

number of collisions is very small for ethyl alcohol, according to Alty's results, and we can presume the same effect for methyl alcohol which has about the same dipole moment as ethyl alcohol. (3) The retardation of the $C_6H_6-C_2H_4Cl_2$ mixture is small because the number of collisions is large and only the ethylene chloride has a condensation coefficient less than unity.

¹ J. W. Westhaver, *Ind. and Eng. Chem.* **34**, 126 (1942).

² M. Bertrand, Ph.D. thesis, University of Montreal (1950).

³ T. Alty, *Nature* **139**, 374 (1937).

Nuclear Magnetic Resonance in Methane*

J. T. THOMAS, N. L. ALPERT, AND H. C. TORREY

Physics Department, Rutgers University, New Brunswick, New Jersey

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NUCLEAR magnetic resonance studies of materials with more than one phase in the solid state have been carried on in this laboratory as a continuation of the earlier work done by one of us.¹

The most interesting and complete results have so far been obtained in methane. Plots of the thermal relaxation time (T_1) and of the line width (ΔH) vs. absolute temperature are shown in Figs. 1 and 2, respectively.

The technique used has been the pulse method recently described by Torrey.² All of the data reported here were taken using a new nuclear resonance cryostat designed and constructed in this laboratory. This cryostat operates on the principle of adiabatic isolation commonly used in specific heat measurements. The cryostat and associated equipment permit the variation, control, and measurement of temperature to within better than 0.1°K in the vicinity of 20°K and lower, and to within better than 0.2°K in the vicinity of 80°K and lower.

The line-width data obtained here on methane do not agree with those previously reported.¹ This is not the case for other materials for which we have obtained close checks. In view of the

comparatively qualitative nature of the data taken in those early, exploratory experiments on methane, this is not surprising. The absence of any change in line width at the λ -point at 20.4°K eliminates the possibility of a rotational transformation, as originally suggested by Pauling.³ This conclusion is in agreement with the x-ray observations of Mooy.⁴

The data for T_1 are more complex. The values reported here are reproducible to about one percent above 65°K and to about five percent below 65°K where the line becomes broad. The salient features are: (1) The extremely small value of T_1 in the vicinity of 2 to 4°K. (2) The behavior of T_1 is anomalous in the vicinity of the λ -point and there may be a small discontinuity in T_1 near the λ -point. This will be studied further. (3) There are two dips in T_1 in the solid state, rather than one as might be expected on the basis of the Bloembergen, Purcell, Pound⁵ theory. (4) T_1 is continuous across the melting point. (5) The small dip in T_1 just above the melting point is unexpected on the basis of existing theories.

At first we suspected the presence of paramagnetic impurity, particularly oxygen, which might explain (1) above.⁶ Since we did not know the impurities in the sample, we condensed a new sample from a tank of Matheson c.p. (better than 99 percent) methane, which is supposed to contain traces of ethane, nitrogen, and carbon dioxide, but no oxygen. This showed roughly the same relaxation times at helium temperatures and gave about the same variation with temperature, according to a few spot checks at various temperatures. We plan to obtain an even purer sample to study this factor as well as other possible impurity effects.

Although data have not yet been taken between 4.2 and 14°K, there is apparently a minimum in T_1 in this range. If we assume that this dip is due to a decrease in the characteristic time⁶ τ_c , we obtain values of τ_c which would require the line width to be much narrower than observed in this range. Other explanations are under study. The minimum at 73°K is qualitatively consistent with the line-width data, as predicted by the Bloembergen, Purcell, Pound theory. On the basis of this theory, τ_c is almost constant from about 30°K to about 55°K, after which it starts dropping rapidly almost up to the melting point. There is apparently sufficient activity in the solid at the melting point so that the additional Brownian motion in the liquid phase has little or no effect on τ_c .

A more detailed account of this work as well as our results on other substances will be submitted for publication in the near future.

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² H. C. Torrey, *Phys. Rev.* **76**, 1059 (1949).

³ L. Pauling, *Phys. Rev.* **36**, 430 (1930).

⁴ H. H. Mooy, *Leiden Comm.* **19**, 213d (1931).

⁵ Bloembergen, Purcell, and Pound, *Phys. Rev.* **73**, 679 (1948).

⁶ N. Bloembergen, *Physica* **XV**, 386 (1949).

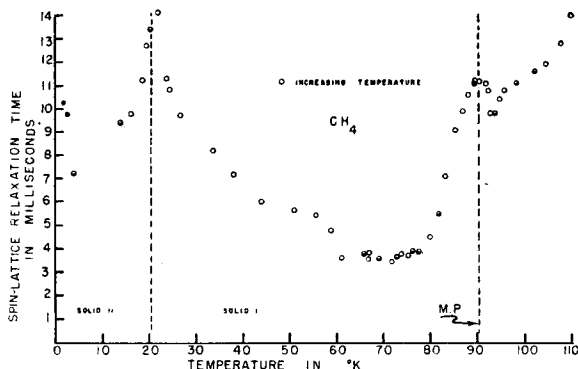


FIG. 1.

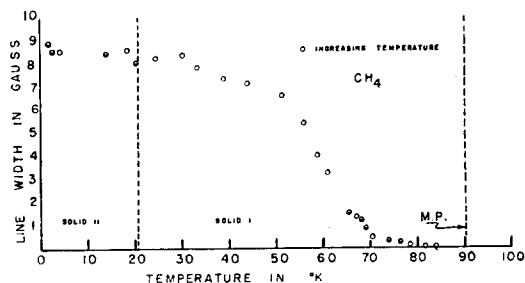


FIG. 2.

The Infra-Red Spectrum and Molecular Structure of HNCS

L. H. JONES AND RICHARD M. BADGER
*Gates and Crellin Laboratories of Chemistry,
California Institute of Technology,*
Pasadena, California*

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FROM an examination of the microwave spectra of four isotopic species of isothiocyanic acid, Beard and Dailey¹ recently obtained the following values for the molecular parameters in the ground vibrational state:

$$\begin{aligned} r_{C-S} &= 1.57 \pm 0.01 \text{ \AA}; & r_{N-C} &= 1.21 \pm 0.01 \text{ \AA}; \\ r_{N-H} &= 1.2 \pm 0.1 \text{ \AA}; & \angle HNC &= 112^\circ \pm 10^\circ. \end{aligned}$$

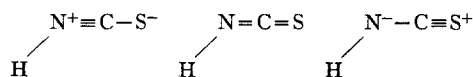
These C-S and N-C distances are not unexpected, but the N-H distance is abnormally long and the HNC angle abnormally

small.² The errors in locating the hydrogen atom from the microwave data are, of course, rather large; indeed we believe they are much larger than are indicated here.

The infra-red spectrum of isothiocyanic vapor has recently been examined in this laboratory and the coarse rotational structure of the first overtone of the N—H vibration at 6914 cm⁻¹ has been resolved with a vacuum grating instrument. The large rotational constant was found to be 43.1±0.4 cm⁻¹ in the ground state. The frequency of the N—H fundamental is 3530 cm⁻¹ as against 3534 cm⁻¹ found³ for HNCO.

Because of the practical equality of these frequencies it is reasonable to believe that the N—H distance in HNCS does not differ appreciably from the 0.99 Å recently found³ for HNCO. Using this distance and the C—S and N—C distances reported by Beard and Dailey, it is found that an HNC angle of 138°40'±1° is required to account for the rotational constant mentioned above. This angle is quite compatible with the observed hybrid structure of the NH bands, which would be difficult to account for if the angle were in the neighborhood of 112°.

The HNC angle is HNCS is about 10° larger than in HNCO which indicates that of the three resonant structures:



the third is less important than the analogous structure in HNCO. This is in agreement with general chemical experience which indicates that structures with a carbon-sulfur triple bond are less important than others.

* Contribution No. 1446 from the Gates and Crellin Laboratories.

¹ C. I. Beard and B. P. Dailey, *J. Chem. Phys.* **15**, 762 (1947).

² L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945).

³ Jones, Shooley, Shulman, and Yost, *J. Chem. Phys.* **18**, 990 (1950).

The Infra-Red Absorption Spectrum of Isothiocyanic Acid (HNCS)

C. REID

National Research Council, Ottawa, Canada

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THE infra-red absorption spectrum of isothiocyanic acid has been studied in the region 400 to 4000 cm⁻¹, for comparison with that of isocyanic acid (HNCO) of which a more detailed study has recently been made.¹

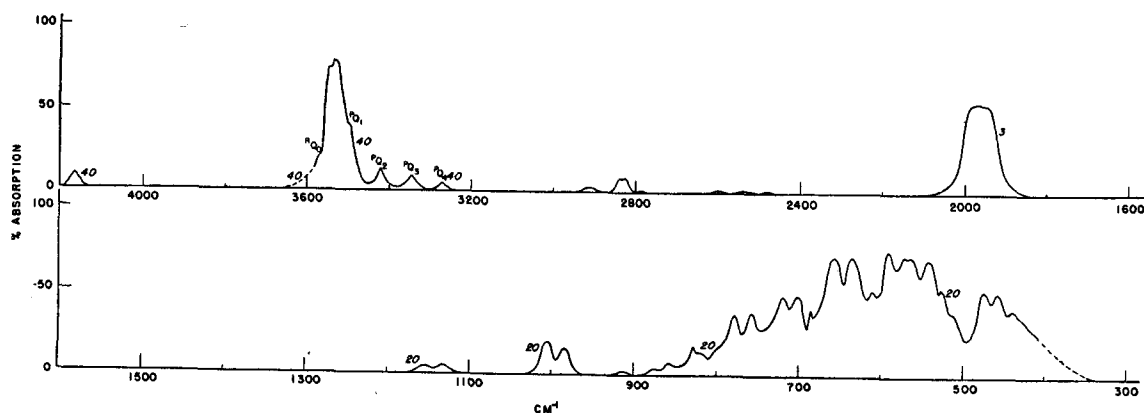


FIG. 1. Infra-red absorption spectrum of HNCS. The figures in italics are the product of gas pressure in centimeters of mercury times path length in centimeters at which the band was observed.

The isothiocyanic acid was prepared by cooling dry potassium thiocyanate to -10°C and slowly adding glacial phosphoric acid while passing a stream of dry nitrogen through the reaction vessel. The gas was condensed at -70°C, and fractionated from a bath at 0° to purify it. HCN was the most troublesome impurity.

At 0°C isothiocyanic acid has a vapor pressure of a few millimeters only, and at higher temperatures rapid decomposition or polymerization to a reddish solid occurs in the condensed phase. By heating quickly above 0°C, however, it is possible to obtain vapor pressures up to 5 cm. At this pressure the vapor is stable at room temperature, although occasionally polymerization occurs after a few hours.

The absorption spectrum was measured using a Perkin-Elmer Model 12B instrument with a 10-cm absorbing path, and gas pressures ranging from 1 to 50 mm. The spectrum obtained is shown in Fig. 1.

On the basis of comparisons with the normal vibrational frequencies of HNCO, COS, and of the NCS ion,² the assignments in Table I have been obtained. The labeling of normal vibrations is

TABLE I. Observed infra-red absorption bands of HNCS.

ν_{vac} observed cm ⁻¹	Assignment and band type		Approximate relative intensity
469	$\nu_5(a')$	Irregular hybrid	125
600	$\nu_6(a'')$	Irregular \perp (?)	200
817(?)	$\nu_4(a')$	Resolved hybrid	75
995	$\nu_3(a')$, P R	50
1145	$\nu_2 - \nu_4(A')$, P R	12
1963	$\nu_2(a')$, P R	1000
2540	$\nu_2 + \nu_6(A')$	Irregular \perp (?)	2.5
2830	$\nu_2 + \nu_4(A')$	Irregular (?)	12
2912	$\nu_2 + \nu_3(A')$	Irregular (?)	4
3536	$\nu_1(a)$	Resolved hybrid	90
4130	$\nu_1 + \nu_6(A')$	Irregular (?)	12

as follows: ν_1 = N—H stretching; ν_2 = asymmetric CNS stretching; ν_3 = symmetric CNS stretching; ν_4 = N—H bending; ν_5 = in-plane CNS bending; ν_6 = out-of-plane CNS bending. Diagrams of the normal vibrations are given in reference 1.

The positions of the two lowest frequency fundamentals are uncertain by about ±10 cm⁻¹ since the values given are approximate centers of irregular bands in which the widely spaced \perp components are interlaced. The origin of ν_4 was tentatively located by the assignment of the series of parallel sub-bands with $K=1, 2$, and 3, respectively, centered at 810, 773, and 712 cm⁻¹. Each of these sub-bands shows P and R, but no Q structure. In view of the