Mean Amplitudes of Vibration of Iodine Trifluoride

E. J. Baran

Centro de Química Inorgánica (CEQUINOR/CONICET,
UNLP), Facultad de Ciencias Exactas,
Universidad Nacional de La Plata, C. Correo 962,
1900-La Plata, Argentina

Reprint requests to Prof. E. J. B.;
E-mail: baran@quimica.unlp.edu.ar

Z. Naturforsch. **56a,** 333–334 (2001);
received January 12, 2001

Mean amplitudes of vibration of IF_3 have been calculated from vibrational spectroscopic data in the temperature range between 0 and 1000 K. Bond properties of the molecule are discussed on the basis of these results. Some comparison with related species are made.

Key words: IF_3; Mean Amplitudes of Vibration: Bond Properties.

Chlorine and bromine trifluoride are two of the best known and well-characterized interhalogen compounds. Information about the corresponding iodine compound is rather scarce, probably due to the fact that it is only stable below −30 °C [1] and decomposes easily to form I_2 and IF_5 [1, 2]. The three XF_3 species have a T-shaped structure of C_{2v} symmetry, consistent with the presence of 10 electrons in the valence shell (formally an sp^3d hybrid orbital) of the central atom [1].

Although the structural [1, 3–5] and spectroscopic [5–8] properties of ClF_3 and BrF_3 are well known, the related information concerning IF_3 is reduced to infrared spectroscopic studies of some of its complexes with organic bases [9] and to an assignment of the infrared spectrum of solid IF_3 measured at −100 °C [2].

Using the last mentioned spectroscopic investigation, and as part of our current studies on the vibrational and bond properties of interhalogen species, we have now performed a calculation of the mean amplitudes of vibration of IF_3 in order to attain a wider insight into the bond characteristics of this molecule.

The calculations were performed using the method of the characteristic vibrations, developed by Müller and coworkers [10] (cf. also [11, 12]). The necessary vibrational frequencies were taken from the paper of Schmeisser et al. [2]. The geometrical parameters (d(I–F(ax)) = 1.98 Å; d(I–F(eq)) = 1.88 Å; < F(ax)-I–F(eq) = 85.0°) were estimated by comparison with the structural data of ClF_3 and BrF_3 [1]. The results of the calculations, in the temperature range between 0 and 1000 K, are shown in Table 1.

Table 1. Calculated mean amplitudes of vibration (in Å) of IF_3.

T (K)	$u_{\mathrm{I-F(ax)}}$	$u_{\mathrm{I-F(eq)}}$	$u_{\mathrm{F(ax)\ldots F(ax)}}$	$u_{\mathrm{F(ax)\ldots F(eq)}}$
0	0.0448	0.0401	0.057	0.057
100	0.0448	0.0401	0.057	0.058
200	0.0460	0.0405	0.058	0.062
298.16	0.0489	0.0420	0.061	0.068
300	0.0489	0.0420	0.061	0.068
400	0.0528	0.0444	0.066	0.075
500	0.0568	0.0474	0.071	0.082
600	0.0609	0.0500	0.075	0.089
700	0.0648	0.0529	0.080	0.095
800	0.0686	0.0558	0.085	0.101
900	0.0723	0.0586	0.089	0.107
1000	0.0759	0.0613	0.094	0.113

Table 2. Comparison of the mean amplitudes of vibration (in Å and at 298.16 K) of the three isostructural XF_3 species.

Molecule	$u_{\mathrm{I-F(ax)}}$	$u_{\mathrm{I-F(eq)}}$	$u_{\mathrm{F(ax)\ldots F(ax)}}$	$u_{\mathrm{F(ax)\ldots F(eq)}}$
ClF_3	0.0505	0.0473	0.077	0.067
BrF_3	0.0473	0.0424	0.086	0.063
IF_3	0.0489	0.0420	0.061	0.068

As it can be seen, the mean amplitudes of vibration of the two axial I–F bonds are somewhat higher than those of the I–F equatorial bond, in the full temperature range. Remembering that lower mean amplitude values imply stronger bonds, these results show that the equatorial bond is slightly stronger than the axial ones. This behavior is also in agreement with the estimated bond lengths. Regarding the mean amplitudes of the non-bonded pairs, they show comparable values at the lowest temperatures, but with increasing temperatures the values corresponding to the F(ax)····F(eq) pair become clearly higher.

A comparison of the calculated values with those of the two isostructural species ClF_3 and BrF_3 seems interesting. This comparison is presented in Table 2, at the temperature of 298.16 K. The values for the chlorine and bromine species were obtained with the same calculation procedure as that employed in the present case [8]. Besides, the two related molecules show a slightly weaker equatorial bond. However, the most remarkable aspect of this comparison is the fact that the equatorial X–F bond suffers a slight reinforcement on going from the chlorine to the iodine species, whereas a similar trend cannot be observed for the axial bonds. In this last case, although the three values are comparable, the IF_3 amplitude is intermediate between those of the other two molecules. Nevertheless, the obtained results confirm the general trend expected for the bonding forces in this type of molecules. i.e., a reinforcement of the interhalogen bond with increasing difference in electronegativity of the involved atoms [13]. Notwithstanding, the present results show that the bond energies of the three molecules are probably not so markedly different as suggested by simple estimation [13].

On the other hand, the above comments and the present results suggest that the ionic contributions to the interhalogen bonds may be important in these molecules. Although the mean amplitude values obtained for the I–F bonds in IF_3 are lower than those calculated for IF_4^- (0.0520 Å at 298.16 K) [14], IF_2^- (0.0566 Å at 298.16 K) [15], and IF_5^{2-} (0.0602 Å at 298.16 K) [16], in which ionic contributions play a central role in the bonding, they are comparable to that of IF (0.0431 Å at 300 K) [17] which posseses the strongest known interhalogen bond [13].

All these observations suggest that the I-F bonds in IF_3 may be adequately described in terms of the semi-ionic three center-four electron bond model [18–20]. Or, more strictly speaking, the equatorial I–F bonds is formed by a regular localized two center-two electron bond through an sp^2 hybridized orbital on the iodine atom, leaving the two lone pairs in these hybridized orbitals. The two axial bonds must then be in 3c–4e bonds generating a more ionic bond [21]. These differences in I–F bonding of the two geometrically different F-atoms also provide a rational explanation for the differences in the bond length and mean amplitude values.

To conclude, the results of the present calculations are compatible with those previously performed for the similar chlorine and bromine trifluorides and confirm that in all these interhalogen molecules, ionic contributions are important in the formation and stabilization of the bonds.

Acknowledgements

This work has been supported by the "Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina", the author being a member of.

[1] N. N. Greenwood and A. Earnshaw: "Chemistry of the Elements", 2nd Edit., Butterworth-Heinenmann, Oxford 1997.
[2] M. Schmeisser, D. Naumann, and E. Lehmann, J. Fluorine Chem. **3,** 441 (1973/74).
[3] D. F. Smith, J. Chem. Phys. **21,** 609 (1953).
[4] R. D. Burbank and F. N. Bensey, J. Chem. Phys. **21,** 602 (1953).
[5] A. Müller and G. Nagarajan, Z.physik. Chem. Leipzig **253,** 113 (1967).
[6] H. Selig, H. H. Claassen, and J. H. Holloway, J. Chem. Phys. **52,** 3517 (1970).
[7] A. Müller, B. Krebs, A. Fadini, O. Glemser, S. J. Cyvin, J. Brunvoll, B. N. Cyvin, I. Elvebredd, G. Hagen, and B. Vizi, Z. Naturforsch. **23a,** 1656 (1968).
[8] E. J. Baran, Z. Naturforsch. **25a,** 1292 (1970).
[9] M. Schmeisser, W. Ludovici, D. Naumann, P. Sartori, and E. Scharf, Chem. Ber. **101,** 4214 (1968).
[10] A. Müller, C. J. Peacock, H. Schulze, and U. Heidborn, J. Mol. Struct. **3,** 252 (1969).
[11] A. Müller, E. J. Baran, and K. H. Schmidt, Characteristic Mean Amplitudes of Vibration; in S. J. Cyvin (Ed.), Molecular Structures and Vibrations, Elsevier, Amsterdam 1972.
[12] E. J. Baran, An. Asoc. Quim. Argent. **61,** 141 (1973).
[13] J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry. Principles of Structures and Reactivity, 4th Edit., Harper Collins, New York 1993.
[14] E. J. Baran, J. Mol. Struct. **21,** 461 (1974).
[15] E. J. Baran, J. Fluorine Chem. **92,** 119 (1998).
[16] E. J. Baran, Z. Naturforsch. **53a,** 931 (1998).
[17] E. J. Baran, Z.physik. Chem. Leipzig **255,** 1022 (1974).
[18] G. C. Pimentel, J. Chem. Phys. **10,** 446 (1951).
[19] R. E. Rundle, J. Amer. Chem. Soc. **85,** 112 (1963).
[20] T. Kar and E. Sánchez Marcos, Chem. Phys. Lett. **192,** 14 (1992).
[21] O. J. Curnow, J. Chem. Educat. **75,** 910 (1998).