

CHAPTER I
INTRODUCTION

Force constants are important quantities which give information concerning bond properties of molecules. They can be calculated from observed vibrational frequencies obtained from infrared and Raman spectra. Occasionally, some vibrational frequencies have not been observed, which may be due to their weak intensities. But unobserved frequencies can be predicted.

To predict unobserved frequencies, the usual methods used are (a) transfer of force constants or fix a few force constants in a particular force field¹, and (b) product rule.

(a) Transfer of force constants has been applied to isotopic molecules and to molecules having chemical groups in similar surroundings. These force constants depend on the model of force fields used in the calculation. Only Urey-Bradley force field (UBFF) is selected here, because Urey-Bradley force constants have a clearer physical meaning than those of the generalized valence force field. The latter, with its forces treated as arising from stretching of the chemical bonds and deformation of bond angles, is also popular with physical chemists.

(b) Product rule is only applicable to isotopic molecules. The present work is undertaken to introduce a third method:

empirical plots of frequencies against the mass of the central atom, or X atoms in MX_4 .

Fifteen tetrahedral inorganic molecules have been chosen for studies. The vibrational spectra of these molecules contain four fundamental frequencies: $\nu_1(a_1)$, $\nu_2(e)$, ν_3 and $\nu_4(f_2)$, where a_1 is totally symmetric, e is doubly and f_2 is triply degenerate. All four frequencies are Raman active and only ν_3 and ν_4 are infrared active. Fig. 1 illustrates the four normal modes of vibration.

These tetrahedral molecules are divided into four families.

They are

- a) The ammonium family consisting of $\text{N}^{14}\text{H}_4^+$, $\text{N}^{15}\text{H}_4^+$, ND_4^+ , and NT_4^+ (ν_1 of $\text{N}^{15}\text{H}_4^+$ and ν_1 of NT_4^+ unobserved);
- b) The group IV ordinary hydride family consisting of CH_4 , SiH_4 , GeH_4 , and SnH_4 (ν_1 of SnH_4 unobserved);
- c) The group IV deuterated hydride family consisting of CD_4 , SiD_4 , GeD_4 and SnD_4 (ν_1 of SnD_4 unobserved)
- and d) The tungsten family consisting of $[\text{WO}_4]^{-2}$, $[\text{WS}_4]^{-2}$, and $[\text{WSe}_4]^{-2}$ (ν_2 of WSe_4^{-2} unobserved).

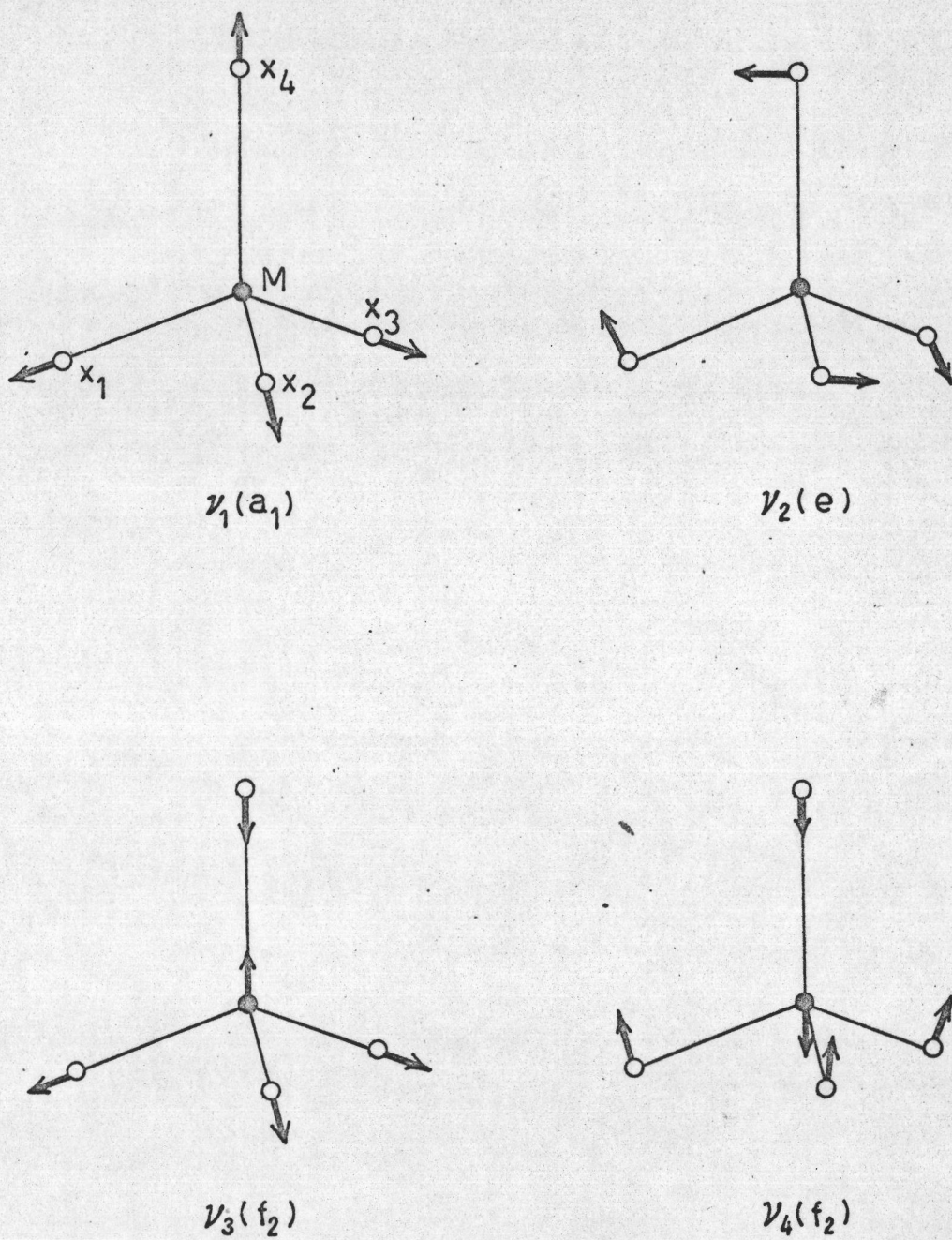


Fig. I Normal modes of vibration of tetrahedral MX_4 molecules.