The Gas-phase Structure of Xenon Hexafluoride

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THE recent publication[1] of the Raman spectra of xenon hexafluoride vapour has prompted the following analysis of the i.r. and Raman vapour spectra of XeF_6 on the basis of a model possessing O_h symmetry.

The occurrence of three lines in the Raman spectrum is in accord with this model of an octahedrally co-ordinated xenon atom.

Using a Urey–Bradley type[2] potential function, a secular equation $|GF - E\lambda| = 0$ was set up with the aid of Wilson's method.[3] The values of G and F elements were obtained from Nakawaga and Shimanouchi.[2] K, H, and F represent the force constants (in mdynes/Å) for bond stretching, angle deformation, and interaction between non-bonded atoms, respectively.

The Raman bands at 609, 520, and 206 cm.$^{-1}$ were assigned to ν_1, ν_2, and ν_5, respectively. Both $\nu_1(A_{1g})$ and $\nu_2(E_g)$ are Raman-active Xe–F stretching modes; $\nu_5(F_{2g})$ is a Raman-active F–Xe–F deformation mode.

On this basis, K, H, and F were calculated to be 2·788, −0·069, and 0·341 mdynes/Å, respectively. Using these force constants, ν_3, ν_4, and ν_6 were calculated to be 607, 158, and 146 cm.$^{-1}$ respectively. Both $\nu_3(F_{1u})$ and $\nu_4(F_{1u})$ are i.r.-active Xe–F stretching and F–Xe–F deformation modes respectively; $\nu_6(F_{2u})$ is an inactive F–Xe–F bending mode. This is substantiated by a calculation of the potential-energy distribution in ν_3 and ν_4.

The i.r. vapour spectrum obtained between 1400 and 400 cm.$^{-1}$ by D. F. Smith[4] shows bands at 1220, 1102, 612, and 520 cm.$^{-1}$. These may now be positively assigned to $(\nu_1 + \nu_3)$; $(\nu_2 + \nu_3)$; ν_3 and $(2\nu_5 + \nu_6)$ respectively. Bands at 1189 and 1154 cm.$^{-1}$ reported by Weaver *et al.*[5] are not apparent in the spectral measurements of Smith.[4]

Both $(\nu_1 + \nu_3)$ and $(\nu_2 + \nu_3)$ are abnormally broad, with about equal intensities. It is of interest that these combination tones occur as fairly narrow bands with similar intensity in various hexafluorides. A broadening of $(\nu_2+\nu_3)$ observed in OsF_6 and ReF_6 is attributable to the Jahn–Teller effect.[6] The band at 520 cm.$^{-1}$ is very weak compared to that at 612 cm.$^{-1}$ and cannot be ascribed to ν_3. The value, ν_4, could not be observed experimentally because it lies below the lower wavenumber limit investigated. The frequencies of ν_1 and ν_3 are almost the same, as in MoF_6.

In the liquid and solid phases, the XeF_6 Raman spectra exhibit many more bands than above. This is due presumably to a lowering of octahedral symmetry by aggregation in a condensed phase.

The bond-stretching force constant obtained for XeF_6 is similar to that of UF_6 (where K, H, F are 2·780, −0·190, 0·554 mdynes/Å, respectively), the bond lengths being *ca.* 2 Å in each case.

The excellent agreement of ν_3 (calculated) with ν_3 (observed), together with the characteristic Raman spectrum, suggest that the ground-state vapour molecules of XeF_6 possess O_h symmetry, but have unusual electronic properties which markedly influence band-widths.

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