

File Copy

Bookcase

THE MICROWAVE SPECTRA OF CH_3NCS AND CH_3SCN

C. I. BEARD and B. P. DAILEY

TECHNICAL REPORT NO. 79

AUGUST 17, 1948

DEPARTMENT OF CHEMISTRY

HARVARD UNIVERSITY

RESEARCH LABORATORY OF ELECTRONICS

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

The research reported in this document was made possible through support extended the Massachusetts Institute of Technology, Research Laboratory of Electronics, jointly by the Army Signal Corps, the Navy Department (Office of Naval Research) and the Air Force (Air Materiel Command), under Signal Corps Contract No. W36-039-sc-32037, Project No. 102B; Department of the Army Project No. 3-99-10-022.

HARVARD UNIVERSITY
Department of Chemistry

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Research Laboratory of Electronics

Technical Report No. 79

August 17, 1948

THE MICROWAVE SPECTRA OF CH_3NCS AND CH_3SCN

C. I. Beard and B. P. Dailey

Abstract

Measurements of the pure rotational spectra of CH_3NCS and CH_3SCN have been made in the frequency range from 20,000 to 30,000 Mc/sec. Experimental techniques used and the interpretation of the spectra of these molecules are discussed. A theoretical spectrum for CH_3NCS has been set up and the complicating effects of the removal of degeneracies by asymmetry and by an external electric field, of centrifugal distortion, of the presence of excited vibrational states, of internal rotation, of isotopic varieties of the molecule, of nuclear quadrupole coupling, and of other allowed asymmetric rotor transitions are calculated. There is good general agreement between the theoretical and observed spectra for CH_3NCS . The spectrum of CH_3SCN was too weak for detailed analysis but values of the average rotational constant $\frac{1}{2}(B+C)$ are presented.



THE MICROWAVE SPECTRA OF CH_3NCS AND CH_3SCN

1. Introduction

The use of microwave absorption spectroscopy in determining the structure of linear and symmetric top molecules is now well established. The application to asymmetric molecules, although of much importance in broadening the scope of the techniques, has been very slow because of the complexity of the spectra which are observed. These complexities arise not only from the pattern (or lack of one) of rotational energy levels for the asymmetric rotor, but from nuclear quadrupole coupling, rotational-vibrational interaction, internal free or hindered rotation, and from experimental difficulties in observing spectra in the microwave region. All of these complications are potential sources of useful information provided an analysis can be carried out. The natural procedure would seem to be to select molecules for study, to begin with, which would exhibit only one or two of these complications. As an example, SO_2 , for whose spectrum a preliminary analysis¹ has appeared, has no quadrupole interactions (except in molecules involving S^{33}), no internal rotation, and possesses a readily observable spectrum in the microwave region.

In this paper results of the investigation of the microwave spectra of the asymmetric tops, methyl isothiocyanate (CH_3NCS) and methyl thiocyanate (CH_3SCN) will be presented. These are members of an interesting class of asymmetric molecules possessing internal rotating groups. Other members of this class whose microwave spectra have been studied are CH_3NO_2 ², CH_3NH_2 ³, CH_3OH ^{3,4}, and CH_3NC ⁵. CH_3NCS would seem to be a favorable case for analysis since it has an easily observable spectrum in a convenient frequency range, has a negligible quadrupole coupling, and should be only slightly asymmetric. In addition the approximate dimensions of the NCS group are known from the microwave study of HNCS⁶.

2. Experimental Details

The CH_3NCS absorption spectrum has been studied in the frequency range from 20,000 to 30,000 Mc/sec by using the Stark modulation spectrometer previously described⁷. The apparatus, shown in block diagram form in Fig. 1, used a waveguide absorption cell ten feet in length with a 100-kc/sec square-wave Stark field. The CH_3NCS was an Eastman Kodak product used without further purification.

With 100 volts/cm Stark field modulation and a vapor pressure of about .05 mm, more than 29 CH_3NCS absorption lines were found in the region from 19,440 to 29,800 Mc/sec (Fig. 2 and Table I). Frequencies in most cases were determined by using lines of the N^{14}H_3 and N^{15}H_3 inversion spectrum as secondary standards, measuring frequency differences by the method of Good and Coles⁸. The frequencies of the lines marked by asterisks in Table I

Table I. Assignment of Lines in the Rotational Spectrum of CH₃NCS

| Transition | ν Mc/sec | Relative Intensity | Assignment |
|------------|--------------|--|--|
| J = 3 → 4 | 19700* | 5 | CH ₃ NCS ³⁴ ; degenerate line, g.s. |
| | 19929* | 1 | CH ₃ NCS ³⁴ ; degenerate line, I |
| | 20020* | < 1 | |
| | 20140 | 10 | CH ₃ NCS; 3 _{1,3} → 4 _{1,4} g. s. |
| | 20216 | 100 | CH ₃ NCS; degenerate line, g. s. |
| | 20230 | < 1 | |
| | 20241 | 7 | CH ₃ NCS; degenerate line, E? |
| | 20350 | 20 | CH ₃ NCS; degenerate line, D |
| | 20413 | < 1 | |
| | 20443 | 40 | CH ₃ NCS; degenerate line, J |
| J = 4 → 5 | 24143* | < 1 | C ¹³ H ₃ NCS; degenerate line, g.s. |
| | 24609* | 5 | CH ₃ NCS ³⁴ ; degenerate line, g.s. |
| | 24824 | 1 | |
| | 24910 | 2 | CH ₃ NCS ³⁴ ; degenerate line, J |
| | 24930* | < 1 | CH ₃ NCS ³³ ; degenerate line, g.s. |
| | 24971* | 1 | |
| | 25002* | < 1 | CH ₃ NC ¹³ S; degenerate line, g.s. |
| | 25077* | 1 | |
| | 25100* | < 1 | |
| | 25161 | < 1 | |
| | 25195 | 10 | CH ₃ NCS; 4 _{1,4} → 5 _{1,5} , g. s. |
| | 25269 | 100 | CH ₃ NCS; degenerate line, g. s. |
| | 25306 | 7 | CH ₃ NCS; degenerate line, E? |
| | 25333 | 10 | CH ₃ NCS; 4 _{1,3} → 5 _{1,4} , g. s. |
| | 25390 | < 1 | |
| | 25409* | 1 | |
| | 25442 | 25 | CH ₃ NCS; degenerate line, D |
| | 25550 | 40 | CH ₃ NCS; degenerate line, J |
| 25653* | < 1 | CH ₃ NCS; 4 _{1,3} → 5 _{1,4} , J | |
| J = 5 → 6 | 19700 | | CH ₃ NCS ³⁴ ; degenerate line, g. s. |

* These frequencies were determined only by cavity wavemeter readings.

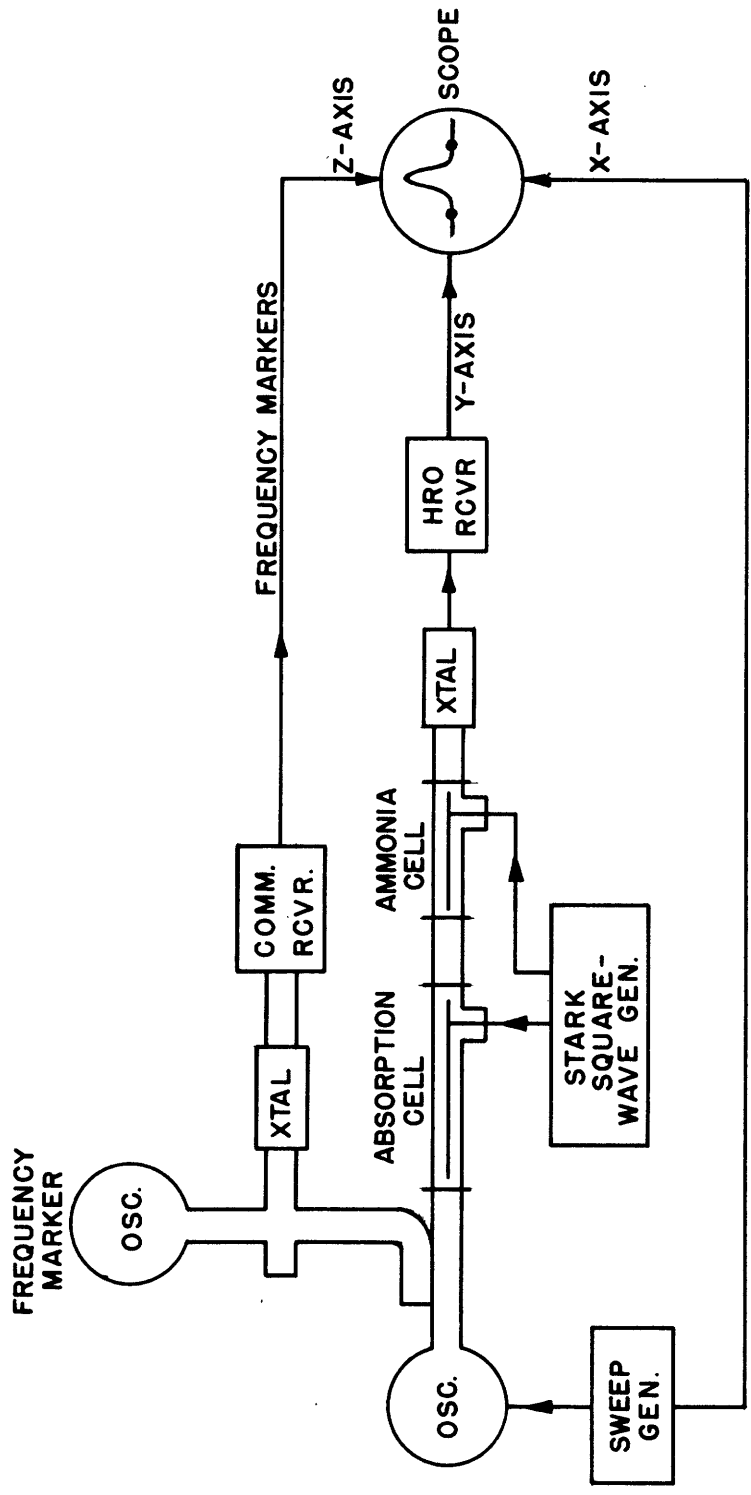


Fig. 1. Arrangements of components in the microwave spectrometer.

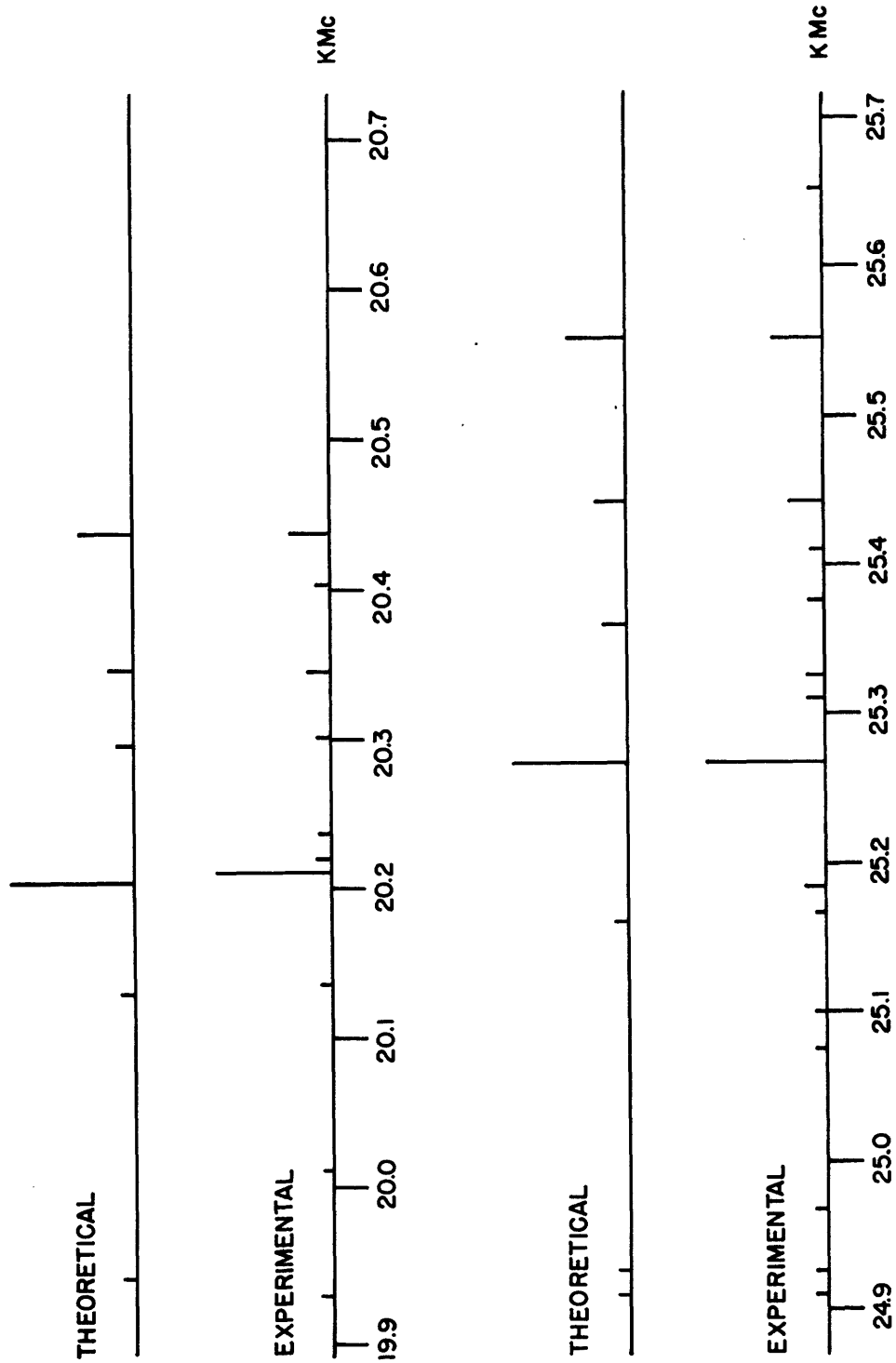


Fig. 2. Microwave spectrum of methyl isothiocyanate.

were determined only by cavity-wavemeter readings. The approximate relative intensities reported represent observed signal strengths at the same power level incident on the terminal crystal detector. These relative intensities are comparable only within each group of lines and are not true relative intensities since they neglect the dependence upon the Stark effect of each line.

3. Theoretical Spectrum

The analysis of the observed spectrum may be most conveniently discussed by setting up a probable structure for the molecule, calculating a theoretical spectrum and comparing with observed results. In view of the microwave data on HNCS we can with some confidence picture CH_3NCS as being a resonance hybrid of the three structures shown in Fig. 3. If we assume

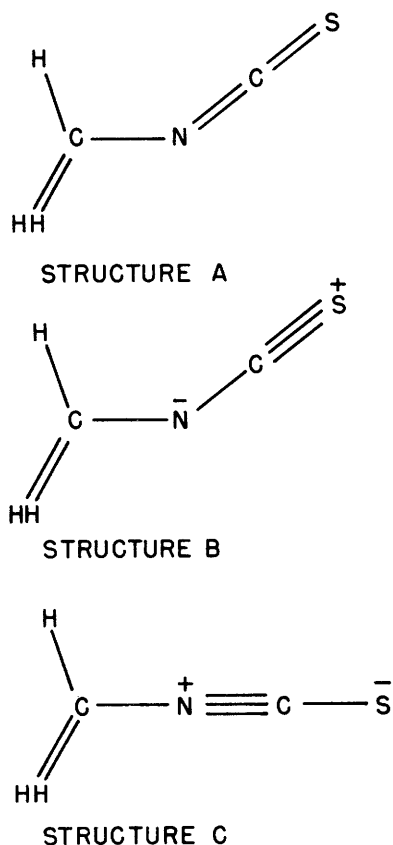


Fig. 3. Resonating structures for CH_3NCS .

that the structure of the NCS group suffers no major changes in going from the acid to the ester, and take the dimensions of the methyl group from the recent accurate work on the methyl halides⁹, we need only choose a value for the $\text{CH}_3\text{-N-C}$ angle to have a complete molecular model. For a first approximation the H-N-C angle could be used although it has been determined only

roughly. The N-C distance in HNCS indicates a predominance of the structure involving the $N \equiv C$ bond and suggests that an angle greater than the average for the resonating structures, 130° , may be the correct one. For the present purpose an angle of 142° has been chosen. The influence of hyperconjugation on the $CH_3-\overset{+}{N} \equiv C-\bar{S}$ structure might lengthen the N-C bonds and shorten the CH_3-N bond but should leave the angle unchanged. The structure illustrated in Fig. 4 should roughly approximate the correct molecular configuration and permit calculation of a theoretical spectrum correct in broad outline.

By using the formula given by Mecke¹⁰ for the energy levels of a slightly asymmetric rotor (which in view of the near degeneracy of the rotational constants B and C should apply in this case),

$$F(J,K) \text{ cm}^{-1} = \frac{(B+C)}{2}J(J+1) + \left[A - \frac{(B+C)}{2} \right] K^2$$

$$\text{where } A = h/8\pi^2 c I_A, \quad B = h/8\pi^2 c I_B, \quad C = h/8\pi^2 c I_C,$$

the following formulas for observed frequencies may be obtained.

$$\text{For } \Delta J = +1, \quad \Delta K = 0$$

$$\nu \text{ cm}^{-1} = (B+C)(J+1).$$

$$\text{For } \Delta J = 0, \quad \Delta K = +1$$

$$\nu \text{ cm}^{-1} = \left[A - \frac{1}{2}(B+C) \right] (2K+1).$$

By using the calculated rotational constants based on the approximate molecular model, spectral lines would be predicted at the frequencies given in Table II. An inspection of this table permits the widely spaced groups of lines at 20,500 and 25,000 Mc/sec to be identified as arising from the parallel type transitions $J = 3 \rightarrow 4$ and $J = 4 \rightarrow 5$. Detailed analysis to be presented later indicates that the lines at 29,800 are the beginning of the $J = 5 \rightarrow 6$ group. On the basis of these simple considerations, however, each of these transitions should consist of but a single line. Since there are more than 19 components in the $J = 4 \rightarrow 5$ group alone, some explanation must be found for the extra lines.

Table II

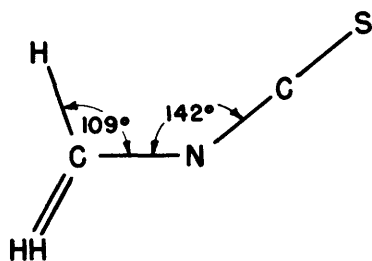
Calculated Rotational Spectrum for CH_3NCS
 Considered as a Nearly Symmetric Rotor.

| J | K | J' | K' | $\nu \text{ cm}^{-1}$ | $\nu \text{ Mc/sec}$ |
|---|---|----|----|-----------------------|----------------------|
| 0 | 0 | 1 | 0 | 0.16856 | 5,053 |
| 1 | 1 | 2 | 1 | 0.33712 | 10,106 |
| 2 | 2 | 3 | 2 | 0.50568 | 15,159 |
| 3 | 3 | 4 | 3 | 0.67424 | 20,212 |
| 4 | 4 | 5 | 4 | 0.84280 | 25,265 |
| 5 | 5 | 6 | 5 | 1.01136 | 30,319 |
| 0 | 0 | 0 | 1 | 2.5257 | 75,716 |
| 1 | 1 | 1 | 2 | 7.5772 | 227,148 |

4. Removal of Degeneracies

By considering the various complicating factors in turn, the removal of degeneracies known to exist in the pattern of symmetric rotor energy levels by the asymmetry of the molecule and by the modulating field will be taken up first. Each J level in the symmetric rotor is made up of $2J + 1$ degenerate levels corresponding to the individual values of K. In turn each J K level is made up of $2J + 1$ levels, degenerate in the absence of an external field corresponding to the individual values of the quantum number M. In the specific case of a molecule having the structure indicated in Fig. 4 the K degeneracy is at least partially removed by the molecular asymmetry. The transition frequencies for such an asymmetric rotor have been calculated with the use of third-order perturbation theory, and the coefficients tabulated by King, Hainer, and Cross¹¹ and are given in Table III. The single line predicted above for the $J = 4 \rightarrow 5$ transition, for example, has been replaced by a pattern of three lines. The lines corresponding to (in the KHC notation) the $4_{1,4;-3} \rightarrow 5_{1,5;-4}$ and $4_{1,3;-2} \rightarrow 5_{1,4;-3}$ transitions have split, not quite symmetrically, some 100 Mc/sec away, on either side of the degenerate line.

Since the spectrometer employs an applied electric field for modulation, the spectrum actually observed is complicated by the presence of lines corresponding to the individual M values. The experimental arrangement is such that the electric radiation vector and the applied electric field are parallel (except for negligible fringing effects near the edges of the waveguide absorption cell) and the selection rule $\Delta M = 0$ is obeyed. Analysis



| | | | |
|--------------|--------|----------------|---|
| C-H DISTANCE | 1.09 Å | I _A | $10.72 \times 10^{-40} \text{ g.cm.}^2$ |
| C-N DISTANCE | 1.47 | I _B | 329.34 |
| N-C DISTANCE | 1.22 | I _C | 334.85 |
| C-S DISTANCE | 1.56 | A | 2.61 cm. ⁻¹ |
| H-C-N ANGLE | 109° | B | 0.08498 |
| C-N-C ANGLE | 142° | C | 0.08358 |

Fig. 4. Approximate molecular configuration of CH₃NCS.

Table III

Calculated Rotational Spectrum For CH₃NCS Considered as an Asymmetric Rotor

| Transition | ν Mc/sec |
|---|--------------|
| ${}^3_{0,3;-3} \rightarrow {}^4_{0,4;-4}$ | 20,215 |
| ${}^3_{1,3;-2} \rightarrow {}^4_{1,4;-3}$ | 20,131 |
| ${}^3_{1,2;-1} \rightarrow {}^4_{1,3;-2}$ | 20,297 |
| ${}^3_{2,2;0} \rightarrow {}^4_{2,3;-1}$ | 20,215 |
| ${}^3_{2,1;+1} \rightarrow {}^4_{2,2;0}$ | 20,216 |
| ${}^3_{3,1;+2} \rightarrow {}^4_{3,2;+1}$ | 20,215 |
| ${}^3_{3,0;+3} \rightarrow {}^4_{3,1;+2}$ | 20,215 |
| ${}^4_{0,4;-4} \rightarrow {}^5_{0,5;-5}$ | 25,262 |
| ${}^4_{1,4;-3} \rightarrow {}^5_{1,5;-4}$ | 25,158 |
| ${}^4_{1,3;-2} \rightarrow {}^5_{1,4;-3}$ | 25,364 |
| ${}^4_{2,3;-1} \rightarrow {}^5_{2,4;-2}$ | 25,265 |
| ${}^4_{2,2;0} \rightarrow {}^5_{2,3;-1}$ | 25,266 |
| ${}^4_{3,2;+1} \rightarrow {}^5_{3,3;0}$ | 25,265 |
| ${}^4_{3,1;+2} \rightarrow {}^5_{3,2;+1}$ | 25,265 |
| ${}^4_{4,1;+3} \rightarrow {}^5_{4,2;+2}$ | 25,265 |
| ${}^4_{4,0;+4} \rightarrow {}^5_{4,1;+3}$ | 25,265 |

of this pattern of Stark components would allow calculation of the component dipole moment along the approximate figure axis of the molecule, but unfortunately the complexity of the not-very-intense spectrum was such that an analysis has not been carried out. In the reported spectrum Stark components have been omitted by eliminating every line whose frequency varied with the electric field. The principal difficulty is that certain lines having only a second-order Stark effect, and appearing in the spectrum only for values of the modulating voltage above a certain minimum, may have been overlooked.

5. Centrifugal Distortion

The foregoing calculations were based on the assumption that the molecule was rigid. The actual molecule is subject to centrifugal distortion which will have an effect on the pattern of rotational energy levels. Slawsky and Dennison¹² give the following expression for the energy levels of a non-rigid symmetric rotor

$$F(J,K) = BJ(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$$

which leads to an expression

$$\nu = 2B(J+1) - D_J (J+1)^3 - D_J' (J+1) + D_{JK} K^2 (J+1)$$

where constants are as previously defined (p.6). Slawsky and Dennison give the following calculated values of the constants for the case of CH_3Cl

$$\begin{aligned} D_J &= 0.0036 \text{ Mc/sec} \\ D_J' &= 0.0414 \text{ Mc/sec} \\ D_{JK} &= 0.4020 \text{ Mc/sec.} \end{aligned}$$

Gordy, Simmons, and Smith⁹ report an experimental value of D_{JK} for CH_3Cl of 0.19 Mc/sec. The term involving D_{JK} is much the largest and should lead to a separation between the $K = 0$ and $K = 4$ components of the degenerate transition of as much as 15 Mc/sec. In the experimental spectrum there is considerable evidence of fine structure on the high-frequency side of the degenerate line but interference from the pattern of Stark components has prevented any accurate measurement of this centrifugal splitting. The term involving D_J will cause deviations from the frequencies predicted by using a linear relation between ν and $J(J+1)$. The example of CH_3Cl makes it seem probable that this effect would be unobservable with the precision of frequency measurement available in this study.

6. Excited Vibrational States

The interaction of vibration and rotation has so far been neglected. The rotational constant B (and A and C as well) actually has different values in the different vibrational states. This dependence of B on the vibrational quantum numbers is indicated by the following formula, taken from Herzberg¹³:

$$B_{[v]} = B_e - \sum_i \alpha_i^B (v_i + d_i/2)$$

where the α_i are small compared to B_e , which is the rotational constant for the equilibrium position; d_i is the degree of degeneracy of the vibration v_i . The summation extends over all vibrations. The constants α_i are usually positive for the non-degenerate vibrations of linear molecules, but may be positive or negative for the degenerate vibrations.

No complete vibrational study and resulting assignment of fundamentals has yet been published for CH_3NCS . Goubeau and Gott¹⁴, however, have determined the stretching frequencies for the linear portion of the molecule, and Eyster and Gillette¹⁵ have made vibrational assignments for similar molecules including CH_3NCO . The approximate vibrational frequencies listed in Table IV should then be at least of the correct order of magnitude. The Boltzmann factors computed from these frequencies indicate roughly the expected ratio of relative intensities of spectral lines due to the same transition for molecules in the ground and excited vibrational states.

The vibrations of series A correspond to CH_3 -N stretching frequencies. Series B and C are stretching frequencies localized within the linear portion of the molecule. B is the N-C stretching and C the C-S stretching frequencies in CH_3NCS . The D vibration corresponds to the bending of the CH_3 -N bond against the linear group. The E vibrations are the perpendicular bending vibrations of the linear group.

The vibrations F through H are the well-known internal vibrations of the methyl group. The I vibrations correspond to the rocking frequencies of the methyl group. The torsional oscillation frequency J requires further discussion.

7. Internal Rotation

The features of the spectrum due to the internal rotation of the methyl group and isothiocyanate group independently about the molecular axis will depend upon the height of the barrier hindering the rotation. If the barrier is of a comparable (although probably somewhat smaller) magnitude to that in the roughly similar case of methanol¹⁶ an appreciable number of molecules will occupy the first excited torsional vibration level. Indeed, if the figure 250 cm^{-1} for the height of this excited state above the ground level listed in Table IV is correct, a line in the observed spectrum due to

Table IV

Approximate Vibration Frequencies For CH₃NCS

| Series | CH ₃ NCO | CH ₃ NCS | CH ₃ NCS |
|--------|---------------------------|---------------------------|---------------------|
| | ω cm ⁻¹ | ω cm ⁻¹ | $e^{-h\nu/kT}$ |
| A | 870 | 850 | 0.0166 |
| B | 2232 | 2162 | <0.0001 |
| C | 1412 | 1087 | 0.0052 |
| D | 353 | 300 | 0.2340 |
| E | 652 607 | 600 550 | 0.0550 0.0699 |
| F | 2994 2951 | 3000 2950 | <0.0001 <0.0001 |
| G | 1453 | 1450 1440 | 0.0009 0.0009 |
| H | 1377 | 1375 | 0.0014 |
| I | 1181 1107 | 1200 1100 | 0.0030 0.0049 |
| J | ? | 250 | 0.2982 |

the second excited state might well appear. In methanol, the ratio of populations for the ground state and first excited state of torsional vibration is 0.18; in the case of CH₃NCS this ratio would probably be somewhat larger.

For low values of the barrier height and in any case for torsional vibration states higher than the second or third, the internal rotation would be essentially free. If we apply the analysis of Koehler and Dennison¹⁶ (which should fit only roughly because of the considerable asymmetry of the NCS group), the following expression for the frequencies of the lines in the $\Delta J = 0$ series may be used:

$$\nu = A_1 - B - 2BK + 2A_1K_1,$$

where A_1 is the rotational constant for the NCS group about the molecular

axis (not the symmetry axis of the methyl group). By using the rotational constants given in Fig. 4 and a minimum value of A_1 of 3.0 cm^{-1} the frequencies for this series were calculated. All lie outside the experimental frequency range for this investigation.

The torsional vibrational states, according to the analysis of the methyl alcohol problem presented by Koehler and Dennison, are actually made up of a number of sublevels with a spread in energy which increases with the torsional vibration quantum number. In general there are three sublevels for each permitted K value although certain degeneracies occur. For methyl alcohol the spread of the energy levels for the first excited state has been calculated to be 33 cm^{-1} . Since this spread varies inversely with the barrier height, an even wider separation of levels would be expected for CH_3NCS . It is difficult to predict whether the first excited torsional state will give rise to a single broad line in the pure rotation spectrum or will have a resolvable structure.

A limit to the complexity introduced into the observed spectrum by excited vibrational states is set only by the available sensitivity of the spectrometer. If the observed spectrum is limited to those lines whose apparent intensity is at least 0.05 of that for the most intense line in the spectrum, the Boltzmann factors listed in Table IV should permit selection of the vibrations whose first excited states might give rise to lines. On this basis the most intense of the excited vibration lines should be due to the torsional vibration J. Next most intense would be the line corresponding to the first excited state of the $\text{CH}_3\text{-N}$ bending vibration, D. Following in order of intensity would be the second excited levels for these two vibrations and the first excited levels for the nearly degenerate bending modes of the NCS group, E. Finally, a line due to the first excited level for the $\text{CH}_3\text{-N}$ stretching vibration, A, might be seen. The α 's for these vibrational states cannot be easily calculated, so that the lines due to excited vibrational states must be identified from their intensities and from the change of intensity with temperature. The experimental measurement of temperature coefficients of intensity was made rather difficult by the small temperature range over which measurements could be made for this molecule and with the present equipment. The rough values obtained, however, definitely serve to establish several of the fairly intense lines as being due to excited vibrational states.

8. Isotopic Spectra

There should be, of course, separate and easily resolvable microwave spectra for each of the different isotopic varieties of the CH_3NCS molecule. The relative intensities of lines due to the more abundant naturally occurring CH_3NCS molecules have been calculated and are given in Table V.

Table V

Relative Abundance of Isotopic Varieties of CH_3NCS

| Molecule | Relative Abundance |
|--|--------------------|
| $\text{C}^{12}\text{H}_3\text{N}^{14}\text{C}^{12}\text{S}^{32}$ | 100.00 |
| $\text{C}^{12}\text{H}_3\text{N}^{14}\text{C}^{12}\text{S}^{34}$ | 4.40 |
| $\text{C}^{12}\text{H}_3\text{N}^{14}\text{C}^{12}\text{S}^{33}$ | 0.76 |
| $\text{C}^{13}\text{H}_3\text{N}^{14}\text{C}^{12}\text{S}^{32}$ | 1.08 |
| $\text{C}^{12}\text{H}_3\text{N}^{14}\text{C}^{13}\text{S}^{32}$ | 1.08 |
| $\text{C}^{12}\text{H}_3\text{N}^{15}\text{C}^{12}\text{S}^{32}$ | 0.38 |

If the same range of relative intensities is used here as was proposed earlier in the discussion of excited vibrational states, any or all of these molecules might give rise to observable spectra. It is even probable that for the molecule involving S^{34} lines due to both the ground and excited vibrational states would be seen.

9. Nuclear Quadrupole Coupling

Two of the nuclei which are concerned in the CH_3NCS molecular species have nuclear quadrupole moments: N^{14} and S^{33} . In the latter case, the intensity of the main transition must be so low that the quadrupole fine structure would be unobservable. For N^{14} intensities of the fine structure components might be sufficient, but it is doubtful that the spectrometer was operated with sufficient resolving power to separate the individual lines. In the closely similar case of N in CH_3NC the quadrupole splitting has been reported as less than 1 Mc/sec. Line widths in this study were considerably larger than this figure. Line widths were, in fact, unusually broad although extra width seems to be a feature of the microwave rotational spectral lines of symmetric rotors possessing large dipole moments.

10. Other Asymmetric Rotor Transitions

In considering the molecule as an asymmetric rotor, certain transitions become possible other than the ones so far dealt with which correspond to the parallel type $\Delta J = 1, \Delta K = 0$ transitions of the prolate symmetric rotor and in the KHC notation¹⁷ are described as $ae_{R_{0,1}}$ or $ao_{R_{0,1}}$. For the most part, however, the intensities of other types of "a" transitions may be shown to be too small to be detected with the present equipment for all reasonable values of the asymmetry parameter K . The only other "a" transitions which might be observable are the $ao_{Q_{0,1}}$ transitions between the split components of each K level. Very high J values would be required to bring the frequencies of such lines into the observed region so that the resulting Boltzmann factors would reduce their intensities to a rather small figure. Such transitions would be so widely spaced that at most they could account for only two or three lines in the entire experimental frequency range.

Since there is no component of the dipole moment along the I_C axis (perpendicular to the C-N-C-S plane) "c" type transitions will have zero intensity. While a small component of the dipole moment does exist along the I_B axis, the intensities of "b" type transitions would be quite small, since the intensity is proportional to the square of the dipole moment component. There are a number of lines of low intensity in the observed spectrum which have not been accounted for (as well as some for whose assignment there is at least a reasonable doubt), so that this possibility cannot be completely ruled out.

11. Analysis of Observed Spectrum

An analysis of the observed spectrum has been made in the light of the discussion above and the results are presented in Table I. The theoretical spectrum, calculated using the molecular model described in Fig. 4, and compared to the experimental spectrum in Fig. 2, reproduces the general features of the experimental spectrum quite well. The features of this spectrum which are advanced with the most confidence are the following. The average rotational constants, $(\frac{B+C}{2})$, for CH_3NCS in the ground vibrational state have the values indicated in Table VI. Certain of the lines in different transition groups reveal by the ratio of their frequencies that they correspond to the same average rotational constant, which is different from the value assigned to the most abundant isotopic variety in the ground vibrational state. The details of the assignment of these rotational constants to different isotopic varieties of the molecule in different vibrational states depend upon measurements of relative intensity and calculations of isotopic frequency shifts. The relative intensities are highly approximate because of

difficulties encountered in their measurement. The calculated frequency shifts, of course, depend upon the assumed molecular model. In the case of the lines assigned to the first excited torsional vibration level, however, the intensities are so large as to rule out most other possible assignments. For the lines assigned to $\text{CH}_3\text{NCS}^{34}$ both the frequency shifts and the intensities are of the right order of magnitude and their agreement lends confidence to the conclusion. The assignment of the next most intense set of lines to the first excited state of the $\text{CH}_3\text{-N}$ bending mode seems reasonable, since in the vibrational assignment for similar molecules this is much the lowest lying vibration exclusive of torsion. The assignment of lines to the nearly degenerate bending modes of the NCS group is much more doubtful, but has been made simply on the basis of the relative intensities. Because of the complexity of the spectrum the interesting question of the effects of the near degeneracy and slight asymmetry on what would be ℓ -type doubling in a linear molecule has not been pursued. Because of the uncertainty in the degeneracy of the line ascribed to the first excited torsional vibration level the assignment of the lines in the neighborhood of 25,500 Mc/sec is rather tentative. It is possible that this group of lines are the resolved components of the degenerate line.

Table VI

Rotational Constants for CH_3NCS Molecules

| Molecule | ν Mc/sec | $(\frac{B+C}{2})^{-1}$ cm ⁻¹ | Transition | Vib. State | I_{av} in units of 10 ⁻⁴⁰ gm·cm ² |
|------------------------------|--------------|---|-----------------------|------------|---|
| CH_3NCS | 20216 | 0.084295 | $J = 3 \rightarrow 4$ | ground | 332.01 |
| | 25268 | 0.084292 | $J = 4 \rightarrow 5$ | ground | 332.02 |
| | 20443 | 0.085241 | $J = 3 \rightarrow 4$ | I | 328.33 |
| | 25550 | 0.085223 | $J = 4 \rightarrow 5$ | I | 328.40 |
| | 20350 | 0.084854 | $J = 3 \rightarrow 4$ | D | 329.83 |
| | 25442 | 0.084869 | $J = 4 \rightarrow 5$ | D | 329.77 |
| $\text{CH}_3\text{NCS}^{34}$ | 19700 | 0.082144 | $J = 3 \rightarrow 4$ | ground | 340.71 |
| | 24609 | 0.082090 | $J = 4 \rightarrow 5$ | ground | 340.93 |
| | 29540 | 0.082116 | $J = 5 \rightarrow 6$ | ground | 340.82 |
| | 19929 | 0.083099 | $J = 3 \rightarrow 4$ | I | 336.79 |
| | 24910 | 0.083094 | $J = 4 \rightarrow 5$ | I | 336.81 |

The designation of certain of the lines as components of the degenerate main transition split by the molecular asymmetry is somewhat difficult because their spacing is quite sensitive to the small changes in the rotational constants and their intensities are low enough to permit confusion with the excited vibrational lines. The spacing of the lines

should be nearly symmetric about the degenerate line and should be greater for the $J = 4 \rightarrow 5$ transition than for the $J = 3 \rightarrow 4$. The relative intensities should be in the calculated ratio. Most of these requirements are at least roughly met by the assignment given above.

12. CH₃SCN Spectrum

With the same Stark modulation apparatus, the region from 20,000 to 30,000 Mc/sec was searched for lines of methyl thiocyanate. The observed spectrum was similar in many respects to that for the tautomeric ester although, of course, occurring at different frequencies. Again the spectrum consisted of complex groups of lines. However, for methyl thiocyanate the intensities were so low that only the strongest lines could be properly studied. The two strongest lines, which by analogy with the tautomeric ester would be assigned to the degenerate transition of the ordinary isotopic form of the molecule, were found to have the frequencies given in the following table.

| Frequency | Transition | Average Rotational Constant |
|---------------|-----------------------|-----------------------------|
| 22,680 Mc/sec | $J = 3 \rightarrow 4$ | 0.09457 cm^{-1} |
| 28,380 | $J = 4 \rightarrow 5$ | 0.09467 |

The frequencies were determined with a cavity wavemeter and are accurate only to ± 10 Mc/sec.

The frequency ratio of these lines enables them to be identified as $\Delta J = 1$, $\Delta K = 0$ transitions of a slightly asymmetric rotor involving the J values listed above. This conclusion is supported by calculations based on various probable structures of the CH₃SCN molecule. By assuming probable values of the interatomic distances, the C-S-C angle corresponding to moments of inertia resulting from the observed value of $(\frac{B+C}{2})$ could be calculated. The CH₃SCN structure shown in Fig. 5 is the one consistent with the above considerations. In order to determine the structure completely from the spectrum independently of the above assumptions, spectra for several different isotopic varieties of the molecule, probably synthesized from enriched material, would have to be observed.

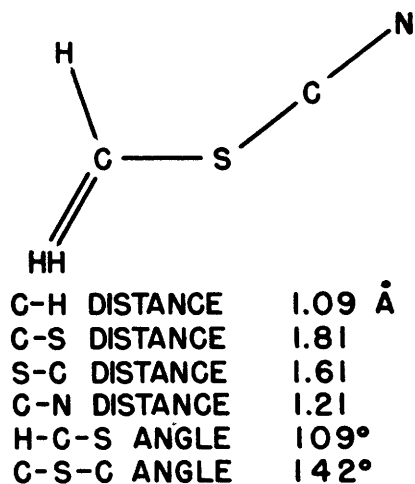


Fig. 5. Approximate molecular configuration of CH_3SCN .

References

1. B. P. Dailey, S. Golden, and E. B. Wilson, Jr., Phys. Rev. 72, 871 (1947).
2. B. P. Dailey and E. B. Wilson, Jr., paper presented at regional meeting of the American Physical Society, Amherst, Mass., May 31, 1947.
3. W. D. Hershberger and J. Turkevitch, Phys. Rev. 71, 554 (1947).
4. B. P. Dailey, Phys. Rev. 72, 84 (1947).
5. H. Ring, H. Edwards, M. Kessler, and W. Gordy, Phys. Rev. 72, 1262 (1947).
6. C. I. Beard and B. P. Dailey, J. Chem. Phys. 15, 762 (1947).
7. R. H. Hughes and E. B. Wilson, Jr., Phys. Rev. 71, 562 (1947).
8. W. E. Good and D. K. Coles, Phys. Rev. 71, 383 (1947).
9. J. W. Simmons, W. Gordy, and A. G. Smith, Phys. Rev. (in press).
10. R. Mecke, Z. Physik, 81, 313 (1933).
11. G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. 11, 27 (1943).
12. Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. 7, 509 (1939).
13. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, 1945, p. 370.
14. J. Goubeau and O. Gott, Ber. 73B, 127 (1940).
15. E. H. Eyster and R. H. Gillette, J. Chem. Phys. 8, 369 (1940).
16. J. S. Koehler and D. M. Dennison, Phys. Rev. 57, 1006 (1940).
17. P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. 12, 210 (1944).

