Electron Diffraction Investigation of the Molecular Structures of Dimethylsilyl Isocyanate and Dimethylsilyl Isothiocyanate

Stephen Cradock,* Christopher M. Huntley, David W. H. Rankin, and Heather E. Robertson
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The molecular structures of dimethylsilyl isocyanate and dimethylsilyl isothiocyanate have been determined by electron diffraction in the gas phase. For both molecules the data are consistent with the presence of a single conformer at room temperature, the NCX group eclipsing the Si–H bond of the dimethylsilyl group. The skeletal parameters found are (NCO, NCS; distances in pm, angles in degrees): *r*(Si–N) 171.9(5), 172.3(8); *r*(Si–C) 185.8(3), 185.0(5); *r*(N=C) 121.8(4), 121.2(5); *r*(C=O) 115.5(4); *r*(C=S) 157.9(5); angle NSiC 111.2(25), 109.7(9); angle CSiC 113.3(50), 112.3(13); angle Si–N=C 153.5(13), 154.7(22). The NCX groups are linear. The large apparent bond angles at nitrogen suggest that these molecules are pseudolinear, like the non-methylated silyl isocyanate, or truly linear like silyl isothiocyanate, both of which show shrinkage effects of similar magnitude due to the effects of a very low-frequency, high-amplitude bending vibration. The results are compared with those for some related molecules.

The molecular structures of isocyanates and isothiocyanates of silicon have been of interest for many years, since early i.r. studies of SiH_3NCS[1] and SiH_3NCO[2] suggested that these compounds had linear or effectively linear skeletons in the gas phase, as the vibrational selection rules and the rotational fine structures of the bands observed were those appropriate to C_{3v} symmetry, with only hydrogen atoms lying off the symmetry axis. For the isothiocyanate the microwave spectrum[3] confirmed the linearity of the skeleton, though the presence of a very low-frequency bending vibration was indicated by the observation of an extensive series of vibrational satellite spectra. For the isocyanate the microwave spectra were even more complex,[4] and it was later shown[5] that the low-frequency vibration was a two-dimensional anharmonic bend at nitrogen. This resulted in a pseudolinear skeleton, whose equilibrium bond angle was *ca.* 156°, but whose lowest vibrational level was only just below the energy of the local maximum at a bond angle of 180°. Consequently the molecule had a very non-rigid structure, with many low-lying vibrational levels populated at room temperature. The low-frequency bending motions have been studied by far-i.r. spectroscopy in the gas phase; they give rise to *two* bands for each compound,[6] corresponding loosely to the fundamental and its overtone, but each spectrum has to be regarded as arising from a large number of overlapping bands due to transitions between the many populated levels.

The molecular structures of SiH_3NCO and SiH_3NCS have been studied by electron diffraction;[7] both showed apparently bent skeletons, but the application of corrections for shrinkage[8] resulted in good agreement with the microwave results. Recent electron diffraction studies of the trimethylsilyl analogues $SiMe_3NCO$[9] and $SiMe_3NCS$[10] show similarly bent skeletons, but again the apparent deviations from linearity can be accounted for by shrinkage effects related to a very low-frequency bend at nitrogen. We are interested to discover how the presence of an asymmetric group R may modify the pseudolinearity of the skeleton of RNCX (X = O or S) molecules, and here report the results of an electron diffraction study of the dimethylsilyl compounds $SiHMe_2NCO$ and $SiHMe_2NCS$.

Experimental

Dimethylsilyl isocyanate and dimethylsilyl isothiocyanate were prepared by modifications of the methods used for their SiH_3 analogues. The isocyanate was prepared by reaction of gaseous HNCO with a slight excess of $NH(SiHMe_2)_2$, giving $SiHMe_2NCO$ in 80% yield, and the isothiocyanate by reaction of $SiClHMe_2$ with solid AgNCS. They were purified by fractional condensation in a vacuum line. Details of the characterisation of these compounds will be reported separately.[11] Electron diffraction scattering intensities were recorded photographically using the Edinburgh apparatus[12] operating at *ca.* 44 kV. Sample and nozzle were at room temperature during data collection. Data were converted to digital form using a computer-controlled Joyce–Loebl microdensitometer as described previously.[13] The electron wavelength was determined by analysis of the scattering patterns of gaseous benzene recorded consecutively with those of the compounds. Data reduction[13] and refinement[12] were carried out with established programs, using the complex scattering factors of Schäfer *et al.*[14] The weighting points used in setting up the off-diagonal weight matrix, *s* ranges, and other pertinent data are given in Table 1. The reduced electron scattering intensities and radial distribution curves for the two compounds with final difference curves in each case are shown in Figures 1 and 2.

Table 1. Camera distances, *s* ranges and weighting points, scale factors, correlation parameters, and electron wavelengths

	$SiHMe_2NCO$		$SiHMe_2NCS$	
	Long	Short	Long	Short
Distance/mm	285.59	128.36	285.67	128.36
Δs/nm^{-1}	2	4	2	4
$s_{min.}$/nm^{-1}	20	60	24	60
sw_1/nm^{-1}	40	90	40	90
sw_2/nm^{-1}	120	290	120	280
$s_{max.}$/nm^{-1}	146	336	146	340
Scale factor	0.874(14)	0.901(18)	0.910(16)	0.902(56)
Correlation	0.398	−0.135	0.264	0.020
Wavelength/pm	5.681(6)	5.682(6)	5.681(6)	5.681(6)

Structural Model and Refinements

The molecules considered here have 13 atoms and up to 78 independent interatomic distances. We have constrained the two methyl groups to be identical, with local C_{3v} symmetry about the Si–C bonds, and the nitrogen and unique hydrogen

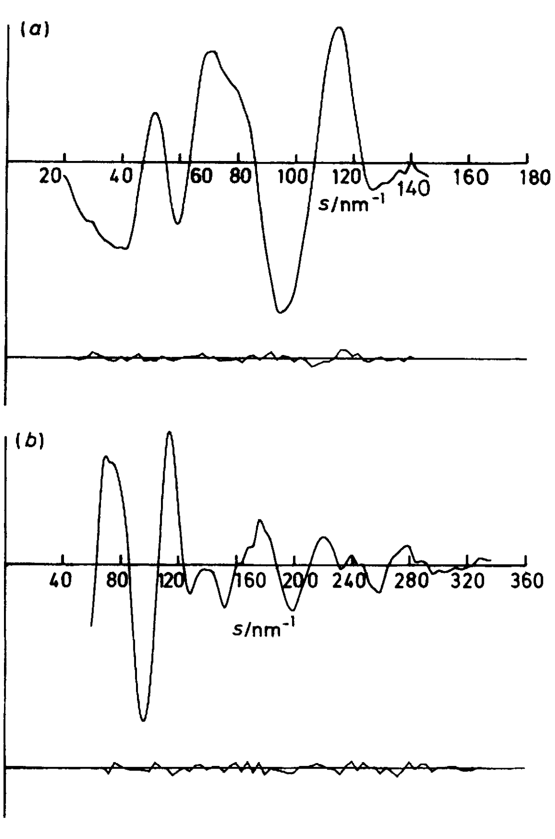

Figure 1. Molecular scattering intensities for dimethylsilyl isocyanate; observed and final difference curves for camera distances of (*a*) 285.59 and (*b*) 128.36 nm

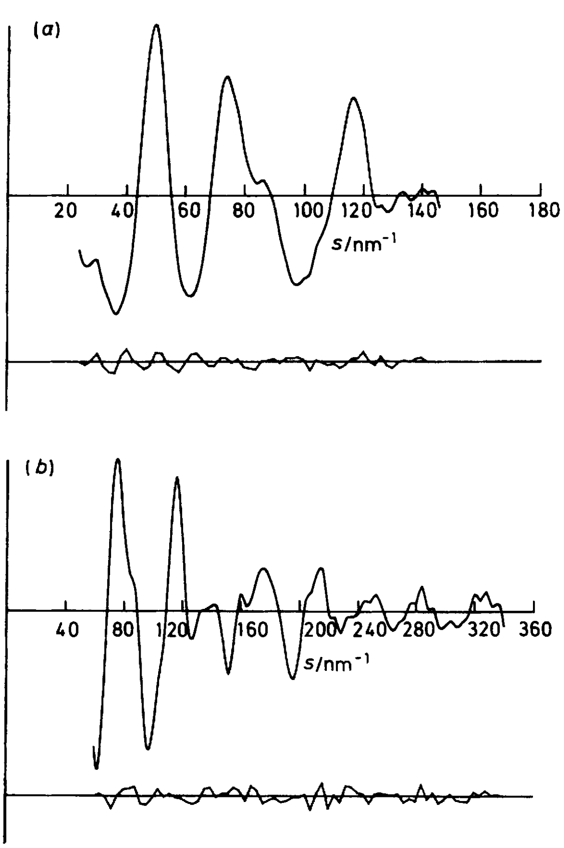

Figure 2. Molecular scattering intensities for dimethylsilyl isothiocyanate; observed and final difference curves for camera distances of (*a*) 285.67 and (*b*) 128.36 nm

atoms to lie in the plane bisecting the CSiC angle. The number of independent distances is thus reduced to 57. The NSiH and SiCH bond angles and SiH bond length were fixed after testing for the minimum *R* factor over a range of values at a late stage of the refinement, a common value being chosen for each parameter that gave acceptable *R* factors for both molecules. The NCX groups were not found to depart from linearity, and the torsion angle about the N=C bond was thus undefined. The NSiC and CSiC bond angles were found to be correlated, and were loosely tied together initially. For the isocyanate the constraint was removed in the final stages of the refinement. For the isothiocyanate a loose constraint (that the difference in angles was 2 ± 1°) was retained to prevent these angles refining to unrealistic values.

All bond distances [except *r*(SiH)] and the Si–N=C bond angle were varied, and were free to refine in the final stages. Suitable values for the torsion angles were selected by testing for the minimum *R* factor as they were varied over a range.

Table 2. Electron diffraction structures of dimethylsilyl isocyanate and dimethylsilyl isothiocyanate (r_a basis)

	$SiHMe_2NCO$	$SiHMe_2NCS$
r(Si–N)/pm	171.9(5)	172.3(8)
r(Si–C)/pm	185.8(3)	185.0(5)
r(N=C)/pm	121.8(4)	121.2(5)
r(C=X)/pm	115.5(4)	157.9(5)
r(C–H)/pm	113.1(7)	112.9(7)
r(Si–H)/pm	150*	150*
Angle NSiC/°	111.2(25)	109.7(9)
Angle CSiC/°	113.3(50)	112.3(13)
Angle Si–N=C/°	153.5(13)	154.7(22)
Angle N=C=X/°	180*	180*
Angle SiCH/°	109*	109*
Angle NSiH/°	105*	105*
CH_3 torsion/°	10*	0*
Si–N torsion/°	0*	0*
R_G	0.073	0.110
R_D	0.060	0.089

* Fixed value (see text).

Amplitudes of vibration were given initial values suggested by experience with related molecules,[9–11] and those corresponding to all important distances were allowed to refine, individually or tied in groups, some being fixed after initial refinement. The final *R* factors were *ca.* 7% (NCO) and 11% (NCS). The difference curves associated with the radial distribution curves (Figure 3) gave no indication that we might be unjustifiably neglecting a significant proportion of a second conformer for the isocyanate, but an obvious discrepancy in the 500—600 pm region for the isothiocyanate suggests that another conformer might be present in this case. Simply adding a second (*trans*) conformer reduced the *R* factor slightly, and a further reduction was achieved by allowing the SiNC bond angle to be different in the two conformers, while all other parameters remained the same. A second difference curve [bottom of Figure 3(*b*)] shows the effect of assuming the presence of 40% of the *trans* conformer; the obvious discrepancy in the radial distribution curve was reduced but not wholly removed by these changes, and we suggest that it is better regarded as due to the effects of the low-frequency bending vibration at nitrogen, which will result in the

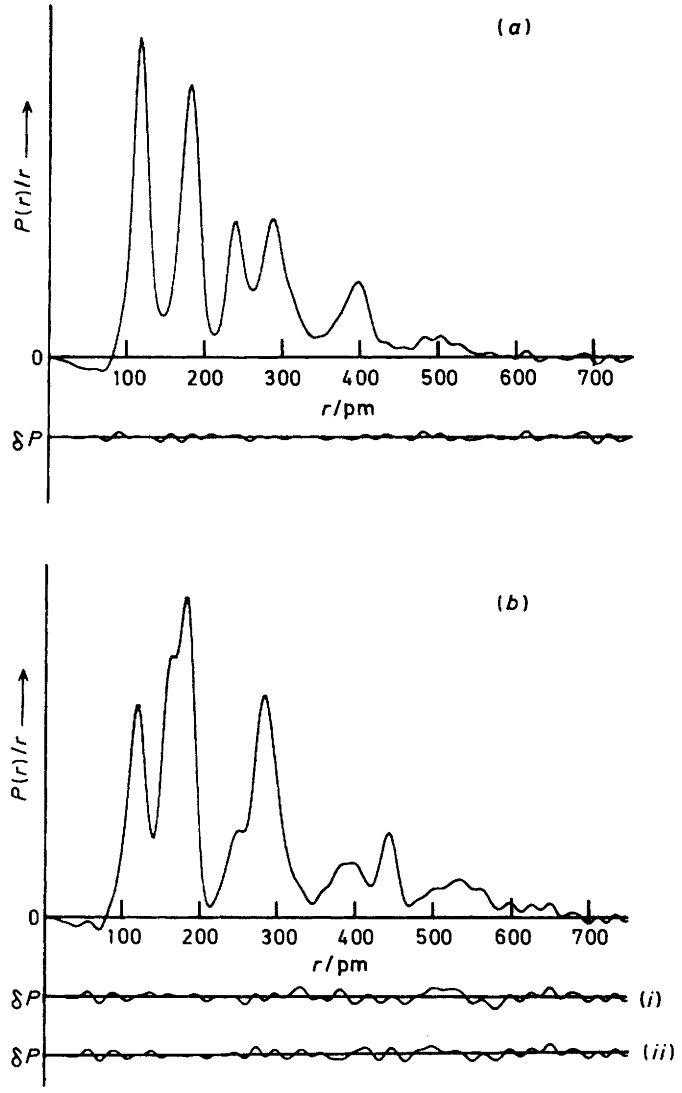

Figure 3. Observed and final difference radial distribution curves $P(r)/r$ for (*a*) $SiHMe_2NCO$ and (*b*) $SiHMe_2NCS$. Before Fourier inversion the data were multiplied by $s \cdot \exp[-0.000\,02s^2/(Z_N - f_N)(Z_{Si} - f_{Si})]$. The upper difference curve (*i*) for (*b*) refers to single conformer (100% *cis*); the lower difference curve (*ii*) for (*b*) refers to a *cis–trans* mixture (60:40)

non-bonded C $\cdots$ S distances in different molecules being on average less than the value appropriate to a linear SiNCS group (a shrinkage effect, see below) but in an unsymmetrical distribution, as found for the silyl-[7] and methyl-pseudohalides.[15–17] We do not believe that our data are good enough to allow us to define the nature of the bending potential function at present. The final structural parameters (r_a basis) and *R* factors are given in Table 2, and a list of interatomic distances and amplitudes in Table 3. Table 4 shows the important correlations between refining parameters and amplitudes.

Table 3. Interatomic distances and amplitudes for dimethylsilyl isocyanate and dimethylsilyl isothiocyanate

	$SiHMe_2NCO$		$SiHMe_2NCS$	
Atoms	d_a/pm	u_a/pm	d_a/pm	u_a/pm
Si–C	185.8	62.3(3)	185.0	5.9(8)
Si–N	171.9	6.2	172.3	6.5(12)
C–H	113.1	11.0(12)	112.9	8.0[a]
Si–H	150.0	5.3(21)	150.0	7.6[a]
N=C	121.8	3.5[a]	121.2	4.9(9)
C=X	115.5	3.5[a]	157.9	4.5[a]
C $\cdots$ C	310.6	16.0(42)	307.3	16.4(24)
C $\cdots$ N	295.3	16.0	292.3	16.4
Si $\cdots$ C	286.1	7.0(8)	286.6	9.8(22)
N $\cdots$ X	237.3	4.2(6)	279.1	6.9(9)
C $\cdots$ C	403.2	34.0(72)	400.1	10.5(20)
Si $\cdots$ X	398.6	10.4(10)	441.1	10.2(8)
C $\cdots$ X	511.3	25.7(38)	549.0	26.2(33)
Si $\cdots$ H	247.0	14.4(13)	246.1	12.1(12)
X $\cdots$ H	423.3	23.0[b]	474.5	23.0[b]
	476.5	25.0[b]	514.5	25.0[b]
	484.2	25.0[b]	514.5	25.0[b]
	554.6	25.0[b]	605.4	25.0[b]
	577.2	25.0[b]	605.4	25.0[b]
	589.3	25.0[b]	635.7	25.0[b]
	604.6	25.0[b]	635.7	25.0[b]
N $\cdots$ H	255.9	13.0[b]	261.1	13.0[b]
	290.5	15.0[b]	288.1	15.0[b]
	360.9	15.0[b]	366.4	15.0[b]
	375.0	15.0[b]	366.4	15.0[b]
C $\cdots$ H	272.1	13.0[a]	275.1	13.0[b]
	303.2	13.0[b]	299.1	13.0[b]
	305.5	13.0[b]	299.1	13.0[b]
	332.3	19.0[b]	334.0	19.0[b]
	370.2	13.0[b]	374.4	23.0[b]
	378.2	23.0[b]	374.4	23.0[b]
	380.1	13.0[b]	378.1	13.0[b]
	382.9	23.0[b]	378.1	13.0[b]
	385.6	13.0[b]	381.4	13.0[b]
	393.3	13.0[b]	381.4	13.0[b]
	454.9	23.0[b]	462.7	23.0[b]
	474.3	23.0[b]	462.7	23.0[b]
	475.9	23.0[b]	480.6	23.0[b]
	390.9	23.0[b]	480.6	23.0[b]
H $\cdots$ H	185.3	14.0[b]	184.9	14.0[b]
	259.7	20.0[b]	249.5	20.0[b]
	271.0	17.0[b]	275.3	17.0[b]
	272.9	17.0[b]	275.3	17.0[b]
	334.1	17.0[b]	344.2	17.0[b]
	342.1	17.0[b]	344.2	17.0[b]
	348.2	17.0[b]	350.8	17.0[b]
	354.5	17.0[b]	350.8	17.0[b]
	358.9	20.0[b]	374.0	20.0[b]
	369.9	20.0[b]	374.0	20.0[b]
	392.2	20.0[b]	376.8	20.0[b]
	396.1	20.0[b]	376.8	20.0[b]
	420.0	20.0[b]	423.7	20.0[b]
	441.8	20.0[b]	431.9	20.0[b]
	458.3	20.0[b]	466.0	20.0[b]
	476.2	20.0[b]	466.0	20.0[b]

[a] Value fixed after refining. [b] Value remained fixed at the initial magnitude throughout.

Discussion

The bond lengths and angles given in Table 2 are unremarkable, but some comparisons may be made with corresponding parameters in other silyl pseudohalides. Thus the SiN bonds, both *ca.* 172 pm, are distinctly shorter than those found in the trimethylsilyl derivatives (*ca.* 174 pm[9,10]), but longer than those in the unsubstituted silyl compounds (just over 170 pm[7]). These variations reflect the inductive effect of the methyl groups. The C=S bond lengths show a similar trend (SiH_3 156, $SiHMe_2$ 158, $SiMe_3$ 159 pm), but no clear trends are apparent for C=O and N=C bonds, partly at least because of strong correlations between these parameters in the isocyanates. Comparison with

Table 4. Correlation matrices (× 100) for refining parameters and amplitudes for (*a*) $\mathrm{SiHMe_2NCO}$ and (*b*) $\mathrm{SiHMe_2NCS}$. Only those elements whose absolute value exceeds 50 are shown

(*a*)	*r*(C=O)	Angle CSiC	*u*(SiN)	*u*(CH)	*u*(C ··· N)	Scale 1
r(CH)	−56					
Angle NSiC		−94			91	
u(C ··· N)		−94			100	
u(Si ··· O)		53				
Scale 1				62		100
Scale 2	−51		51	73		65

(*b*)	*r*(C=S)	Angle SiNC	*u*(SiC)	*u*(SiN)	*u*(Si ··· C)
r(SiN)	56	70	80	72	
r(SiC)			−52	−76	
r(N=C)					54
Angle NSiC					−56
Angle SiNC	61	100	60	57	
u(SiN)	60	57	81	100	

Table 5. Shrinkages (pm) and apparent bond angles (°) at nitrogen[a]

RNYX	$\delta(\mathrm{R}\cdots\mathrm{Y})$	Angle RNY	Ref.
$\mathrm{SiH_3NCS}$	2.8	163	7
$\mathrm{SiMe_3NCS}$	5.1	158	10
$\mathrm{SiMe_3NCO}$	5.8	157	9
$\mathrm{SiHMe_2NCS}$	6.9	155	*b*
$\mathrm{SiHMe_2NCO}$	7.6	154	*b*
$\mathrm{SiH_3NCO}$	8.6	152	7
EtNCS	11.0	143	18
MeNCS	14.6	141	17
MeNCO	15.4	140	17
$\mathrm{Pr^iNCS}$	19.3	136	19
$\mathrm{Pr^iNCO}$	22.3	133	19
EtNCO	23.3	129	18
MeNNN	39.4	117	17

[a] Shrinkage $\delta(\mathrm{R}\cdots\mathrm{Y})$ is defined as $[r(\mathrm{R{-}N}) + r(\mathrm{N{=}Y}) - d(\mathrm{R}\cdots\mathrm{Y})]$. This is a true shrinkage only for those molecules with linear or pseudo-linear skeletons, not for those with bent skeletons, but it provides a convenient basis for comparison. [b] This work.

alkyl compounds[17–19] shows the C=O and C=S bonds appear to be some 2 pm shorter in silicon compounds than in the analogous carbon compounds with the same number of methyl groups.

We have not so far taken account of shrinkage effects in the SiNCX group, though we have noted above some aspects of the radial distribution curve for the isothiocyanate that are attributal to shrinkage effects in the longest C ··· S distances. The three-bond Si ··· X distances give rise to distinct peaks in the radial distribution curves, but they are overlapped (almost completely in the case of the isocyanate and on the short side in the isothiocyanate) by other non-bonded distance peaks including those due to the C ··· C distances, and this makes it hard to compare them directly with those reported for the $\mathrm{SiH_3}$ analogues.[7] It does not appear that the Si ··· S peak is markedly asymmetric, however, and the refined amplitudes of vibration (*ca.* 10 pm in each case) are quite low for such long distances. The amplitudes found here are very similar to those reported in the $\mathrm{SiH_3}$ analogues,[7] and are distinctly larger than the values calculated[20,21] assuming a linear skeleton in these compounds. We therefore concentrate on the two-bond distances Si ··· C, which effectively determine the apparent bond angles at nitrogen. Without a normal co-ordinate analysis we cannot claim that the observed two-bond shrinkages δ(SiC), given by $[r(\mathrm{Si{-}N}) + r(\mathrm{N{=}C}) - d(\mathrm{Si}\cdots\mathrm{C})]$, and the apparent bond angles at nitrogen (Table 5), are consistent with any particular bending frequency, but comparison with the results of normal co-ordinate calculations[20,21] on $\mathrm{SiH_3NCO}$ and $\mathrm{SiH_3NCS}$ shows that shrinkages of the order of 5—10 pm, as found here, are associated with rectilinear, simple harmonic bending frequencies of some 50—100 $\mathrm{cm^{-1}}$ in such molecules. As we are not expecting the bending motion to be harmonic, rectilinear, or of small amplitude we can only say that the observed shrinkages are quite compatible with the existence of a pseudolinear skeleton in each case, with a large amplitude vibration associated with the bending motion at nitrogen. As Table 5 shows, the dimethylsilyl compounds are clearly more similar to the silyl and trimethylsilyl compounds than to alkyl pseudohalides. The conformation defined by the electron diffraction data is thus only an apparent one, representing the most probable deformation of the linear skeleton. It is noteworthy that the conformational preference found for ethyl and isopropyl pseudohalides RNCX,[18,19] where the NCX group eclipses a carbon–carbon bond in each case, is here replaced by a tendency to eclipse the Si–H bond. This may be related to the differing polarities of the C–H and Si–H bonds, as the $\delta^-\mathrm{N{=}C}\delta^+$ dipole will be attracted to a $\delta^+\mathrm{Si{-}H}\delta^-$ group and repelled from a $\delta^-\mathrm{C{-}H}\delta^+$ group.

References

1 A. G. MacDiarmid and A. G. Maddock, *J. Inorg. Nucl. Chem.*, 1955, **1**, 411.

2 E. A. V. Ebsworth and M. J. Mays, *J. Chem. Soc.*, 1962, 4844.

3 K. F. Dössel and A. G. Robiette, *Z. Naturforsch., Teil A*, 1977, **32**, 462.

4 M. C. L. Gerry, T. M. Sugden, and J. C. Thompson, *Nature (London)*, 1966, **211**, 846.

5 J. A. Duckett, A. G. Robiette, and I. M. Mills, *J. Mol. Spectrosc.*, 1976, **62**, 34.

6 S. Cradock and D. C. J. Skea, *J. Chem. Soc., Faraday Trans. 2*, 1980, 860.

7 C. Glidewell, A. G. Robiette, and G. M. Sheldrick, *Chem. Phys. Lett.*, 1972, **16**, 526.

8 S. J. Cyvin, 'Molecular Vibrations and Mean-square Amplitudes,' Elsevier, Amsterdam, 1968, ch. 14.

9 S. Cradock, C. M. Huntley, and J. R. Durig, *J. Mol. Struct.*, 1985, **127**, 319.

10 C. M. Huntley, D. W. H. Rankin, and H. E. Robertson, unpublished work.

11 S. Cradock, C. M. Huntley, and D. W. H. Rankin, unpublished work.

12 S. Cradock, J. K. Koprowski, and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **77**, 113.

13 C. M. Huntley, G. S. Laurenson, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1980, 954.

14 L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, 1971, **55**, 3055.

15 J. Koput, *J. Mol. Spectrosc.*, 1984, **106**, 12.

16 S. Cradock, *J. Mol. Spectrosc.*, 1982, **92**, 170.

17 D. W. W. Anderson, D. W. H. Rankin, and A. Robertson, *J. Mol. Struct.*, 1972, **14**, 385.

18 S. Cradock, J. R. Durig, and J. F. Sullivan, *J. Mol. Struct.*, in the press.

19 S. Cradock, J. F. Sullivan, and J. R. Durig, *J. Mol. Struct.*, in the press.

20 S. Cradock and D. C. J. Skea, *J. Chem. Soc., Faraday Trans. 2*, 1982, 787.

21 S. J. Cyvin, J. Brunvoll, and A. G. Robiette, *Chem. Phys. Lett.*, 1971, **11**, 263.

Received 12*th July* 1985; *Paper* 5/1179