Microwave Spectrum of a Gas-phase Charge-transfer Complex

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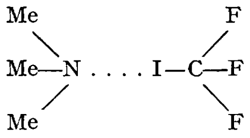
Summary The microwave spectrum of a charge-transfer complex formed between two molecules having closed electron shells [($Me_3N\cdots ICF_3$) has been observed for the first time and a bond length [r ($N\cdots I$) $= 2{\cdot}93$ Å] reported.

CHARGE-TRANSFER complexes have been the subject of many theoretical studies,[1] which refer for the most part to the isolated complex in the gas phase, while the vast majority of experimental studies have been of condensed phases, and although in recent years there has been increasing interest in experimental investigations of gas-phase complexes[2] these do not appear so far to have included any determination of structural parameters. Microwave spectroscopy is a well established method of gas-phase structure determination and has already been applied to the study of strong complexes involving Me_3N with molecules BX_3 ($X = F$,[3] Me [4]), which have open electron shells. Recently, some weak gas-phase hydrogen-bonded complexes have been investigated by the same technique[5] and this suggested that it might also be possible to obtain microwave spectra for another group of weak complexes, namely charge-transfer complexes formed by two molecules having closed electron shells. We now report for the first time the observation of the microwave spectrum of a complex which falls into the last-named group *i.e.* between trimethylamine and trifluoroiodomethane.

The formation of a 1:1 complex $Me_3N \cdots ICF_3$ in this system for both gaseous and condensed phases has already been conclusively established by Pullin and his coworkers,[6–8] by i.r. and other evidence. In microwave spectra of mixtures of the two gases, below −25 °C and at a total pressure of 2·5 Torr, we find new bands, which we attribute to the complex since they disappear and reappear reversibly as the temperature is raised and lowered. The bands are equi-spaced as expected for a symmetric rotor complex having the geometry shown. The centre frequencies of the bands and their assignments are listed in the Table.



TABLE

Frequency/MHz	B/MHz	Assignment $J+1 \leftarrow J$
26760	431·61	31 ← 30
28510	431·97	33 ← 32
29370	431·91	34 → 33
31120	432·22	36 → 35
31970	432·03	37 ← 36
32830	431·97	38 ← 37

Average B = 431·95 ± 0·20 MHz

The bands, which have halfwidths of *ca.* 200 MHz, probably include a number of unresolved vibrational satellites. Broad bands were also found in spectra of complexes formed by trimethylamine with BF_3[3] and BMe_3[4] and interpreted similarly. From the observed B value the $N \cdots I$ distance may be readily calculated to be 2·932 Å, if it is assumed that the structures of Me_3N[9] and ICF_3[10] remain unchanged on formation of the complex. This assumption is probably satisfactory for the present type of complex, unlike the cases of complexes with open electron shell molecules BF_3 and Me_3 where there are major changes in the angles at the boron atom. Possibly there may be some C–I bond lengthening on complex formation, but the suggested lengthening of 0·06 Å[7] leads only to a change of 0·009 Å in the $N \cdots I$ distance. A more serious source of uncertainty is that B obtained from the centre of the band may differ significantly from B_0, and therefore the $N \cdots I$ distance correspondingly from the r_0 value. However, even changing B by an amount equal to the halfwidth of a band changes the $N \cdots I$ distance by only ±0·015 Å. It is thus clear that the $N \cdots I$ distance is much longer than that for $Me_3N \cdots I_2$ or $Me_3N \cdots ICl$ for which crystallographic studies give 2·27[11] and 2·30 Å[12] respectively. A much closer comparison can be made with the $N \cdots I$ distance of 2·94 Å obtained for the hexamethylenetetramine–triodomethane complex.[13] However, this is a comparison with a three-dimensional network and more gas phase work is needed before reliable comparisons can be made.

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