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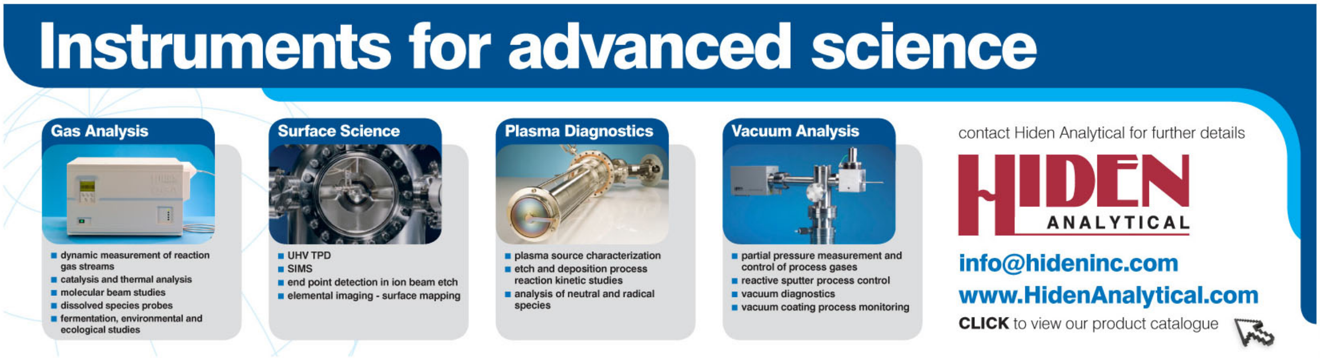

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Microwave Spectrum of Methyl Isocyanate*

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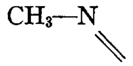
The $J0\rightarrow1$ and $J1\rightarrow2$ a-type transitions of CH_3NCO and CD_3NCO have been studied. These transitions are complicated by the population of a number of internal rotation states. Several absorptions arising from the lowest energy internal rotation states have been assigned. The barrier to internal rotation of the methyl group in CH_3NCO has been found to be 49±3 cal/mole from the splitting of the $J3\rightarrow4$, $K=\pm1$, $m=\pm3$ transition by the barrier. The component of electric dipole moment parallel to the a axis has been found to be 2.81±0.06 D by measurement of the Stark effect. The nitrogen quadrupole coupling constant has been found to be $eqQ=+2.3$ Mc/sec.

INTRODUCTION

IN the past few years the barriers to internal rotation of methyl groups have been measured in a number of molecules by analysis of characteristic internal rotation splittings found in their microwave spectra. None of these molecules contained the



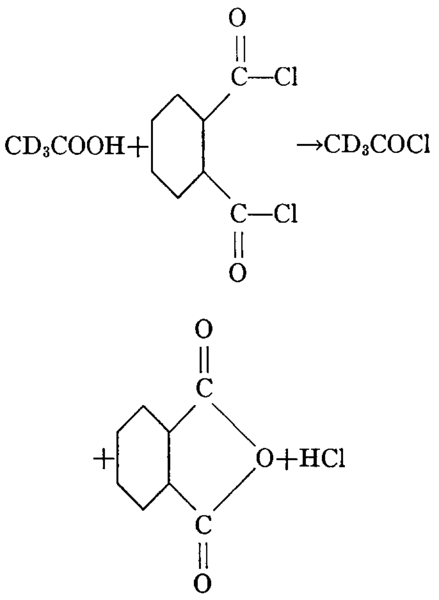
group which is found in methyl isocyanate, methyl isothiocyanate, methyl azide, or N-methylmethylenimine. The only recent study specifically aimed at dedetermining the barrier to internal rotation of such a compound of which the authors are aware was that made by Siegel[1] on methyl isothiocyanate.

The results of that investigation were inconclusive as far as the barrier to internal rotation was concerned. The transitions observed were the a-type R branches. The $J1\rightarrow2$ absorptions instead of consisting of three lines of comparable intensity as would be expected for a rigid molecule, consisted of some 19 lines of comparable intensity. The many additional lines presumably arise from excited internal rotation and excited vibrational states. The richness of the spectrum probably indicates that the barrier to internal rotation is low. Without an assignment of internal rotation and vibrational quantum numbers, the barrier could not be determined. Such an assignment appears to be very difficult to make for methylisothiocyanate. When methylisocyanate was investigated it was quickly established that a similar situation exists for that molecule, but the assignment of quantum numbers proved to be easier.

EXPERIMENTAL

A sample of methyl isocyanate was obtained from the Ott Chemical Company and used without further purification. The spectrum was observed on a conventional Stark modulation spectrograph. The modulation frequency was 100 kc/sec. The lines were broadened by nitrogen quadrupole structure which was not usually resolved. The estimated uncertainty in the frequencies from this source is ±0.4 Mc/sec. Most of the investigation was carried out with the absorption cell cooled by dry ice, and the estimates of relative intensities given were made with the dry-ice cooling.

CD_3NCO was prepared by the sequence of reactions:



$$CD_3COCl+NaN_3\rightarrow CD_3CON_3+NaCl,$$

$$CD_3CON_3\rightarrow CD_3NCO+N_2.$$

The last two reactions take place in the same reaction vessel.

The 99% deuteroacetic acid was purchased from the Isomet Corporation. The procedure followed in the first step was a modification of that of Cox and Turner.[2] In our preparation 5.8 ml of CD_3COOD was mixed

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[†] Alfred P. Sloan Foundation Fellow.

[1] S. Siegel, thesis, Harvard University, Cambridge, Massachusetts, 1958.

[2] J. D. Cox and H. S. Turner, J. Chem. Soc. **1950**, 3176.

TABLE I. Observed frequencies of methyl isocyanate.

	Frequency (Mc/sec)	Intensity[a]	Tentative *m* assignment
CH_3NCO			
$J0\to1$			
$K=0^b$			
	8 661.2	1.3	
	8 671.8	12.0	0^c
	8 692.3	0.7	
	8 706.5	3.5	
	8 712.1	9.7	2
	8 714.3	10.4	1
	8 722.6	10.4	±3
	8 726.4	3.5	
	8 732.9	1.0	
	8 736.6	3.2	4
	8 747.6	1.2	
	8 755.4	2.5	5
	8 775.1	<1	±6
	8 796.5	<1	7
$J1\to2$			
$K=0$			
	17 342.9	8	0^c
	17 421.2		
	17 425.4	10	2
	17 426.3		
	17 427.7		1
	17 444.1	5	±3
	17 445.8		
	17 453.7[d]	3	
	17 463.4	1	
	17 475.3	3	4
	17 510.4[d]	5	5
	17 551.5	2	±6
$K=1$			
	17 131.7	2	
	17 140.0	3	+1
	17 175.6	1	
	17 190.5	5	$0^c(1_{11}\to2_{12})$
	17 381.5	1	
	17 403.4	2	
	17 408.7	1	−3±
	17 413.1	1	
	17 453.7[d]	3	
	17 489.5	3	
	17 504.3	6	$0^c(1_{10}\to2_{11})$, $+3+^c$
	17 510.4[d]	5	$+3-^c$
	17 533.2	0	
	17 540.4	0	
$J2\to3^e$			
$K=0$			
	25 763.9	mw	
	25 983.6		
	26 010.9	s	
	26 013.2	vs	0^c
	26 053.0	w	
	26 106.7	s	
	26 131.3	s	2
	26 136.9	s	1
	26 166.1	m	±3
	26 168.4	m	
	26 179.0	ms	
$J2\to3^e$			
$K=0$			
	26 181.0	ms	
	26 212.1	m	4
	26 217.7	mw	
	26 326.6	mw	±6
	26 386.6	w	7
	26 390.9	vw	
$K=1$			
	25 696.9	mw	
	25 711.2	mw	+1
	25 765.9	mw	
	25 782.3	ms	$0^c(2_{12}\to3_{13})$
	25 784.9		
	26 106.7	s	
	26 108.8	s	−3±
	26 118.8	w	
	26 227.2	m	
	26 229.4	m	
	26 258.7	m	$0^c(2_{11}\to3_{12})$, $+3+^c$
	26 265.3	m	$+3-^c$
	26 300.0	mw	
$K=2$			
	25 665.2	mw	
	26 037.9	s	±0
	26 101.2	s	
	26 141.1	w	
	26 149.1	w	
	26 173.0	mw	
$J3\to4^f$			
$K=1$			
	35 008.8	s	$0^c(3_{12}\to4_{13})$
	35 012.0	s	$+3+^c$
	35 020.5	s	$+3-^c$
CD_3NCO			
$J0\to1$			
$K=0$			
	7 668.6		
	7 672.8		
	7 674.2	8	0^c
	7 693.2	2	
	7 703.0	6	
	7 708.7	16	1, 2
	7 715.1	9	±3
	7 719.9	5	
	7 727.5	6	4
	7 735.3	3.5	
	7 742.3	3.5	5
	7 754.4	2	
	7 758.5	3.4	±6
	7 769.4	1.5	
	7 777.4	2	7
	7 779.4		
	7 787.0	2	
	7 797.3	2	8
	7 819.5	1	±9

TABLE I (*Continued*)

	Frequency (Mc/sec)	Intensity[a]	Tentative m assignment
$J1\rightarrow 2$			
$K=0$			
	15 348.1	12.5	0[c]
	15 407.0	1	
	15 413.9	9	
	15 415.5	15	2
	15 416.6	13.5	1
	15 429.2	7.5	±3
	15 431.4	7.5	
	15 438.5	3	
	15 440.1	4.3	
	15 455.1	7.5	4
	15 467.1	3.5	
	15 470.9	4.2	
	15 484.8[d]	7.3	5
	15 507.6	1.8	
	15 516.8	4.8	±6
	15 536.3	1.3	
	15 539.9	3.0	
	15 553 9	2.6	7
$K=1$			
	15 182.9	4.2	+1
	15 211.7	6.5	0[c]($1_{11}\rightarrow 2_{12}$)
	15 366.2	2.0	
	15 376.2	~2.	
	15 383.6	~2.	
	15 403.7	2.1	
	15 480.5	4 0	
	15 484.8[d]	7.3	
	15 488 1	5.1	0($1_{10}\rightarrow 2_{11}$)
	15 490.9	3.2	
	15 495.1	1.8	
	15 498.8	0.9	
	15 502.4	2.1	
$J2\rightarrow 3$[f]			
$K=1$			
	22 775.4		+1
	22 816 8		0[c]($2_{12}\rightarrow 3_{13}$)
	23 049 6		
	23 064.5		
	23 106.7		
	23 231.3		0[c]($2_{11}\rightarrow 3_{12}$)

[a] The scale of intensities is arbitrary and no comparison is possible between different $J\rightarrow J+1$ transitions or different isotopes. The intensities should be accurate to ±15% or ±0.5 unit, whichever is larger.

[b] The assignment of K quantum number is made by the second-order Stark of $K=0$ lines and the $J\rightarrow J+1$ transition for which a line first appears. The quantity $\nu/(J+1)$ is very accurately constant. Naturally the distinction between $K=0$ and $K=1$ is more reliable than between $K=1$ and $K=2$, since the Stark effect can be used in the former case.

[c] These assignments are considered definite not tentative.

[d] There are two different K-value lines not resolved at this frequency.

[e] This region has not been as thoroughly investigated as the others.

[f] Only a few lines have been studied in this region.

with 35 ml of phthaloyl chloride. This mixture was placed in a small distillation apparatus with the condenser cooled with ice water and heated gently with a small flame. When the temperature of the mixture reached about 70°C, a rapid reaction occurred with the evolution of a large amount of HCl. At the same time, liquid began to collect in the receiver. After the reaction had ceased, the mixture was heated gradually to 210°C. Most of the deuterated acetyl chloride distilled over a vapor temperature of 51°C. The vapor temperature never exceeded 55°C. The yield was not measured but appeared to be good.

The conversion of deuteroacetyl chloride to CD_3NCO seemed much more difficult. Several trial runs were unsuccessful, probably because of the presence of traces of moisture in the NaN_3. The procedure followed was similar to that of Schroeder.[3] The sodium azide was activated by a modification[4] of the method of Nelles.

The yield from the first reaction was placed in a 60-ml pear-shaped flask with 10 ml of xylene and cooled to −78°C. Then 8.0 g of NaN_3 was added. The pear-shaped flask was connected to an ice-water-cooled reflux condenser. The reflux condenser was connected in turn to a cold trap which was in dry ice. The trap was protected from atmospheric moisture with a drying tube. The mixture was allowed to stand overnight and then refluxed for several hours. Finally, the dry ice on the trap was replaced with liquid nitrogen, the reaction vessel was cooled with ice and salt, and the methyl isocyanate distilled over under vacuum. The product contained xylene and acetyl chloride. The yield was reasonable for microwave purposes.

SPECTRUM OF METHYL ISOCYANATE

Only the regions of the a-type 0→1, 1→2, and 2→3 absorptions have been investigated thoroughly. Outside these regions the spectrum is sparse. No other lines have been observed. The observed spectrum is shown in Table I and Fig. 1. The assignments shown in Table I must be regarded as tentative except where they are indicated as unequivocal. They will be discussed later.

All of the lines observed in the 0→1 region appeared to have a single second-order Stark lobe to high frequency. The corresponding lines in the 1→2 region have one second-order lobe to high and one second-order lobe to low. All the remaining lines in the 1→2 region appear at very low Stark voltages of about 10–20 V/cm. Where the spectrum was uncrowded and it was possible to study the Stark lobes of these lines with rapid Stark effects, it was found that there is a rapid Stark lobe to each side of the line with one ex-

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[3] G. Schroeder, Ber. **42**, 3356 (1909).

[4] P. A. S. Smith, *Organic Reactions* (John Wiley & Sons, Inc., New York, 1946), Vol. III, p. 382.

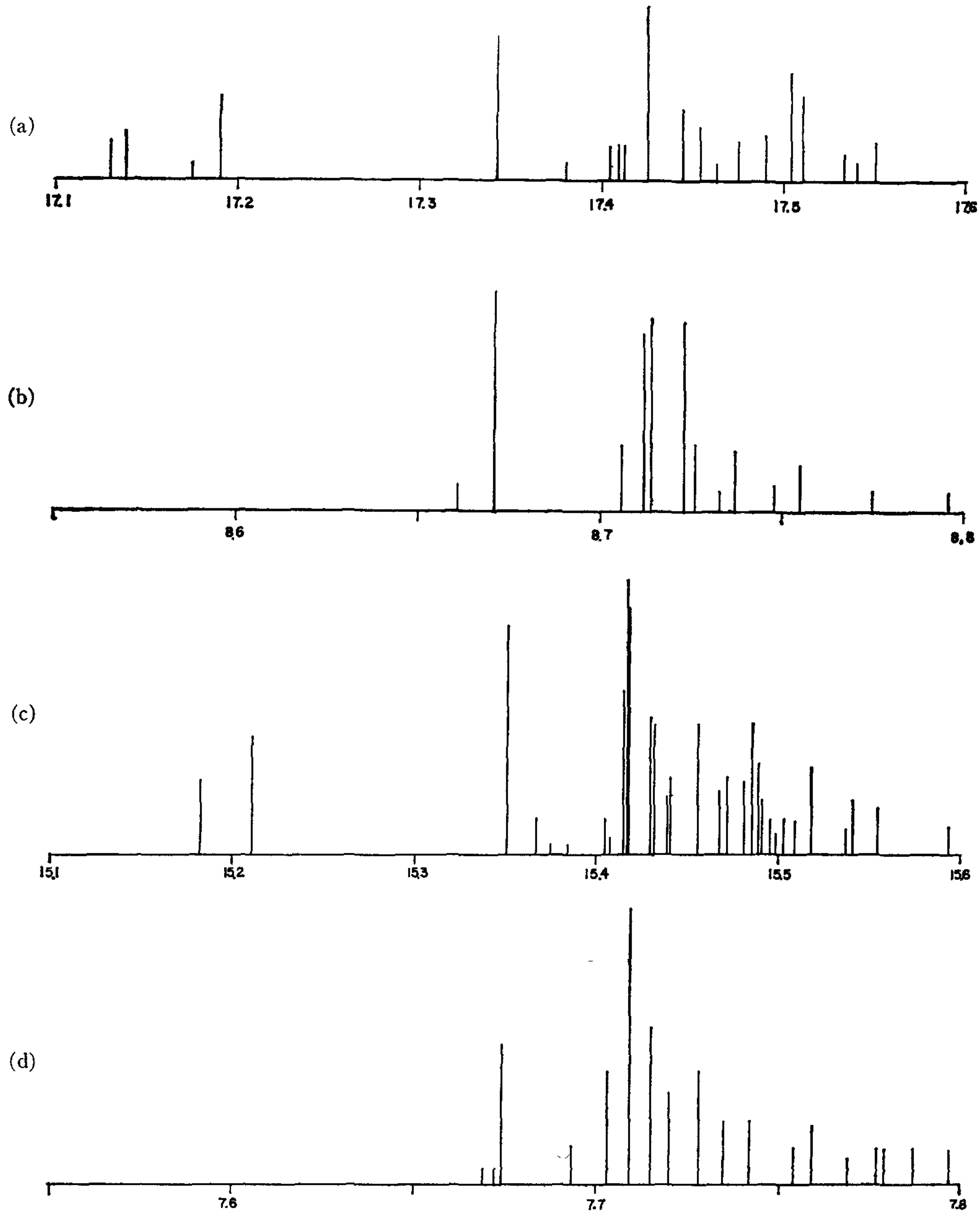

FIG. 1. Observed spectra: (a) of CH_3NCO 1→2; (b) of CH_3NCO 0→1; (c) of CD_3NCO 1→2; (d) of CD_3NCO 0→1. kMc/sec units.

ception. The line at 17 190.5 exhibited a single rapid Stark lobe to high frequency.

The same situation with respect to Stark effects was found for CD_3NCO. The line in the $J1\rightarrow2$ region which has a rapid Stark lobe to high frequency is at 15 211.0 The $J2\rightarrow3$ region has not been completely investigated for CD_3NCO.

ASSIGNMENT OF QUANTUM NUMBERS

A computer program was written to calculate the energy levels and transition frequencies for any value of the barrier for a molecule containing a methyl group and a plane of symmetry. The model assumed was a rigid methyl group attached to a rigid frame. The basis chosen was that appropriate for free internal rotation. Usually 11 internal rotation basis functions were chosen so that for the E levels the size of the matrix to be diagonalized was $11\times(2J+1)$. This leads to a 99×99 matrix for $J=4$. The matrix was diagonalized by the Givens[5] method. The roots of the continued fraction secular equation were obtained by use of the Rutishauser algorithm described by Bennett, Ross, and Wells.[6] Naturally rounding errors must be feared in the diagonalization of such a large matrix.

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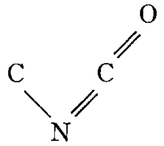
[5] W. Givens, Natl. Bur. Std. (U.S.) Appl. Math. Ser. **29**, 117 (1953).

[6] J. M. Bennett, I. G. Ross, and E. J. Wells, J. Mol. Spectry. **4**, 342 (1960).

These were checked by comparison of the sum of the eigenvalues after diagonalization to the trace of the Hamiltonian matrix before diagonalization. It was felt that the rounding errors would not preserve the trace check. The traces before and after diagonalization usually agreed to 0.01 Mc/sec. In addition, some matrices were run both by the Given's method program and by a Jacobi method program. The energy levels usually agreed to 0.01 Mc/sec. The Rice University computer on which the calculations were carried out carries about 12 decimal digits.

The spectrum of methyl isocyanate was predicted for a range of values of the barrier from 0 to 1500 cal/mole and for a range of values of the ∠CNC from 130° to 140°. The structure assumed for methyl isocyanate was that determined by Eyster, Gillette, and Brockway[7] by electron diffraction. It is given in Table II. The effect of varying the ∠CNC was primarily to change the size of the *a*-type *R*-branch regions. When this angle was made smaller, the *a*-type *R* branches are spread over larger regions. The effect of varying the barrier was quite complicated. As the barrier to internal rotation is increased from zero some absorptions move very rapidly, selection rules change, and degeneracies split.

In spite of the variation of the spectrum which could be obtained by varying the barrier, it soon began to appear that the spectrum could not be fit by the model of a rigid methyl group attached to a rigid frame. This was confirmed by calculating the effect of the



in-plane bending motion on the spectrum. The approach used for this calculation was similar to that used by Hecht and Dennison[8] on methanol.

The assignment was made on the basis of the splitting of degeneracies by the barrier and the characteristic Stark effects caused by this. The barrier to internal rotation of the methyl group destroys the degeneracy between $+m$ $+K$ and $-m$ $-K$ if m is a multiple of three. If $K\neq 0$, this splitting causes a qualitative change in the Stark effect. There is no longer a first-order Stark effect. Instead, the two levels which are split are connected by a dipole moment matrix element. If the splitting is greater in the higher J level involved in the observed absorptions, this gives rise to a Stark pattern in which the lower line of the $\pm m$ $\pm K$ pair has a rapid second-order Stark lobe to high frequency, and the upper line has a rapid second-order lobe to low frequency.

TABLE II. Electron-diffraction structure of methyl isocyanate.[a]

r(C—H) = 1.09 Å	∠HCH = 109.5°
r(C—N) = 1.47	∠C—N=C = 125° (140° consistent with the microwave)
r(N—C) = 1.19	
r(C=O) = 1.18	

[a] As determined by Eyster, Gillette, and Brockway.

TABLE III. CH$_3$NCO dipole moment.

Lobe	$\Delta\nu/E^2$ (Mc/sec·cm^2/V^2)	μ parallel (debyes)
$m=0$		
0→1		
$M=0$	1.21×10^{-4}	2.78
1→2		
$M=0$	-3.58×10^{-5}	2.84
$M=1$	2.88×10^{-5}	2.82
Average		2.81
HNCO[a]		1.59

[a] As measured by Shoolery and Sharbaugh.

If the barrier to internal rotation is at least 150 cal/mole, there should be at least three such pairs in the 1→2 region. If the barrier is zero, there should be one such pair corresponding to $m=0$. Only one line 17 190.5, in the 1→2 region, exhibited such a Stark effect as mentioned previously. Of course, many lines are crowded by nearby lines and the Stark effect is difficult to study.

For a barrier less than 150 cal/mole and a bond angle of 140°C, the calculated spectrum is in fair qualitative agreement with the observed spectrum. The line at 17 190.5 was assigned as $1_{11}\rightarrow 2_{12}$ $m=0$. In order to improve the value of the barrier a split pair such as $m=\pm3$, $K=\pm1$ had to be assigned. The region in which this pair might fall had a pair of strong lines at 17 504.5 and 17 510.4 Mc/sec. The lines are too close together to study the Stark effect. However, when the corresponding lines at 26 257.8 and 26 265.3 in the 2→3 region were examined, they were found to have the proper Stark effect for $K=\pm1$, $m=\pm3$. That is, the 26 257.8-Mc/sec line had a rapid Stark lobe only to high and the 26 265.3-Mc/sec line had a rapid Stark lobe only to low. It was necessary to assign 17 504.5 and 26 257.8 Mc/sec also to $1_{10}\rightarrow 2_{11}$ $m=0$, and $2_{11}\rightarrow 3_{12}$ $m=0$, respectively. However, at the voltages used for making the 2→3 $K=\pm1$, $m=\pm3$ assignment, the $2_{11}\rightarrow 3_{12}$ $m=0$ line is not expected to appear. This ambiguity was cleared up by examining the 3→4

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[7] E. H. Eyster, R. H. Gillette, and L. O. Brockway, J. Am. Chem. Soc. **62**, 3236 (1940).

[8] K. T. Hecht and D. M. Dennison, J. Chem. Phys. **26**, 48 (1957).

TABLE IV. Quadrupole coupling splittings and constants of methyl isocyanate.[a]

	$J0\rightarrow1 \quad m=0$	
	CH_3NCO	CD_3NCO
$F1\rightarrow0$	8670.7	7672.8
$1\rightarrow1$	8672.3	7674 7
$1\rightarrow2$	8671.6	7674 0
eqQ[b]	+2.3	+2.3

[a] All values in Mc/sec.

[b] Based on the 1→1, 1→2 splitting. The 1→0 was weak enough to make its measurement somewhat unreliable.

region. Three lines appeared in this region. One at 35 008.8 Mc/sec appeared only at fairly high Stark voltage and was assigned to $3_{12}\rightarrow4_{13}$ $m=0$. The other two appeared at very low Stark voltage with the proper Stark effect to be assigned to $K=\pm1$ $m=\pm3$. The frequencies observed were 35 012.0 and 35 020.5 Mc/sec. The barrier to internal rotation calculated from this splitting is 49±3 cal/mole. The uncertainty quoted is estimated from experimental error and does not consider a possible V_6 term. Two additional lines are present on the high-frequency side of 35 020.5. If the highest of these, 35 022.4, is used, the barrier is 59 cal/mole.

The assignment of quantum numbers for CD_3NCO proceeded in the same way. Again the $m=0$ $1_{10}\rightarrow2_{11}$, and $m=\pm3$ $K=\pm1$ lines fell close together in a crowded region. By going to the $J2\rightarrow3$ region it was possible to assign the $m=0$ $2_{11}\rightarrow3_{12}$ line by its Stark effect. However, the Stark effects of $J2\rightarrow3$ $m=\pm3$ $K=\pm1$ are still not clear in CD_3NCO.

ATTEMPTS TO FIT THE SPECTRUM

Most of the foregoing explanations of how the assignments were made and the barrier to internal rotation was determined would be unnecessary if the spectrum could be fitted. Attempts to include the effects of nonrigidity and fit a reasonable number of lines have given standard deviations of at least 4 Mc/sec. This is fair qualitative agreement with the observed spectrum, but far from pleasing.

The formula used to fit these a-type R-branch frequencies $J\rightarrow J+1$ was

$$\nu=\nu\ (\text{rigid})-2(J+1)[D_{JK}K^2+D_{Jm}m^2+D_{JKm}mK]. \qquad (1)$$

There seems to be little value in reporting values of the constants obtained or details of the fits.

DIPOLE MOMENT

The Stark effect of the $0\rightarrow1$ $m=0$ and $1_{01}\rightarrow2_{02}$ $m=0$ was measured. The waveguide spacing was determined by measuring the Stark effect of the $0\rightarrow1$ transition of OCS. A simple calculation showed that these Stark lobes are not sensitive to μ_b^2. This was verified experimentally by the nearly equal values of μ_a^2 obtained from the three lobes measured assuming that the entire Stark effect came from μ_a^2. These results are shown in Table III. For some of the higher J lines the Stark effect will be sensitive to μ_b^2, but without a more accurate value of I_a it is hard to predict which lines will be more sensitive.

The value of the dipole moment obtained, 2.81 D, can be compared to 1.59 D, the parallel component of HNCO determined by Shoolery and Sharbaugh[9] from Stark effect measurements. The great change in the dipole moment caused by replacing a proton with a methyl group is difficult to explain. A similar trend has been found for HNCS[10]: $\mu_{||}=1.72$ D and CH_3NCS [11] $\mu=3.18$ D. It appears that there is also a large change in the bond angle in going from HNCO to CH_3NCO. The bond angle in HNCO has been found[12] to be 128.5° while that in CH_3NCO appears to be 140°.

QUADRUPOLE COUPLING CONSTANTS

The nitrogen nuclear quadrupole splittings were usually not resolved. In order to determine the quadrupole coupling constant three transitions were studied carefully. These were the $m=0$ $0\rightarrow1$ and $1_{11}\rightarrow2_{12}$ of CH_3NCO and the $m=0$ $0\rightarrow1$ of CD_3NCO. The $0\rightarrow1$ transitions showed the characteristic triplet pattern. The frequencies are given in Table IV. From these splittings eqQ can be determined and is also given in Table IV. Unfortunately the $m=0$ $1_{11}\rightarrow2_{12}$ could not be resolved. There appears to be another line close by on the high-frequency side. Therefore η could not be determined.

ACKNOWLEDGMENTS

The help of Mr. Ernest Sibert with the numerical computations is gratefully acknowledged.

The numerical computations were carried out on the Rice University digital computer constructed under U. S. Atomic Energy Commission Contract No. AT-(40-1)-1825.

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[9] J. N. Shoolery and A. H. Sharbaugh, Phys. Rev. **82**, 95L (1951).

[10] C. I. Beard and B. P. Dailey, J. Chem. Phys. **18**, 1437 (1950).

[11] E. C. E. Hunter and J. R. Partington, J. Chem. Soc. **1932**, 2812.

[12] L. H. Jones, J. N Shoolery, R. G. Shulman, and D. M. Yost, J. Chem. Phys. **18**, 990L.