Reassignment of Some Phenyl Vibrations in Benzotrifluoride

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A reassignment of the substituent sensitive phenyl vibrations in benzotrifluoride is made. The unambiguous reassignment of the C-CF$_3$ stretching vibration leads to the reassignment discussed here.

VIBRATIONAL spectrum of benzotrifluoride has been extensively studied and the assignment of the fundamentals have been proposed by a number of workers[1-4]. Both absorption and fluorescence studies[5-7] lend further support to the vibrational assignment.

The diverse assignments of $\nu C-CF_3$, as shown in Table 1, leave a cloud of uncertainty. A thorough discussion in our earlier publication[8] has removed the ambiguity and the $\nu C-CF_3$ could be assigned with certainty at 770 cm^{-1}. This change of $C-CF_3$ assignment leads to the reassignment of some of the phenyl vibrations, which are reported in this note.

TABLE 1 — DIVERSE ASSIGNMENTS OF νC-CF$_3$

Author	Frequency (cm^{-1})
Narasimhan *et al.*[3]	1028
Scott *et al.*[4]	1072
Cave and Thompson[6]	1035 (excited state)
Sponer and Lowe[5]	751 (excited state)
Sponer and Sastri[7]	771 (ground state)
D'Cunha[12]	1327
Varsanyi[9]	338

In substituted benzenes the substituent is known to influence the frequency and intensity of the phenyl vibrations. Most important vibrations are corresponding to modes 1, 12 and 6a (Wilson's notation) which are usually termed as substituent sensitive vibrations. In deciding frequencies of these modes, the mass and the bonding character of the substituents are to be considered.

The change in frequency of vibration-1 depends on two factors, namely (i) the extent of coupling and (ii) the frequency of the C-substituent stretching mode.

The character of CF$_3$ substituent in benzotrifluoride is not very definite. CF$_3$ is bonded to the benzene ring with a C-C bond which is rather weak. Thus for the ring radical skeletal vibrations it would behave like a heavy substituent. For the C-substituent vibrations, however, CF$_3$ may be classed as light and will show the characteristics of a light substituent to certain extent.

Varsanyi[9] has made a detailed discussion on the frequency ranges of various vibrations, taking into consideration the coupling nature of the C-substituent stretching vibration. It is well established now that in the case of monosubstituted benzenes with a heavy substituent, mode-6a couples strongly with the C-substituent stretching vibration and weakly with mode-1 resulting in an increase of the frequency of mode-1 and lowering that of vibration-6a. At the same time the frequency of mode-12 lies around that of benzene (990 cm^{-1}) without being affected by substitution.

The general frequency range of vibration-1 in the case of a heavy substituent is between 1050 and 1000 cm^{-1}. In fact, earlier workers have assigned a vibration in the range of 770 to 1072 cm^{-1} to this vibration, e.g. 770 cm^{-1} by Narasimham *et al.*[3] and 1004 cm^{-1} by Scott *et al.*[4]. Discussion in the earlier paper[8] rules out the possibility of assigning 770 cm^{-1} to vibration-1. Mode-1 is totally symmetric vibration which should give rise to a polarized Raman and a strong infrared band. All these conditions are met with, in the case of the 1072 cm^{-1} band, assigned by Narasimham *et al.*[3] to $\nu C-CF_3$. On the basis of this discussion, 1072 cm^{-1} band more appropriately fits the assignment to vibration-1, which agrees with that of Varsanyi[8]. Further confirmation has been found in substituted benzotrifluorides[11].

Vibration-13 is not expected to change its frequency on account of substitution with a heavy substituent. So, the frequency 657 cm^{-1} assigned by Scott *et al.*[4] to this mode is quite improbable. The 1004 cm^{-1} band which is assigned by them to mode-1 actually corresponds to mode-12 as discussed earlier. Narasimham *et al.*[3] too have made the same assignment.

Mode-6a, which is also a substituent sensitive mode along with modes 1 and 12, is more or less definite in its assignment (336 cm^{-1}). Garg's[10] empirical calculations also lead to the same frequency, which Varsanyi[8] assigns to $\nu C-CF_3$, under the assumption that the CF$_3$ group behaves as a heavy substituent. But the vibration is well established to be due to another mode as shown in our earlier work[8].

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