the lattice region of the spectrum and evidence has been found for more than one crystalline form. These studies represent a continuation of earlier investigations[2-5] of the frequencies of the lattice vibrations of molecular crystals.

Experimental

The sample of isothiocyanic acid was prepared by the solid-phase reaction of KSCN and $KHSO_4$ at 200 °C. The reaction mixture was connected to a vacuum line and the volatile products were trapped in a U-tube immersed in liquid nitrogen. The HNCS which was liberated in the above reaction was purified by pumping on the collection tube at −80 °C for a period of 1 hour. To insure that all traces of CS_2, HCN and SO_2 were removed, the sample was pumped on at 0 °C for an additional 10 minutes. The purified HNCS was maintained at a temperature of −80 °C prior to use so as to prevent decomposition and polymerization. The deuterated isothiocyanic acid was prepared in a similar fashion by reacting KSCN and $KDSO_4$. The isotopic purity of DNCS was confirmed by its mid infrared spectrum.

The Raman spectra of polycrystalline HNCS and DNCS were recorded on a Cary Model-81 Raman spectrophotometer equipped with a Spectra Physics Model 125 He–Ne laser. A cold cell similar to that described by Carlson[6] was used to study the samples at liquid nitrogen temperature. The sensitivity and scanning times were varied to give the optimum resolution and presentation and representative spectra may be seen in Figs. 1–3. The instrument was calibrated with the emission lines from a neon lamp and the frequencies for all sharp lines are expected to be accurate to ± 2 cm^{-1}.

The mid-infrared spectra were recorded on a Perkin–Elmer Model 621 spectrophotometer. The instrument housing was purged with

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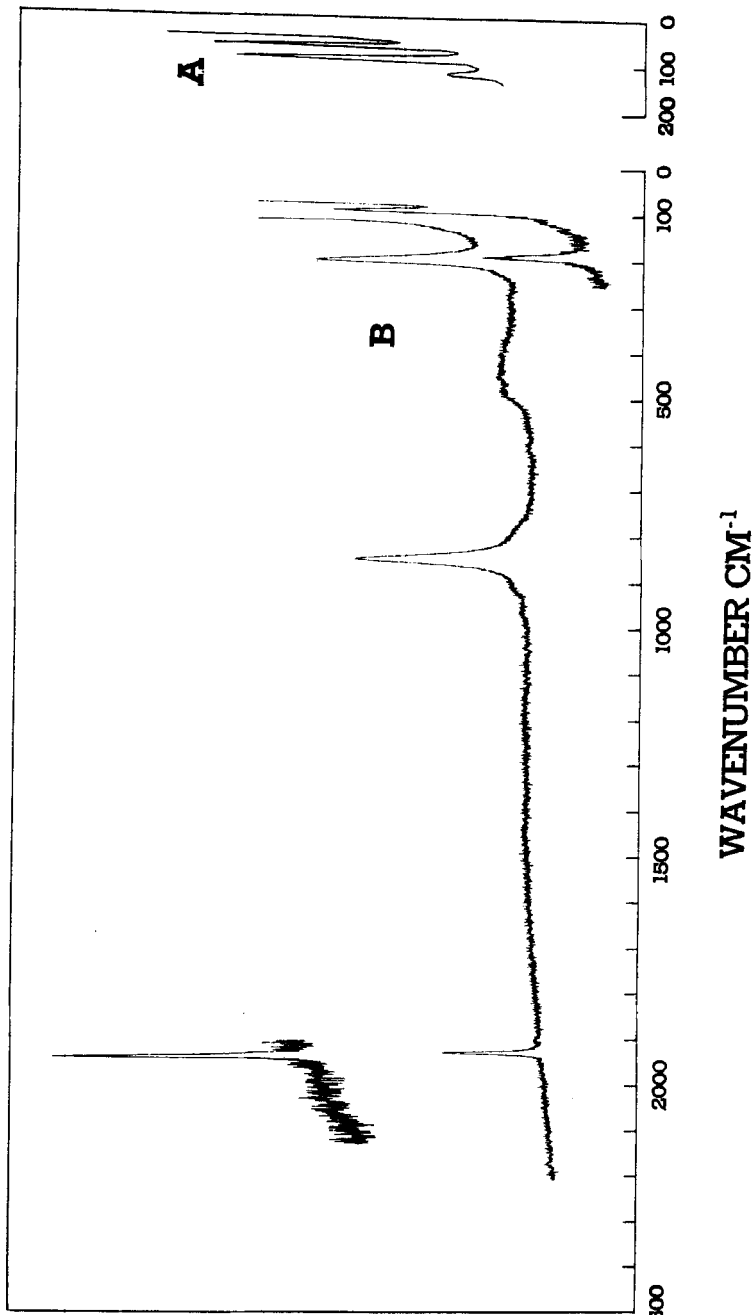

Figure 1. Raman spectra of solid HNCS (– 190 °C) phase I. (A) Single slits; (B) Double slits.

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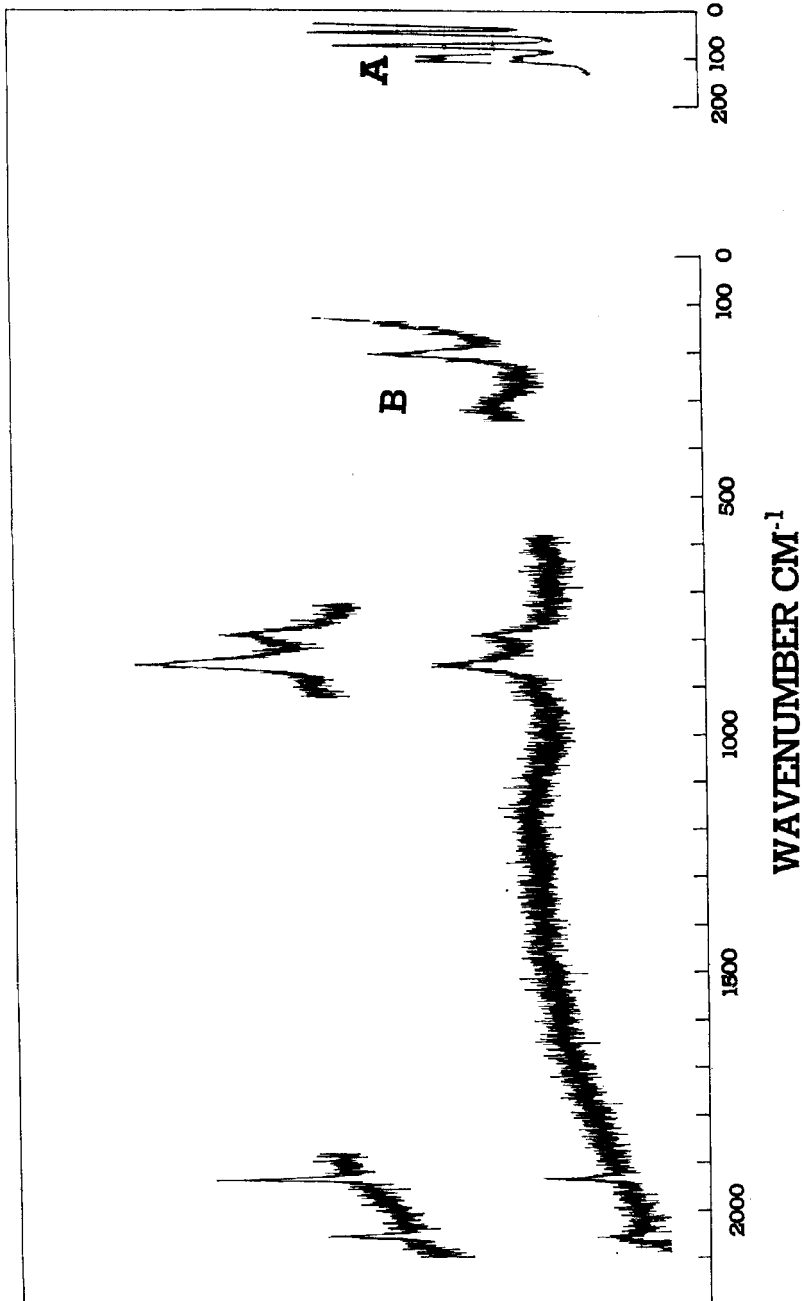

Figure 2. Raman spectra of solid HNCS (– 190 °C) phase II. (A) Single slits; (B) Double slits.

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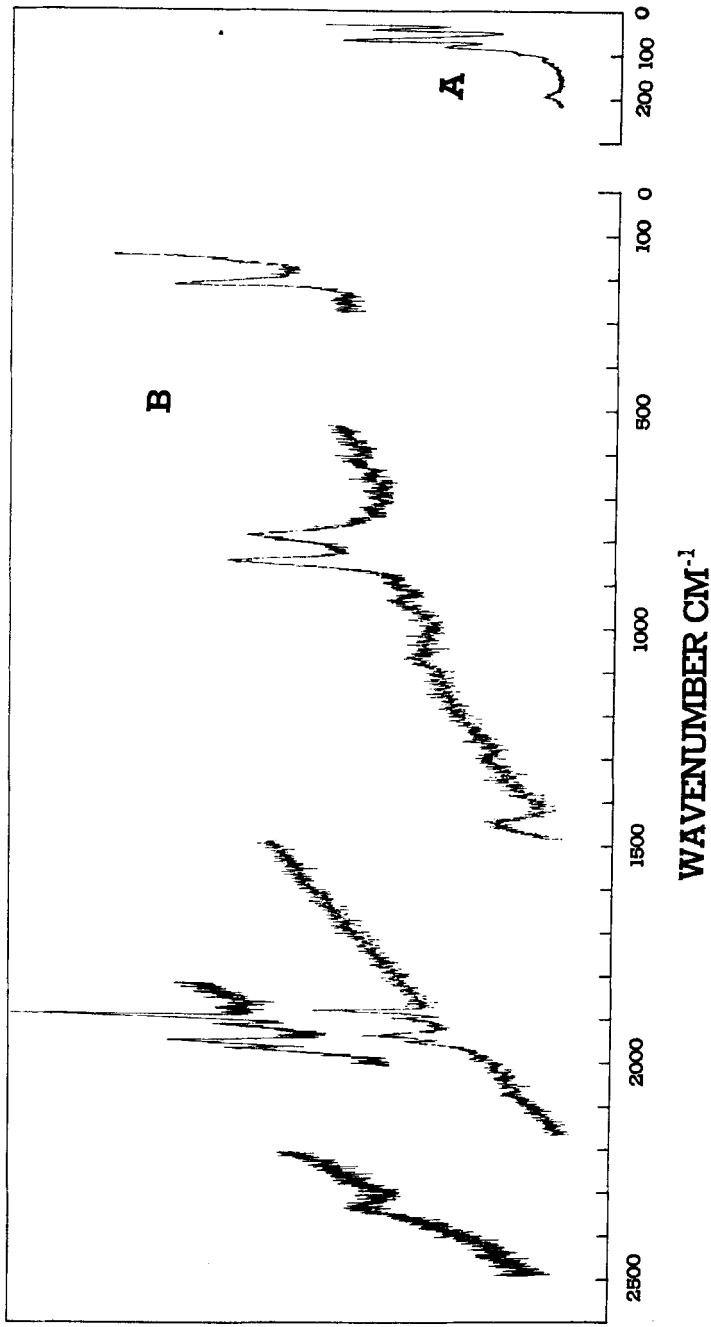

Figure 3. Raman spectra of solid DNCS (– 190 °C) phase II. (A) Single slits; (B) Double slits.

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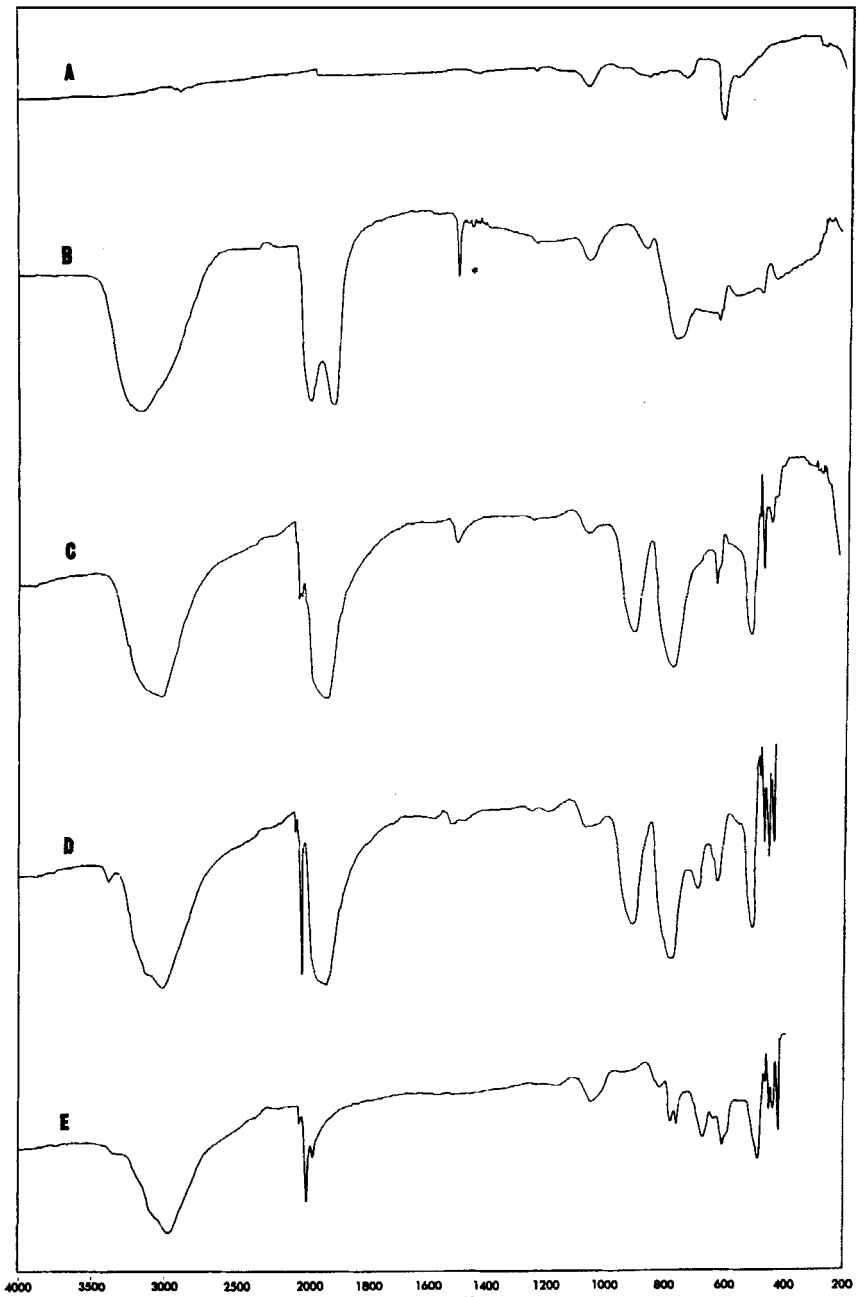

Figure 4. Mid-infrared spectra of polycrystalline HNCS (– 190 °C) recorded on a silicon substrate. (A) " Background " spectrum of the cell; (B) Spectrum of rapidly deposited HNCS; the sample was not annealed; (C) Spectrum of HNCS annealed to – 150 °C; (D) Spectrum of HNCS annealed to – 115 °C; (E) Spectrum of HNCS annealed to – 103 °C (melting point).

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dry air to remove atmospheric water vapor. The spectrophotometer was calibrated by using standard gases in the higher-frequency region[7] whereas the lower-frequency region[8] was calibrated with atmospheric water vapor. The spectra of the polycrystalline samples were obtained by slowly subliming the compounds onto a silicon support maintained at liquid nitrogen temperature. The far infrared spectra were recorded on a Beckman IR-11 spectrophotometer from 33 to 500 cm^{-1}. The instrument was calibrated with atmospheric water vapor and the assignments of Hall and Dowling.[8] A cold cell, which has previously been described,[2] was utilized to study the spectra of the solid samples and typical spectra may be seen in Fig. 4. The observed frequencies are summarized in Tables 1 and 2.

Results and Discussion

Microwave investigations have suggested[9] that HNCS has a relatively short N—H bond distance. Such a result appears to be consistent with the high N—H stretching frequency (3538 cm^{-1}) observed for gaseous HNCS and the large frequency shift which was

TABLE 1 Raman Spectra of Solid HNCS and DNCS

HNCS		DNCS	Assignment
Phase I	*Phase II*	*Phase II*	
44 vs	44 vs	44 vs	lattice
72 vs	72 vs	70 vs	lattice
	95 s	85 s	lattice
103 s	104 s	98 sh, w	lattice
		117 sh, m	lattice
196 s	196 s	201 s	lattice
	312 w		second order line
	789 m	789 s	ν_3 C=S stretch
851 s	851 s	843 s	
		930 w	
		1059 w	
		1295 w	
		1440 m	
		1874 s	
1934 m	1934 m	1890 m	ν_2, C=N stretch
	2055 m	1931 s	
		1946 m	
		2326 m	ν_1, N—D stretch

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TABLE 2 Mid Infrared Spectra of Solid HNCS (- 190 °C)

B	C	D	E
		3385 W	3380 VW
3170 S	3030 S	3020 S	3000 S
	2100 W		
2008 S	2080 W	2098 W	2100 W
1930 S	2060 W	2062 S	2060 S
	1950 S	1950 S	2010 M
1505 M	1503 W	1510 VW	—
860 W	900 S	903 S	825 W
			788 M
755 M	770 S	775 S	768 M
		682 M	682 M
			650 VW
555 W	502 S	500 S	498 S
	468 W	467 W	468 W
465 W	457 M	455 M	456 M
	427 W	440 M	441 M
420 W	410 VW	421 M	423 M

(B) not annealed; (C) annealed to - 150 °C; (D) annealed to - 115 °C; (E) annealed to - 103 °C (M.P.).

found upon solidification (538 cm^{-1}). By employing an empirical expression[10] which relates the vapor-solid frequency shift to the length of the N—H———N bond, one calculates a very short N—H———N distance of 2.95 Å for solid HNCS. Such a value implies a very strong hydrogen bond and a similar result has been found for HNCO by X-ray studies.[11]

In HNCO the N—H———N separation is 3.07 Å and the molecules are linked into infinite zigzag chains by the hydrogen bonds.[11] Although a similar structure is expected for HNCS, there have been no published data on the crystalline sample. As a result the present vibrational study was undertaken to try and determine whether or not the crystal structure has a center of symmetry. In principal, vibrational spectroscopy can also provide information with regard to the number of phase transitions by studying the spectra at various temperatures; furthermore, the observation of factor group splitting often permits the elimination of certain space groups from consideration.

The emphasis in this study has, of course, been placed on the

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Raman study since the Raman spectrum of this sample has yet to be reported. Thus, we shall discuss the Raman spectra of polycrystalline HNCS and DNCS in some detail prior to considering the low frequency infrared data. It should be pointed out that considerable difficulty was experienced in obtaining the respective spectra, and this is thought to result in part from sampling problems. Thus, despite the fact that the spectra always had a similar appearance, the reproducibility in band centers and relative intensity presented a formidable problem.

Since HNCS is a planar molecule it has C_S symmetry and the 6 fundamental vibrations are permitted in both the infrared and Raman spectra. The normal vibrations belong to the following irreducible representations: $5a' + 1a''$. The vibrations of a' symmetry may be described approximately as: an N—H stretch (ν_1), a C=N stretch (ν_2), a C=S stretch (ν_3), an in-plane C=N=S bend (ν_4), and an N—H bend (ν_5). The only vibration of a'' symmetry is the C=N=S out-of-plane bend (ν_6). It should be noted that since ν_6 is the only vibration of a'' symmetry, the Teller–Redlich product rule predicts that it should not show an appreciable shift upon N-deuteration ($\tau = 1.02$).

Raman Spectra

The Raman spectra of HNCS have been reproduced in Figs. 1 and 2 whereas the spectrum of DNCS may be seen in Fig. 3. In Fig. 1 the spectrum is quite simple and there is no apparent doubling of the two skeletal stretching modes as was observed in the spectrum reproduced in Fig. 2. It should be noted that each of the spectra of HNCS was obtained approximately an equal number of times and that it was not actually possible to predict when either spectrum would be observed. This was a very disturbing factor, but it is most likely a result of the sampling difficulties encountered For example, the design of the low temperature Raman cell is such that partial annealing of the sample always occurs when the brass rod which contains the sample is placed against the light pipe which is initially near room temperature. With this design, different degrees of annealing always seem to result and this is probably quite dependent on the amount of sample on the brass rod. Because the low frequency spectral region in both

Figs. 1 and 2 is so well defined, it is thought that each spectrum results from a different crystalline form rather than a " glass " phase. The spectra of DNCS always appeared to correspond to the HNCS spectrum shown in Fig. 2 with each mode showing the expected shift factor. No spectrum of DNCS corresponding to that observed in Fig. 1 for HNCS was ever obtained.

There is little question about the assignment of the N—H stretching fundamental since it has a well-established group frequency. Thus, the band at ~ 3000 cm^{-1} in HNCS shifts upon N-deuteration to 2326 which confirms the assignment to an N—H motion. As previously noted the large vapor-solid frequency shifts result from the formation of relatively strong hydrogen bonds

The two skeletal stretching modes in HNCS may be approximately described as C=N and C=S motions, respectively. These motions should involve a large polarizability change and, thus, should give rise to relatively intense Raman lines. For KNCS the C=N and C=S stretching modes were observed[12] at 2053 and 749 cm^{-1}, and similar frequencies were expected for polycrystalline HNCS. Therefore, the lines at 1934 and 851 cm^{-1} in Fig. 1 have been attributed to the fundamentals in HNCS which involve primarily C=N and C=S motions, respectively. In addition to the bands at 1934 and 851 cm^{-1} shown in Fig. 2, lines were also observed at 2055 and 789 cm^{-1}. Several possible explanations can be given for the origin of these bands. Foremost is the possibility that the spectrum shown in Fig. 2 represents that of a second phase of solid HNCS and the doubling of the two skeletal modes can be attributed to factor group splitting. Also it should be pointed out that the spectrum shown in Fig. 2 may actually be a composite of the spectra from two crystalline modifications. However, since the relative intensities of both doublets remain always the same, this alternative does not appear to be as attractive as the former one. A third possible explanation is that the different spectra are due to orientational phenomena; however, because of the polycrystalline nature of the sample, such an interpretation does not seem very probable.

The spectrum of DNCS in the region of the two skeletal stretching modes is somewhat more complicated than that for the " light " molecule. The two rather strong lines at 1874 and 1931 cm^{-1} both have high frequency shoulders (see Table 1). Additional splittings

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have been previously reported for other deuterium compounds so the increased complexity is not totally unexpected.[13] The two lines assigned to ν_3 are very similar for both molecules but the lines in both spectra are considerably broader than those assigned to ν_2 and the additional splitting would be much more difficult to detect for ν_3.

In conclusion, on the basis of the current evidence, it seems certain that two crystalline modifications of HNCS exist and the observed spectra correspond to the two different phases.

The fact that the low frequency region of the Raman spectra is nearly the same in Figs. 1 and 2 is somewhat surprising. However, if the number of molecules per unit cell is doubling then the in- and out-of-phase motions of the inter-molecular modes may only cause a broadening or slight splitting of the lattice modes. Only the 103 cm^{-1} line shows a definite splitting in the spectrum shown in Fig. 2.

Unfortunately, neither of the skeletal bending nor the N—H bending modes were observed in the Raman spectrum. For the linear NCS ion the skeletal bending mode was not reported in the original Raman work[14] but has recently been observed as a very weak line at 481 cm^{-1} in the Raman spectrum of solid KNCS.[15] Apparently the presence of the hydrogen atom on the NCS ion does not sufficiently alter the polarizability change during the skeletal bending motions for them to be observed in the Raman effect. However, it might be mentioned that the quality of the Raman spectra of the HNCS and DNCS polycrystalline samples was not nearly as good as that for the KNCS sample and a slight increase in the polarizability change would not have led to a detectable Raman line. The N—H bending modes are frequently quite weak in the Raman effect,[16,17] and its absence in the Raman spectrum was not entirely unexpected.

The frequencies observed for both HNCS and DNCS are listed in Table 1. The low frequency lines at 72 and 44 cm^{-1} for the " light " molecule were observed at 70 and 44 cm^{-1}, respectively, in the spectrum of DNCS. As such these lines are attributed to motions of translatory origin. The line centered at 95 cm^{-1} for HNCS appears to shift to 85 cm^{-1} upon deuteration which suggests that it results from a librational mode. The band located near 200 cm^{-1} shows little change with deuteration and is believed to represent a stretching mode of the N—H————N hydrogen bond. This frequency is in the range observed for the O—H————O bond and reflects the strength

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TABLE 3 Far Infrared Spectra of Solid HNCS and DNCS (− 190 °C)

HNCS B	HNCS C	HNCS D	DNCS B	DNCS C
	92 W	86 M	88 W	86 M
106 M	109 S	109 M	108 W	113 W
		155 S		149 S
195 VS	195 VS	195 S	200 VS	188 S
		225 M	255 W	
315 W	310 W	300 W	278 W	290 M
	432 W		329 W	
	447 M		415 M	410 M
472 M	458 M		463 S	440 S
	471 M			458 S
				540 S
515 S	515 S			

of the hydrogen bonding in HNCS. The ramifications of the Raman spectra on the crystal structure will be considered in a later section.

Mid-Infrared

In Fig. 4 is shown the mid-infrared spectrum of HNCS with repeated annealing to both − 150 °C and − 115 °C. The spectra were taken with a silicon substrate since the alkali halides initiate decomposition.[18] The spectrum indicated as B probably represents a glass since the sample was sprayed on the substrate, which was maintained at liquid nitrogen temperature, and it was not annealed. The spectrum represented in Fig. 4C is that of a sample which was repeatedly annealed to − 150 °C until no further changes were noted in the spectrum. One readily notes that the N—H stretching mode shifts to lower frequency, and the skeletal stretching mode at 2008 practically disappears. Also, relatively strong bands are observed at 900 and 502 cm^{-1} and a very complex absorption is centered near 475 cm^{-1}.

The spectrum reproduced in Fig. 4D was obtained after the sample was repeatedly annealed to − 115 °C. The spectral changes are again quite dramatic since the shoulder at 2060 cm^{-1} in Fig 4C is now an intense band. Additionally, a new band is seen at 682 cm^{-1} and the absorption centered near 457 cm^{-1} consists of four sharp bands. The bands at 457 cm^{-1} are believed to result from ν_5, the

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N—H bending fundamental. The fact that four bands are observed implies that there are at least four molecules per unit cell. Upon warming the sample to its melting point, and then rapidly cooling it, the spectrum in Fig. 4E results. The strong bands at 1950 and 903 cm^{-1} have disappeared and the remaining bands have been assigned to the six fundamental modes as may be seen in Table 4. The most reasonable explanation of the disappearance of the bands at 1950 and 903 cm^{-1} is that more than one crystalline phase was giving rise to the spectra in Figs. 4C and 4D, whereas only a single phase results after the sample has been annealed to its melting point (Fig. 4E). The frequencies observed for the C=N stretching mode (ν_2) in the infrared and Raman spectra do not coincide. Such a result suggests that the molecules are arranged in a centrosymmetric fashion and thus, there may actually be at least eight, rather than four molecules per unit cell. However, since it was not possible to perform identical annealing procedures for the Raman and infrared samples, this latter conclusion must be considered tentative.

It should be pointed out that the band at 619 cm^{-1} in each trace shown in Fig. 4 results from the silicon plate. The out-of-plane skeletal bending mode, which has not previously been observed, has been assigned to the band at 682 cm^{-1}. Such an assignment appears reasonable since ν_6 was originally[1] thought to be somewhere between 600 and 800 cm^{-1}. Despite the fact that the frequency difference between the a' and a'' skeleton bending modes is relatively large, the 682 cm^{-1} band appeared in both Figs. 4D and 4E and it may well be concealed by the breadth of the 770 cm^{-1} band in Fig. 4C. No reasonable combination or overtone assignment could be established for this band; furthermore, factor group splitting does not appear realistic on the basis of the observed splitting of the N—H bending fundamental. On the basis of the current experimental evidence, then, ν_6 has been tentatively assigned to the 682 cm^{-1} band.

Far-Infrared

The far-infrared spectra of HNCS and DNCS may be seen in Figs. 5 and 6, respectively. Each spectrum was obtained from a freshly deposited sample which had been annealed to different temperatures. Although the spectra appear to have some differences, on the whole

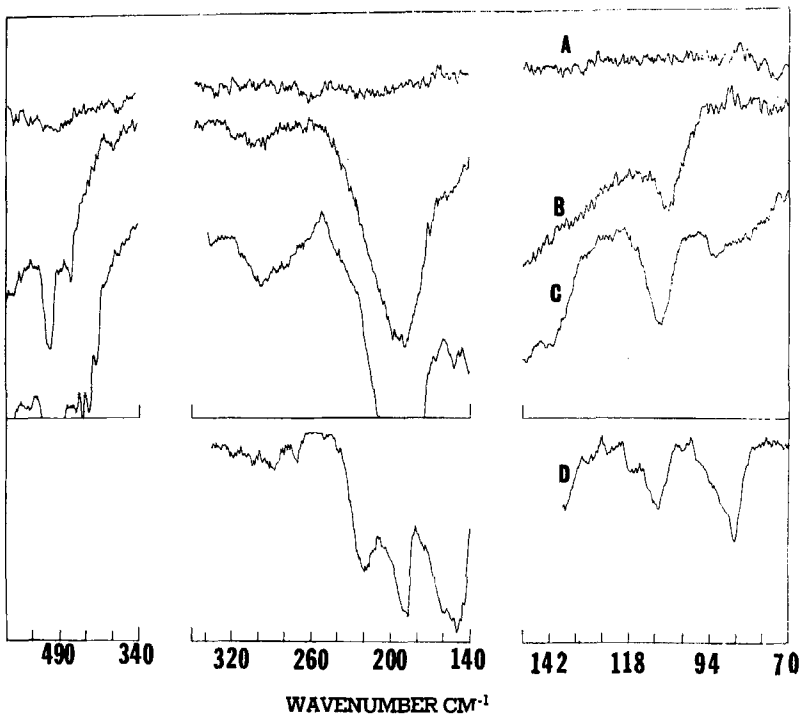

Figure 5. Far infrared spectra of solid HNCS (−190 °C). (A) "Background" spectrum of the cell; (B), (C), and (D) represent different depositions of HNCS which have been annealed to different temperatures.

there is essentially a one-to-one correspondence in the number of bands observed (see Table 4). The spectra in Figs. 5B and 5C are thought to correspond, respectively, with those of the mid-infrared shown in Figs. 4C and 4D. In Fig. 5D, three bands appear in the region of 150 to 225 cm^{-1}, whereas only a single band was resolved in the upper traces, although there is some indication of a shoulder near 160 cm^{-1}. The lower frequency bands in all three spectra appear to correspond, but there is an obvious intensity variation. The bands centered at 195, 109, and 92 cm^{-1} (Fig. 5B) have been attributed to lattice modes, whereas the bands in the 500 cm^{-1} region have previously been ascribed to ν_4 and ν_5. The weak feature in the low frequency spectrum of HNCS centered near 300 cm^{-1} probably results from a multiphonon process, although experimental evidence could not be obtained which verified such an assignment.

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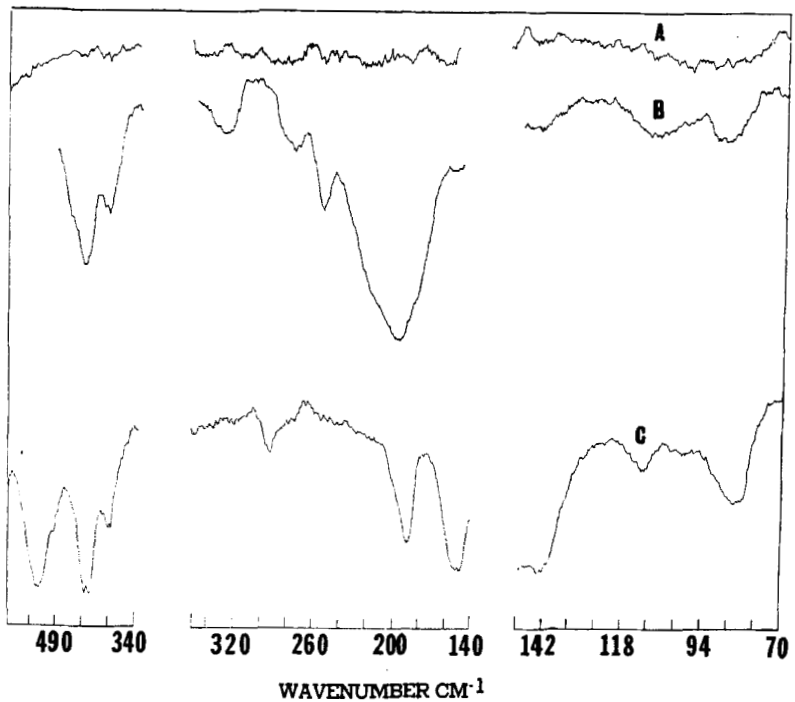

Figure 6. Far Infrared spectra of solid DNCS (- 190 °C). (A) " Background " spectrum of the cell; (B) and (C) represent different depositions of DNCS which have been annealed to different temperatures.

In the spectrum of DNCS (see Fig. 6B), the bands at 200, 108 and 88 cm^{-1} are believed to correspond to the bands of similar frequency in HNCS (Table 4). The weak bands at 329, 278, and 255 cm^{-1} may be a result of multiphonon transitions. The spectrum shown in Fig. 6C is thought to correspond with that of 5D where one has again observed a greater multiplicity of bands in the 150–200 cm^{-1} region. Clearly, the far-infrared spectra of HNCS and DNCS are very similar. The fact that we obtained what appear to be two different spectra suggests that the spectral changes result from distinct phases. The far infrared bands of both isotopic species were quite distinct and in no instance did annealing result in broad bands characteristic of the lattice spectrum of a polymer or decomposed material. Although there has been no detailed report of the number and structure of the phases in HNCS, the oxygen analog (HNCO) is known to have

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two stable crystalline phases.[11] Thus it is concluded that when the isothiocyanic acid crystal is annealed to $-150\,^{\circ}C$ a phase which we will designate as Phase II is obtained, and is mainly represented by the spectra in Figs. 4C and 5B. When the sample is further annealed to $-115\,^{\circ}C$ a second crystalline phase is obtained which can be designated as Phase I. The spectra in Figs. 4D, 5C and 6B are all believed to be representative of this phase. The spectra shown in Figs. 5D and 6C are also believed to originate from samples in Phase I, but with different relative orientations of the H-bond in reference to the incident radiation. There can be little doubt that the relatively strong band near $200\,cm^{-1}$ originates from the N—H———N stretching motion and it may be possible to grow crystals with different relative orientations of this bond in relation to the substrate. These two types of spectra appeared randomly and neither spectrum could be obtained preferentially by changing the sampling techniques. As evidenced in Tables 1 and 4, the low frequency infrared and Raman bands do not correspond exactly in frequency. Because of this fact and the previously mentioned sampling problems, it is actually not possible to assign this spectral region uniquely, although there is little doubt these bands result from external modes.

Summary and Conclusions

The infrared and Raman spectra of polycrystalline HNCS have been recorded and a vibrational assignment is suggested for the six internal fundamentals. The previously unassigned out-of-plane skeleton bending mode has been tentatively assigned to the band at $682\,cm^{-1}$. The infrared and Raman counterparts of the C=N stretching fundamental were widely separated which suggests that the crystal structure may be centrosymmetric. Factor group splitting was observed for several of the bands and was most apparent for the N—H bending vibration where four bands were clearly defined. On the basis of the observed factor group splitting for ν_5, it would appear that HNCS has at least four or eight molecules per unit cell depending upon whether or not it has an inversion center. The vibrational data also provide strong evidence for the existence of at least two different crystalline phases, and the vapor-solid frequency shift for ν_1 suggests a relatively short N—H———N distance.

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