The Laser Raman Spectrum of Nitrogen Trichloride

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THE vibrational spectra of highly explosive species are seldom cited in the literature. Thus neither of two familiar texts used by inorganic chemists, those by Nakomoto[1] and by Siebert,[2] contain details of the tetra-atomic system nitrogen trichloride, other than a brief mention of some i.r. vapour phase data obtained by Moore and Badger.[3] Spectra of the compounds NH_2Cl, $NHCl_2$, and NCl_3 were discussed by these workers who suggested that bands at 1273 and 1021 cm.$^{-1}$ were due to overtone and combination modes of NCl_3 respectively. As the compound studied was obtained as a decomposition product in the vapour of $NHCl_2$, the data obtained and the assignments suggested are unlikely to be very accurate. Furthermore the use of a KBr-prism spectrometer limited the range of the investigation to frequencies above 400 cm.$^{-1}$

In a pyramidal molecule of the AX_3 type (and almost certainly this structure can be assigned to NCl_3 as to NF_3[4]) the Raman spectrum should be most informative as it should contain four features due to a symmetric stretch ν_1, which will be polarised, an asymmetric stretch $\nu_{2,4}$, and to two deformations ν_6, which will be polarised, and $\nu_{3,5}$. The paucity of spectroscopic information with respect to this alarming compound, however, is explained perhaps by a quotation from Partington's familiar text:[4] "NCl_3 was obtained in 1911 as a yellow explosive oil by the action of chlorine on a solution of ammonium chloride by Dulong, who lost an eye and three fingers by an explosion."

The use of a laser source has two major advantages in studies of compounds of this type; firstly only small samples (*ca.* 3—5 mg.) of pure liquid are required and secondly, owing to the low frequency of the source (in this case emission at 6328 Å from a helium–neon laser), photosensitive species remain relatively unaffected by the intense exciting radiation.

The nitrogen trichloride was prepared by passing fine bubbles of chlorine through a 20% w/v solution of ammonium chloride in water (contrary to the report by Noyes[5] this salt was found to give a better and more rapid yield of the product than the sulphate). Fine droplets of a yellow oil, thought to be $NCl_3 + Cl_2$, were formed. These rapidly coalesced into larger globules which fell to the bottom of the vessel, from which the product was removed *via* a delivery tube of heavy-wall glass capillary bent into a 'swan-neck'.

Three samples were prepared and used as

follows. Sample A was dried over magnesium perchlorate and introduced into a 1 mm. bore capillary sealed at one end. This was filled to a depth of 6—8 mm. and transferred to a specially designed explosion-proof cell. The spectrum was recorded with a Cary 81 Laser Raman Spectrometer.

Samples B and C were dissolved in carbon tetrachloride and cyclohexane respectively, prior to drying. These solutions containing 10—15% w/v were examined in the spectrometer using open glass tubes of *ca.* 8 mm. diameter. No special precautions were necessary in the manipulation of these since previous tests had shown that solutions at this concentration level had little tendency to detonate. However, it must be stressed that the preparation and manipulation of pure nitrogen trichloride, particularly when dry, *is an extremely hazardous* operation (see cautionary note).

TABLE *Vibrational frequencies of the Group V trichlorides*

		$\nu_{3,5}$	ν_6	$\nu_{2,4}$	ν_1
NCl_3	.. ..	254 dp m	347 p s	637 dp vw	535 p s
PCl_3[9]	.. ..	189 (190 dp) s	260 (257 p) ms	494 (480 dp) w	507 (510 p) s
$AsCl_3$[9]	.. ..	155 (159 dp) s	194 (193 p) ms	307 ? (370 dp) ms	412 (410 p) s
$SbCl_3$[9]	.. ..	128 (134) s	164 (165) m	356 (320) s	377 (360) s

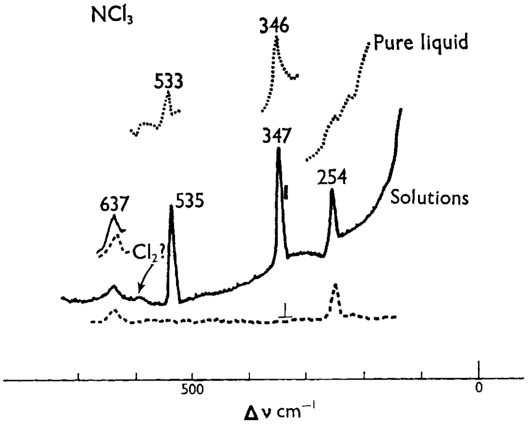
Results in brackets due to Kohlrausch.[8]

The spectra from the two solutions were indistinguishable and confirmed the existence of two strongly polarised bands, one at 535 cm.$^{-1}$ and the other at 347 cm.$^{-1}$. The spectrum of the pure liquid was less well defined but it was clear that certainly two, and probably three, of the lines recognised in the solution spectra were definitely attributable to nitrogen trichloride. A weak plateau near 230 cm.$^{-1}$ was attributed to a familiar spurious line of unknown origin while a very weak band near 550 cm.$^{-1}$ was probably due to dissolved chlorine, as this halogen has a reported frequency of 557 cm.$^{-1}$ (for the system $^{35}Cl-^{35}Cl$).

Turning to the question of assignment, the two bands at higher frequencies must be assigned to the stretching modes $\nu_{2,4}$ and ν_1. Polarisation data distinguish these immediately. In addition, reported data for the trichlorides of the heavier Group IV elements show that the Raman lines due to $\nu_{2,4}$ are always weaker than the line due to the symmetric mode. Polarisation data similarly enable one to distinguish between the remaining two bands. We are left with a frequency order $\nu_{2,4} > \nu_6 > \nu_{3,5}$. This is to be contrasted with the remaining trichlorides of Group V where $\nu_{2,4}$ is always of lower frequency than ν_1. Yet such behaviour is similar to that of the tetra-halides of Group IV where $\nu_3(F_2)$ is higher in frequency than $\nu_1(A_1)$. It is encouraging to note, however, that in planar tetra-atomic systems of similar mass to nitrogen trichloride, *viz.* the CS_3^{z-} ion of BCl_3 molecule, the frequencies of the asymmetric-stretching mode exceed that of the symmetric mode ($BaCS_3$:[6] $-E'_3 = 920$ cm.$^{-1}$, $A'_1 = 510$ cm.$^{-1}$, and BCl_3:[7] $-E'_3 = 995$ cm.$^{-}{}_{1}$, $A'^1 =$ cm.$^{-1}$).

The observed results and the proposed assignments are compared with similar data reported for the heavier trichlorides of Group V elements in the Table.

Since a full satisfactory assignment of the Raman spectrum of nitrogen trichloride can be prepared on the basis of a structure of C_{3v} symmetry but not of D_{3h} (one Raman line, A'_1, polarised and two, E', depolarised) it may be concluded that the nitrogen trichloride molecule is pyramidal like its analogues in Group V.



Cautionary note. The authors emphasise that the unpredictable and dangerously explosive properties of nitrogen trichloride have NOT been exaggerated in the literature. Extremely violent and destructive explosions have occurred during the course of this work, fortunately without causing serious injury. In consequence extreme care and adequate safety precautions are essential to ANY study of this compound.

(*Received, May 3rd,* 1968; *Com.* 540.)

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