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THE VIBRATIONAL SPECTRA OF N—Cl MALEIMIDE

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ABSTRACT

The infrared spectra of N—Cl maleimide as a Nujol mull and dissolved in various solvents were recorded between 4000 and 30 cm^{-1}. Raman spectra of the crystalline solid and saturated solution in CH_3CN were recorded and semiquantitative polarization measurements were made.

The fundamental frequencies have been tentatively assigned in terms of C_{2v} symmetry, based upon Raman polarization data and analogies with the spectra of maleimide and maleic anhydride. A force field was derived by initially transferring force constants from maleimide. After small iterations a satisfactory correspondance was achieved between the observed and calculated in-plane modes whereas larger discrepancies remained for some of the out-of-plane vibrations.

INTRODUCTION

As a continuation of our vibrational spectroscopic studies of maleic anhydride [1, 2] and halogenated maleic anhydrides [3, 4] we have recently reported the results for maleimide and N—D maleimide [5]. We felt it would be of value to prepare derivatives of maleimide leaving the unsaturated heterocyclic ring virtually unchanged and have therefore synthesized the N—Cl and N—Br maleimides. The spectra of these compounds were compared with those of maleimide [5] and the *N*-halogenated succinimides [6] to determine the effect of the electronegative halogen substituents on the cyclic imides. However, unlike the *N*-halogenated succinimides which are stable compounds of practical importance in organic synthesis, the corresponding maleimides, which to our knowledge have not been prepared earlier, were fairly unstable compounds. Particularly N—Br maleimide decomposed rapidly at room temperature both as a crystalline solid and in solution. Therefore, it was not possible to obtain reproducible spectra for this compound.

The present paper will refer closely to our previous work on maleimide, N—D maleimide [5] and maleic anhydride [2].

EXPERIMENTAL

N—Cl maleimide was prepared from maleimide dissolved in acetic acid and potassium hypochlorite at —20°C, in a reaction analogous to one described for synthesizing N—Cl succinimide [7]. The mixture was kept at 0°C for an hour. The precipitate was dried in vacuum and recrystallized twice from benzene just prior to use (m.p. 103°C). A similar procedure (maleimide + potassium hypobromite) for preparing N—Br maleimide gave a product which was purified by sublimation at 50°C at 0.02 torr (m.p. 116°C). However, the infrared and Raman spectra of this compound changed rapidly with time and will therefore not be reported in the present communication.

Saturated solutions of N—Cl maleimide in CS_2, CCl_4, CH_2Cl_2, C_6H_6 and CH_3CN were recorded in the infrared. The sample had highest solubility in CH_3CN and this solvent was employed for the Raman recordings. No significant spectral changes with time were detected for any of the solutions. Attempts to prepare pellets of N—Cl maleimide in KBr, KI or CsI matrices were unsuccessful since rapid spectral variations were observed. Nujol mulls were reasonably stable, but slight spectral changes occurred with time. These spectral changes were avoided by cooling the mulls to —80°C in a cryostat, also leading to sharper peaks and crystal splitting. The pure crystalline solid appeared quite stable at room temperature when irradiated with the 4880 or 5143 Å argon laser lines.

The infrared, far infrared and Raman spectrometers, cells, etc., have been described [2, 5].

RESULTS

Since N—Cl maleimide was prepared and studied for the first time, no structural data are available. Only slight deviations from planarity in the crystalline state were reported for the *N*-halogenated succinimides [8, 9] and we have assumed C_{2v} (planar structure) for N—Cl maleimide as well as for maleimide itself [5]. However, no definite conclusions about the symmetry can be drawn from the present spectra, and point groups C_s (Cl situated outside the plane) or C_2 (twisted ring) cannot be excluded. The 24 fundamentals of N—Cl maleimide will be divided into the following symmetry species: $9a_1 + 3a_2 + 4b_1 + 8b_2$ corresponding to those of maleimide. With no infrared spectra of the vapour or oriented crystalline film available the assignments were partly based upon the incomplete Raman polarization data. Further support was provided by the results of the normal coordinate analysis as well as comparison with maleimide, N—D maleimide [5], succinimide, *N*-halogenated succinimides [6] and maleic anhydride [1, 2].

Obviously, the *N*-halogenated succinimides or maleimides cannot form H-bonding like the parent molecules. Therefore, we expect the *N*-halogenated derivatives to be monomeric in all the states of aggregation and no abnormal frequency shifts would be expected.

Spectral interpretations

The infrared and Raman spectra of crystalline N—Cl maleimide are shown in Figs. 1 and 2, respectively. The observed frequencies are listed in Table 1, whereas the assigned fundamentals are compared with the results of the force constant calculations in Table 2. In Table 3 the fundamental frequencies of maleic anhydride [1, 2], maleimide, N—D and N—Cl maleimide are compared. Because of the striking similarity between the present spectra and those of maleimide [5] only brief comments regarding the interpretations will be given.

The C—H stretching modes are found at 3111 (b_2) and 3105 cm^{-1} (a_1) and the C=O stretches at 1765 (a_1) and 1705 cm^{-1} (b_2). Two Raman bands were observed around 1600 cm^{-1} (only one band for maleimide) and the most intense at 1581 cm^{-1} was attributed as ν_3 characteristic of the C=C stretch.

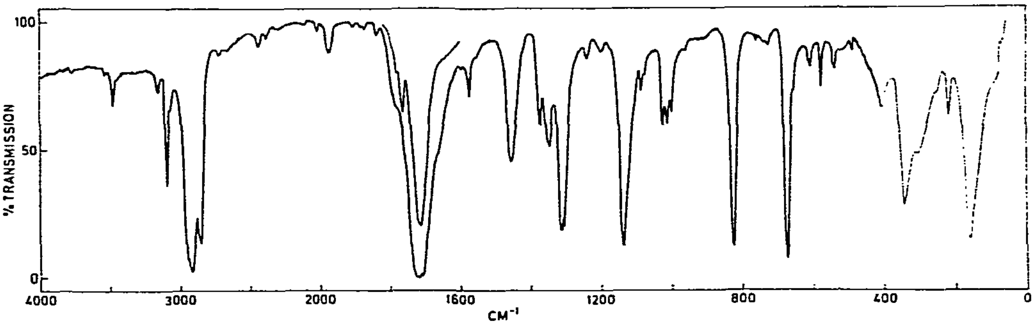


Fig. 1. The infrared spectrum of N—Cl maleimide at ambient temperature as Nujol mull (4000—400 cm^{-1}) and polyethylene pellet (400—30 cm^{-1}).

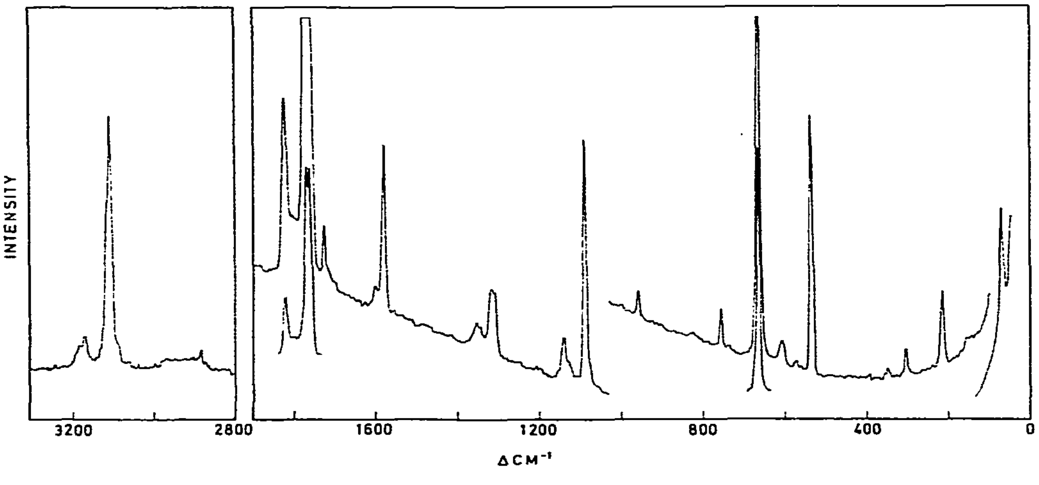


Fig. 2. The Raman spectrum of solid N—Cl maleimide.

TABLE 1

Infrared[a] and Raman spectral data for N—Cl maleimide

Infrared		Raman		Assignments[b]	
Solid ∿—80°C Nujol	Solution CCl_4	Solid	Solution CH_3CN		
3480 w[c]	3502 w			$\nu_2 + \nu_{18}$	B_2
	3440 w			$2 \times \nu_{18}$	A_1
3170 vw sh		3181 w			
3160 w	3160 vw	3166 m	3173 m P	$2 \times \nu_3$	A_1 FR
3105 sh		3111 sh	3111 sh D	ν_{17}	b_2
3098 m	3100 w	3105 vs	3106 vs P	ν_1	a_1
3072 vw sh		3084 w sh	3083 w P	$\nu_2 + \nu_4$	A_1
		2881 w		$\nu_3 + \nu_4$	A_1
		2000 w	2000 vw	$2 \times \nu_6$	A_1
1984 w	1976 w			$\nu_2 + \nu_{15}$	B_1
1893 vw				$\nu_3 + \nu_9$	A_1
1881 vw	1869 w	1882 w		$\nu_4 + \nu_8$	A_1
1845 w	1838 w			$\nu_4 + \nu_{23}$	B_2
		1827 vs	1826 vs P	$\nu_{20} + \nu_{22}$	A_1 FR
1805 sh	1800 sh	1802 w		$\nu_7 + \nu_{20}$	B_2
1791 w sh				$\nu_6 + \nu_{13}$	B_1
1765 m	1785 m	1775 vs 1768 vs	1779 vs P	ν_2	a_1
1737 sh 1722 sh 1705 vs	1740 vs	1729 m	1745 m sh D	ν_{18}	b_2
	1715 m	1719 w sh	1715 w sh	$\nu_3 + \nu_{24}$	B_2 FR
1700 sh		1700 w		$\nu_{21} + \nu_{22}$	A_1
1670 vw sh	1663 w			$\nu_6 + \nu_{22}$	B_2
	1594 w[d]	1606 m	1601 w	$\nu_6 + \nu_8$	A_1 FR
1587 w				$\nu_8 + \nu_{21}$	B_2
1579 w 1575 vw sh	1571 w[d]	1581 vs	1582 m P	ν_3	a_1
1556 w	1550 w[d]	1559 w	1559 vw	$\nu_{21} + \nu_{23}$	A_1
	1490 vw[d]			$\nu_{10} + \nu_{23}$	B_1
1474 vw				$\nu_9 + \nu_{20}$	B_2
	1405 vw[e]			$\nu_{11} + \nu_{14}$	B_2
1352 m 1344 sh	1347 m	1355 m	1350 w	$\nu_6 + \nu_9$	A_1 FR
1318 s	1305 s	1320 s	1315 w	ν_4	a_1
1309 s		1311 s		ν_{19}	b_2
1242 w	1237 w[e]	1250 vw	1248 vw	$\nu_{10} + \nu_{12}$	A_1
1205 vw	1205 vw sh[e]	1208 w	1200 vw	$\nu_{22} + \nu_{23}$	A_1
	1147 sh			$\nu_{21} + \nu_{24}$	A_1
1146 s	1129 s	1143 s	1138 w	ν_{20}	b_2
1129 sh		1128 sh		$2 \times \nu_8$	A_1
1110 sh	1104 w sh[f]			$\nu_{12} + \nu_{13}$	B_2

TABLE 1 (continued)

Infrared		Raman		Assignments[b]	
Solid ∿—80°C Nujol	Solution CCl_4	Solid	Solution CH_3CN		
1091 vw sh 1087 w	1098 w	1092 s	1087 s P	ν_5	a_1
1077 w sh	1075 vw[e]			$\nu_{10} + \nu_{16}$	B_2
1064 vw sh	1065 vw[e]			$2 \times \nu_{23}$	A_1
1027 m	1017 m[e]	1032 vw		ν_{21}	b_2
1010 m	1002 m[e]	1002 vw	1006 vw	ν_6	a_1
1000 m	989 m[e]			$\nu_7 + \nu_9$	A_1 FR
961 w		962 m		ν_{10}	a_2
940 vw				$\nu_{13} + \nu_{16}$	A_1
910 vw				$\nu_8 + \nu_9$	A_1
850 vw	840 w sh[f]			$\nu_{14} + \nu_{15}$	A_1
828 s 823 s	820 s[e]	827 w	822 w	ν_{13}	b_1
757 vw		759 m	759 w	ν_{11}	a_2
737 vw		738 vw		$\nu_8 + \nu_{24}$	B_2
677 s	672 s	676 sh	678 sh D	ν_{22}	b_2
668 s sh	667 sh	667 s	663 s P	ν_7	a_1
660 m sh	657 m			ν_{14}	b_1
609 w 603 w	590 vw[e]	608 m	604 m P	$2 \times \nu_{12}$	A_1 FR
574 sh 572 w 565 w	566 m[e]	576 w		ν_8	a_1
541 w sh 537 w 535 w	533 w[e]	538 m	538 s D	ν_{23}	b_2
417 w				$2 \times \nu_{15}$	A_1
342 s[g]	338 m[h]	345 w	341 w P	ν_9	a_1
305 sh		304 m	299 m D	ν_{12}	a_2
215 m	207 w[h]	217 s	213 m D	ν_{15}	b_1
158 s	144 s[h]	150 m	150 vw	ν_{24}	b_2
138 sh				ν_{16}	b_1
77 w		79 s		lattice vib.	

[a] The weakest infrared bands in the regions 5000—3500 cm^{-1} and 2800—2000 cm^{-1} are omitted.

[b] When available the combination frequencies and overtones are calculated from infrared solid data.

[c] w, weak; m, medium; s, strong; v, very; bd, broad; sh, shoulder; P, polarized; D, depolarized; FR, Fermi resonance.

[d] CH_2Cl_2 solution.

[e] CS_2 solution.

[f] CH_3CN solution.

[g] Solid state frequencies below 400 cm^{-1} are from polyethylene (Rigidex) pellet.

[h] C_6H_6 solution.

TABLE 2

Calculated (ν_{calc} cm^{-1}) and observed (ν_{obs} cm^{-1}) fundamentals and potential energy distribution (PED) for N—Cl maleimide

Species and No.		ν_{calc}[a]	ν_{obs}	PED[b]
a_1	ν_1	3107	3105	98l[c,d]
	ν_2	1797	1765	32s + 30d + 24r
	ν_3	1581	1579	45s + 42d
	ν_4	1315	1318	58a + 17b
	ν_5	1045	1087	$42\phi + 34\psi$
	ν_6	997	1010	41r + 30b + 19s
	ν_7	684	668	$47b + 25\alpha$
	ν_8	557	572	$24b + 20\alpha$
	ν_9	329	342	$37\xi + 34\eta$
a_2	ν_{10}	970	961	$33\tau_7 + 17\pi_5 + 17\pi_4 + 16\tau_8$
	ν_{11}	627	757	$24\pi_1 + 19\pi_2 + 15\tau_8 + 15\pi_3$
	ν_{12}	289	305	$35\tau_{10} + 32\tau_9$
b_1	ν_{13}	905	828	$38\tau_7 + 15\tau_8$
	ν_{14}	674	660	$22\tau_6 + 20\pi_1 + 16\pi_2$
	ν_{15}	211	215	$18\tau_3 + 15\tau_9$
	ν_{16}	99	138	$27\tau_3 + 25\tau_1$
b_2	ν_{17}	3100	3111	99l
	ν_{18}	1690	1705	63s + 33r
	ν_{19}	1311	1309	$34\phi + 33s + 16\psi$
	ν_{20}	1149	1146	$83a + 16\alpha + 15r$
	ν_{21}	1024	1027	$22\psi + 17a + 16r$
	ν_{22}	660	677	$37a + 32\epsilon + 16\eta$
	ν_{23}	551	537	$36\xi + 25\eta + 15r$
	ν_{24}	155	158	85μ

[a] When possible frequencies are taken from the infrared spectra of the solid state.

[b] The potential energy distribution defined as $x_{ik} = 100\ F_{ii}L_{ik}^2/\lambda_k$.

[c] For meaning of symbols, see Fig. 4, ref. 5.

[d] The coefficient indicates the total fraction of energy of the mode distributed among the equal coordinates, and terms below 15 are neglected.

The neighbouring bands at 1318 and 1309 cm^{-1} of the solid are attributed as ν_4 and ν_{19}, respectively, although only one band was detected in solution. An alternative choice for ν_4 is the medium intense band around 1350 cm^{-1}, but a comparison with the *N*-halogenated succinimides supports the former choice.

An intense infrared band at 1146 cm^{-1} was attributed as the asymmetric CNC stretch ν_{20}. The polarized Raman band at 1087 cm^{-1} was assigned as ν_5 (mainly C—H deformation). Three medium intense infrared bands were observed around 1000 cm^{-1}. Those at 1027 and 1010 cm^{-1}, both having weak Raman counterparts, were tentatively considered to be the fundamentals ν_{21} and ν_6, respectively, and the low frequency line at 1000 cm^{-1} was interpreted as a combination band.

Medium intense Raman bands at 962, 759 and 304 cm^{-1} had weak counterparts in the infrared crystal spectra (but none in solution) and they were accordingly assigned as the three a_2 modes ν_{10}, ν_{11} and ν_{12} in good agreement with the results for maleimide [5]. The four out-of-plane modes of species b_1 were rather uncertain, but were tentatively assigned to the infrared bands at 828, 660, 215 and 138 cm^{-1}. As apparent from Table 2 and in agreement with the calculations for maleimide and N—D maleimide [5] the out-of-plane force field led partly to large discrepancies between the observed and calculated wavenumbers for fundamentals of species a_2 and b_1. Therefore, the calculated frequencies were of limited help for the assignments of these modes.

Two bands were observed at 677 and 668 cm^{-1}, the former strong in infrared, the latter in Raman. They were assigned as a b_2 and an a_1 fundamental, respectively, whereas a band around 600 cm^{-1} was interpreted as an overtone, enhanced by Fermi resonance. The weak infrared and Raman bands around 570 cm^{-1} were assigned as the a_1 mode ν_8, and the PED's of Table 2 indicate that ν_6, ν_7 and ν_8 all have significant contributions from N—Cl stretch.

In the corresponding N—Cl succinimide [6] the "N—Cl stretching mode" was found at 527 cm^{-1}. A weak infrared band at 537 cm^{-1} and the depolarized Raman counterpart were taken as ν_{23}.

The bands around 342 cm^{-1} were interpreted as the lowest a_1 mode ν_9 and the PED as well as comparison with maleimide [5] and the succinimides [6] reveal the C=O bend to make significant contributions to this fundamental. We have assigned the bands around 158 cm^{-1} as the lowest b_2 mode involving N—X in plane bending, partly overlapping the b_1 mode around 138 cm^{-1}. The low frequency bands around 79 cm^{-1}, only observed in the crystalline state, were interpreted as a lattice vibration. However, it cannot be completely ruled out that these bands should instead be interpreted as ν_{16} or ν_{24}.

The close relationship between the spectra of maleimide, N—D and N—Cl maleimide which also includes maleic anhydride is demonstrated in Table 3. Here, we have attempted to describe the fundamentals in terms of localized vibrational modes arranged monotonically for maleimide. The weakness of this procedure is obvious for the N—X (X=H,D,Cl) stretching and bending modes (which are absent for maleic anhydride). However, the similarity between the spectra of these molecules is well demonstrated, supporting our assignments.

NORMAL COORDINATE ANALYSIS

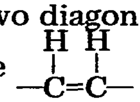
The in-plane force field was constructed by an iteration program [10] described previously [5]. We employed the force field for maleimide and N—D maleimide as a starting point. Two diagonal stretching (Table 4) (K_d and K_1) and two diagonal bending force constants (H_ψ and H_ϕ) were kept fixed since the  $-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-$ moiety should be virtually unchanged from maleimide to N—Cl maleimide. Among the seven off-diagonal force constants included,

TABLE 3

Vibrational fundamentals for N—H, N—D, N—Cl maleimide and maleic anhydride

N—X maleimide			Maleic anhydride[a]	Assignments	Species
X = H[b]	X = D[b]	X = Cl[c]			
3200	2368	572		N—X stretch	a_1
3108	3105	3105	3117	C—H in-phase stretch	a_1
3108	3115	3111	3117	C—H out-of-phase stretch	b_2
1772	1769	1765	1852	C=O in-phase stretch	a_1
1710	1690	1705	1782	C=O out-of-phase stretch	b_2
1581	1578	1579	1592	C=C stretch	a_1
1365	837	158		N—X bend	b_2
1350	1338	1318	1235	C—N[d]—C in-phase stretch	a_1
1295	1300	1309	1305	C—H out-of-phase bend	b_2
1140	1204	1146	1054	C—N[d]—C out-of-phase stretch	b_2
1067	1062	1087	1060	C—H in-phase bend	a_1
972	972	961	959	C—H out-of-plane bend	a_2
937	1085	1027	889	skeletal mode	b_2
900	888	1010	864	C—C in-phase stretch	a_1
851	850	828	839	C—H out-of-plane bend	b_1
776	773	757	768	skeletal mode	a_2
721	518	215		N—X out-of-plane bend	b_1
680	666	677	697	skeletal mode	b_2
647	641	668	632	skeletal mode	a_1
635	635	660	642	skeletal mode	b_1
552	538	537	557	C=O out-of-phase bend	b_2
415	414	342	403	C=O in-phase bend	a_1
301	300	305	275	C=O out-of-plane bend	a_2
175	175	138	173	C=O out-of-plane bend	b_1

[a] Frequencies taken from ref. 2.

[b] When possible frequencies are taken from the infrared solid state [5].

[c] This work.

[d] For maleic anhydride C—O—C.

the three stretch—bend interactions ($F_{a\eta}$, $F_{r\xi}$ and $F_{s\alpha}$) were not varied.

An additional term $F_{b\beta}(r(\text{N—Cl}) - \alpha(\text{CNC}))$ was added to the previous [5] force field. The remaining force constants were included in the iteration procedure, and the calculated frequencies are given in Table 2, together with the potential energy distribution (PED). The in-plane force field appears physically reasonable, and the discrepancies between the observed and calculated frequencies could easily be diminished by introducing additional interaction terms (only seven are included).

The out-of-plane force field for maleimide [5] (previously constructed by trial and error) was transferred directly to N—Cl maleimide. Attempts to employ an iteration procedure for these force constants led to unacceptable force constants, indicating that certain interaction terms should have been added to the diagonal terms. As apparent from Table 2, the deviations between the observed and calculated frequencies were quite large for some of the a_2 and b_1 modes (using the force field of Table 4 of ref. 5).

ACKNOWLEDGEMENT

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TABLE 4

Final valence force constants for N—Cl maleimide

Force type[a]	Constants		Force type	Constants	
	Symbol[b]	Value[c]		Symbol	Value[c]
stretch	K_a	4.942		H^*_ψ	0.415
	K_s	10.274		H_ϕ^*	0.415
	K_r	5.619		H_α	1.916
	K^*_d	8.230		H_ϵ	0.872
	K^*_l	5.219		H^*_β	1.188
	K_b	5.239		H_μ	0.372
stretch—stretch	$K_{a_1a_2}$	1.359	stretch—bend	$F^*_{a\eta}$	0.141
	K_{as}	1.856		$F^*_{r\xi}$	0.141
	K_{ar}	0.935		$F^*_{s\alpha}$	—1.276
in-plane bend	H_η	0.774		$F_{b\beta}$	—1.800
	H_ξ	0.774			

[a] For out-of-plane bending and torsional force constants see ref. 5, Table 4.
[b] For meaning of symbols see Fig. 4, ref. 5. Asterisks denote force constants kept constant.
[c] In units of mdyn A^{-1} (stretch constants), mdyn rad^{-1} (stretch—bend interaction constants) and mdyn A rad^{-2} (bending constants).

REFERENCES

1 H. Baranska, D. H. Christensen, F. Nicolaisen, O. F. Nielsen and P. Klæboe, Acta Chem. Scand., 25 (1971) 2364.

2 A. Rogstad, P. Klæboe, H. Baranska, E. Bjarnov, D. H. Christensen, F. Nicolaisen, O. F. Nielsen, B. N. Cyvin and S. J. Cyvin, J. Mol. Struct., 20 (1974) 403.

3 A. Rogstad, P. Klæboe, B. N. Cyvin, S. J. Cyvin and D. H. Christensen, Spectrochim. Acta Part A, 28 (1972) 123.

4 A. Rogstad, P. Klæboe, B. N. Cyvin, S. J. Cyvin and D. H. Christensen, Spectrochim. Acta, Part A, 28 (1972) 111.

5 T. Woldbæk, P. Klæboe and C. J. Nielsen, J. Mol. Struct., 27 (1975) 283.

6 T. Woldbæk, P. Klæboe and D. H. Christensen, to be published.

7 J. Tscherniac, Ber. Deut. Chem. Ges., B 34 (1901) 4209.

8 R. Mason, Acta Crystallogr., 14 (1961) 720; 9(1956) 405.

9 R. N. Brown, Acta Crystallogr., 14 (1961) 711.

10 G. O. Sørensen, in (Ed. S. J. Cyvin), Moleculer Structures and Vibrations, Elsevier, Amsterdam, 1972.