

CHAPTER 4

STRUCTURAL STUDY BY INFRARED SPECTROSCOPY

Infrared spectroscopy is a technique that finds a wide variety of uses both in industrial analytical laboratories and in research laboratories of all types, as it furnishes information that is useful in qualitative and quantitative analysis. It is a convenient type of analysis which is useful for microsamples (down to the submicrogram range).

The method is rapid and easy to reproduce and can be applied to any physical state. Moreover, spectra are easily to handle documents, it has the particular advantage that all organic and most inorganic substances have their own characteristic spectra in the infrared region.

Infrared absorption spectra can be employed for the identification of pure compounds or for the detection and identification of impurities. Thus, for the identification of pure compound the spectrum of the unknown is compared with the spectra of a limited number of possible substances suggested by other properties, when a match between the spectra is obtained, then identification is complete.

The spectrum of a mixture of compounds is essentially that of the sum of the spectra of the individual components, while association, dissociation, polymerisation, or compound formation does not take place. In order to detect impurity in a substance,

a comparison can be made of the spectrum of the substance with that of the pure compound; impurities will cause extra absorption bands to appear in the spectrum. (25)

The application of infrared spectroscopy to the identification of inorganic compounds has been somewhat less successful. Many simple inorganic compounds such as the borides, silicides, nitrides and oxides do not absorb radiation in the region between 4000 and 600 cm^{-1} . Only within the last 10 years, instruments became available with which include the region below 600 cm^{-1} and it has been developed to cover the far-infrared region between 200 and 10 cm^{-1} . These are the regions in which most inorganic compounds absorb infrared radiation.

When standard spectra are available, a compound such as KNO_3 can easily be distinguished from NaNO_3 or $\text{Ca}(\text{NO}_3)_2$, but in the absence of standard spectra, specific identification of a cation-anion pair is usually not possible by infrared spectroscopy. The differences between the spectra of KNO_3 and $\text{Ca}(\text{NO}_3)_2$ for example, are largely due to two effects

- 1) the extent to which the cation perturbs the internal vibration of the anion
- 2) changes in the crystal structure of the system. The second effect is pronounced in the far-infrared region than in the region $4000 - 600\text{ cm}^{-1}$.

In obtaining infrared spectra of inorganic solids, an experimental complication arises from possible chemical reaction (cation exchange) between the inorganic compound and the infrared

window material or support medium. Care has been exercised in the selection of method preparing samples here so as to avoid their difficulty.⁽²⁶⁾

When the composition of compound is known, infrared spectroscopy can provide information about structural determination. Suppose that a molecule has several possible structures, each of which belongs to a different point group. Then the number of infrared active fundamentals should be different for each structure. Therefore the most probable model can be selected by comparing the observed number of infrared active fundamentals with that predicted theoretically for each model.

Consider the XeF_4 molecule as an example. It may be either tetrahedral or square planar. Using the method of selection rules for infrared spectra, the number of infrared active fundamentals can be found easily for each structure.

Selection Rules for Infrared Spectra

According to quantum mechanics, the selection rules for the infrared spectrum is determined by the integral:

$$[\mu]_{v'v''} = \int \psi_{v'}(Q_a) \mu \psi_{v''}(Q_a) dQ_a$$

Here μ is the dipole moment in the electronic ground state, ψ is the vibrational eigenfunction, and v' and v'' are the vibrational quantum numbers before and after the transition, respectively. The activity of the normal vibration whose normal coordinate, Q_a , is being determined.

By resolving the dipole moment into the three components in the x, y and z directions, we obtain the result

$$[\mu_x]_{\nu, \nu'} = \int \psi_{\nu'}(Q_a) \mu_x \psi_{\nu}(Q_a) dQ_a$$

$$[\mu_y]_{\nu, \nu'} = \int \psi_{\nu'}(Q_a) \mu_y \psi_{\nu}(Q_a) dQ_a$$

$$[\mu_z]_{\nu, \nu'} = \int \psi_{\nu'}(Q_a) \mu_z \psi_{\nu}(Q_a) dQ_a$$

If one of these integrals is not zero, the normal vibration associated with ν is infrared active. If all the integrals are zero, the vibration is infrared inactive. It is seen in the result of selection rules that the tetrahedral structure has two infrared active fundamentals (one stretching and one bending), whereas the square-planar structure has three infrared active fundamentals (one stretching and two bendings). The infrared spectrum of XeF_4 in the vapour phase exhibits one Xe-F stretching at 586 cm^{-1} and two FXeF bendings at 291 and 123 cm^{-1} . Thus, the square planar structure of D_{4h} symmetry is preferable to the tetrahedral structure of T_d symmetry. This method is widely used for the elucidation of molecular structure of inorganic, organic, and coordination compounds. Recently, the structures of various metal carbonyl compounds have been determined by this simple technique.

It should be noted, however, that this method does not give a clear-cut answer if the predicted number of infrared active fundamentals is similar for various probable structures. Furthermore, a practical difficulty arises in determining the number of fundamentals from the observed spectrum, since the intensities of overtone and combination bands are sometimes comparable to those of fundamentals when they appear as satellite bands of the fundamentals. Finally, it

should be remember that the molecular symmetry in the isolated state is not necessary the same as that in the crystalline state. (27)

The discussion of infrared fundamentals for inorganic compounds are divided by number of atoms and structures involved in the molecules, i.e.,

1. Diatomic molecules.
2. Linear triatomic molecules.
3. Bent triatomic molecules.
4. Pyramidal four-atom molecules.
5. Planar four-atom molecules.
6. Other four-atom molecules.
7. Five-atom molecules, tetrahedral and square planar.
8. More than five-atom molecules such as XY_5 , XY_6 , XY_7 etc.

1) In diatomic molecules, there is only one vibration along the chemical bond, its frequency is given by

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where k is the force constant, μ the reduced mass, and c the velocity of light. In homopolar X-X molecules, the vibration is not infrared active, whereas in heteropolar X-Y molecules, it is infrared active.

- 2) For linear triatomic molecules, the three normal modes of vibration of linear X_3 and YXY molecules are shown in Fig 4.1

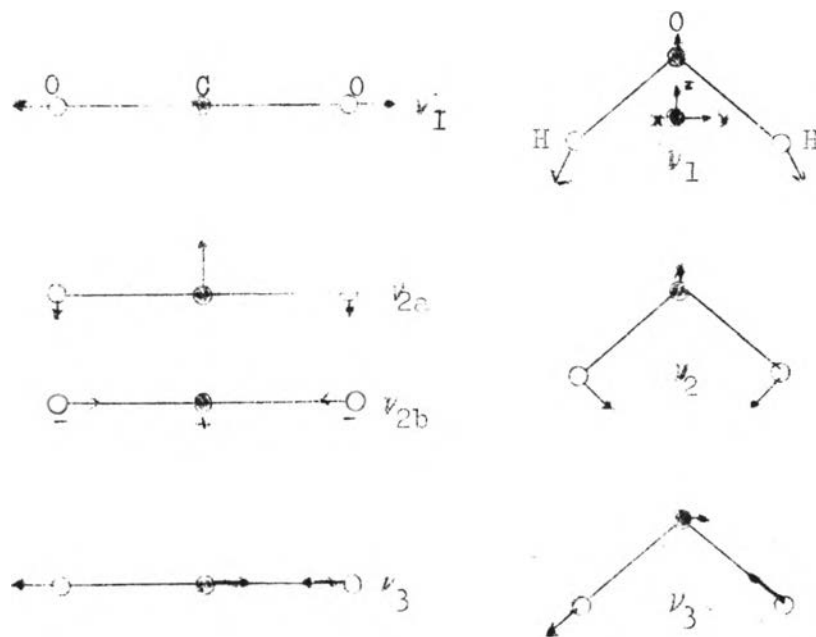


Fig 4.1 Normal modes of vibration in CO_2 and H_2O molecules (+ and - denote the vibrations going upward and downward, respectively, in the direction perpendicular to the paper plane)⁽²⁷⁾

The frequency ν_1 is not infrared active whereas ν_2 and ν_3 are infrared active but in linear molecules XYZ, the three normal modes of vibration shown in Fig. 4.2 are infrared active.

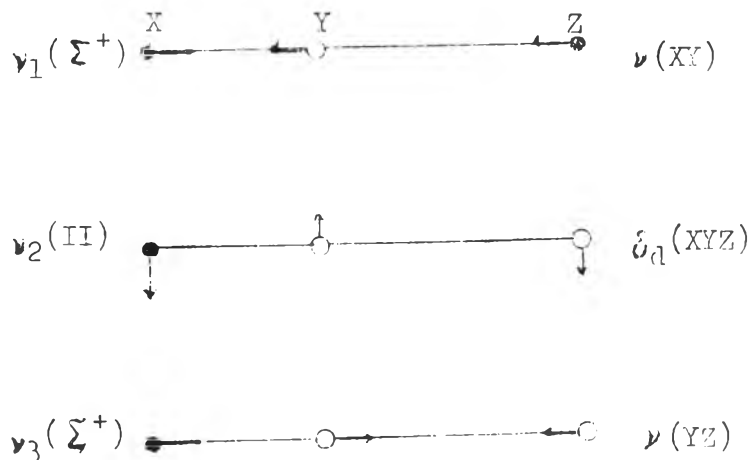


Fig. 4.2 Normal modes of vibration of linear XYZ molecules (27)

3) Bent triatomic molecules have three normal modes of vibration that are shown in Fig. 4.1 as normal modes of vibration in H_2O molecules. The vibrations are infrared active whether the molecule is symmetrical (X_2Y and X_3) or asymmetrical (XYZ , XXY). In many compounds of this type, the antisymmetric stretching frequency (ν_3) is higher than the symmetrical one (ν_1) however, this is not true for O_3 , F_2O , $(\text{NO}_2)^-$ and H_2O (ice).

Vibrational frequencies of water in various organic solvents have been studied by Greinacher et al. For example, dioxane solutions of water exhibit three bands at 3518, 1638 and 3584 cm^{-1} . Apparently, hydrogen bonding between water and dioxane is responsible for the shifts of the stretching modes to lower frequencies and for

the shift of the bending mode to higher frequencies.

4) The four normal modes of vibration of a pyramidal four atom XY_3 molecules (C_{3v}) are shown in Fig. 4.3

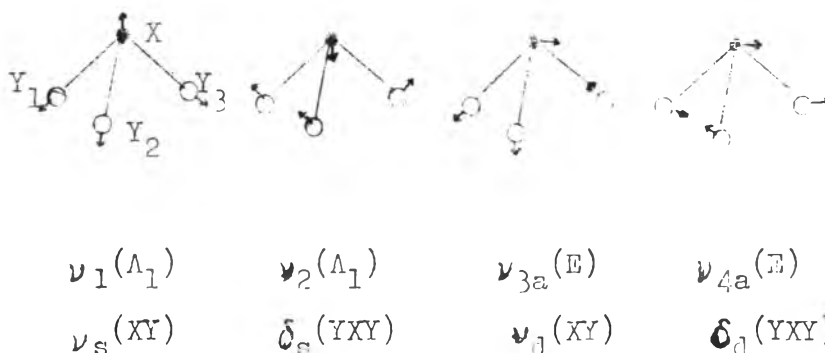


Fig. 4.3 Normal modes of vibration of pyramidal XY_3 molecules⁽²⁷⁾

These four vibrations are infrared active, each band of spectra is split up into two, because of inversion doubling. This arises in pyramidal XY_3 molecules, whereas the two configurations shown in the sketch are equally probable. If the potential barrier between these two configurations is small, the molecule may resonate between the two structures. As a result, each vibrational level also splits up into two. Substitution of a Z atom for one Y atom in the XY_3 (pyramidal four-atom molecules) lowers the symmetry to C_{2v} , as a result, the degenerate vibrations split up into two bands, thus six vibrations are observed. All of which are infrared active. If two of the Y atoms are replaced by two different atoms, W and Z, the symmetry is lowered to C_1 . Six vibrations are observed. All of which are also infrared active.⁽²⁸⁾

5) In planar four atoms molecule XY_3 , the four normal modes of vibration are shown in Fig. 4.4

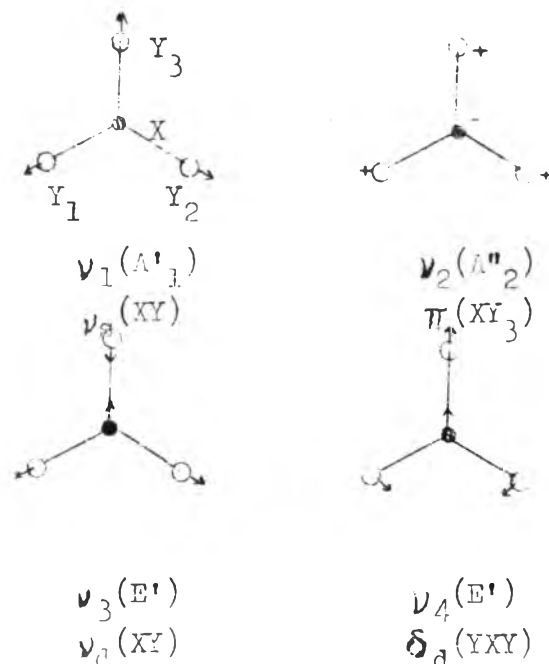


Fig. 4.4 Normal modes of vibration of planar XY_3 molecules⁽²⁷⁾

The vibrations ν_2 , ν_3 , ν_4 , are infrared active, calcite and aragonite ($CaCO_3$) exhibit different spectra although their chemical composition are the same, owing to the difference in crystal structures. Because of intermolecular interactions, the symmetry of a molecule is generally lower in the crystalline state than in the gaseous (isolated) state. The change in symmetry may split the degenerate vibrations and activate infrared inactive vibration. In addition, the spectra obtained in the crystalline state exhibit lattice modes—vibrations due to translatory and rotatory motions of a molecules in the crystalline lattice. Although their frequencies are usually lower than 300 cm^{-1} they may appear in the high frequency region

as the combination bands with internal modes.

If one of the Y atoms of a planar XY₃ molecule is replaced by a Z atom (ZXY₂ molecule), the symmetry is lower. If two of the Y atoms are replaced by two different atoms, W and Z, the symmetry is lowered further. For both cases, all six vibrations become active in the infrared spectra.

For four-atom molecules X₂Y₂ like H₂C₂, several different models have been suggested, but the nonpolar (twisted about the X₁-X₂ axis) and planar models are most probable, six normal modes of vibration and the band assignments for these two models are shown in

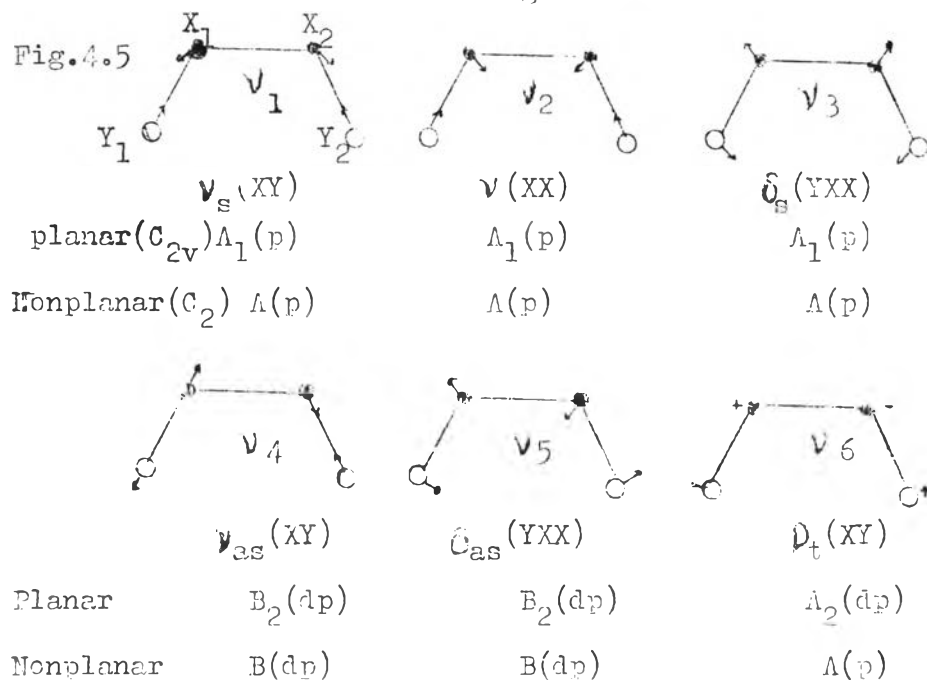


Fig. 4.5 Normal modes of vibration of nonlinear molecules (27)

It is not easy to distinguish between the two models from the vibrational spectra, since the only difference between the two occurs in the ν_1 vibration, it is infrared inactive in the planar model but infrared active in the nonplanar mode. A recent study of neutron diffraction on solid H_2O_2 indicates that the dihedral angle between two OOH planes is about 90° .

6) Other planar four-atom molecules of the XY_3 , $XYZX$ and $WXYZ$ types have six modes of vibration such as shown in Fig 4.6

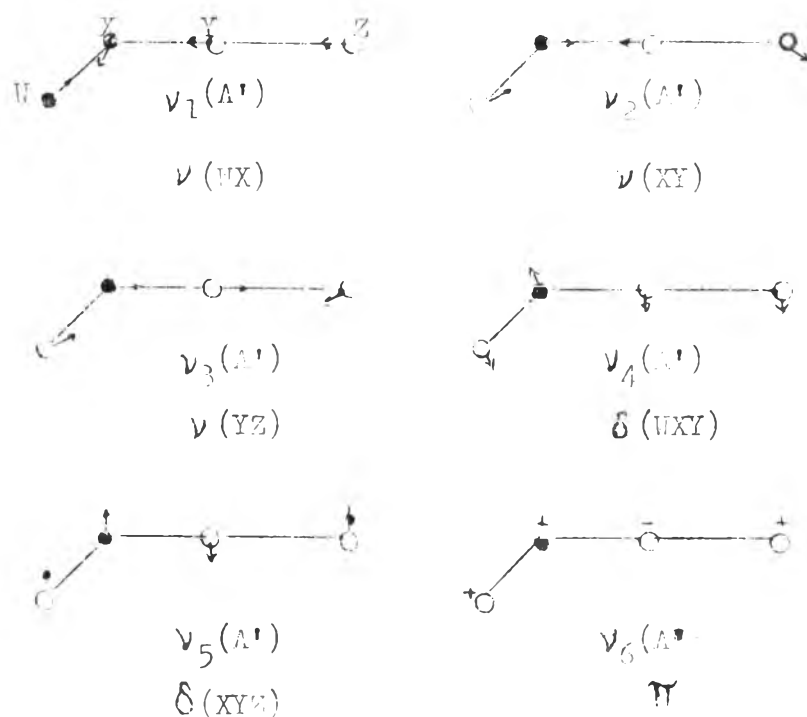


Fig. 4.6 Normal modes of vibration of nonlinear $WXYZ$ molecules⁽²⁷⁾

All these vibration are infrared active

7) In five-atom molecules, tetrahedral and square planar

7.1 Tetrahedral structures are studied as shown in

Fig. 4.7.

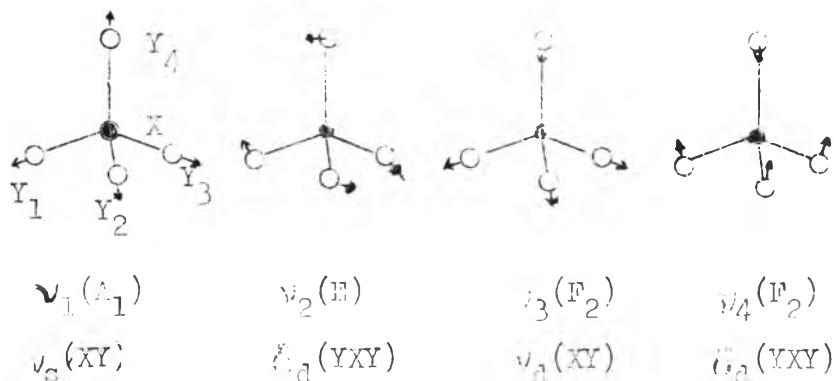


Fig. 4.7 Normal modes of vibration of tetrahedral XY_4 molecules⁽²⁷⁾

The four normal modes of vibration of a tetrahedral XY_4 molecules, only ν_3 and ν_4 are infrared active. Among the many XII_4 molecules, the NH_4^+ ion is chemically the most important. Hornig and co-worker⁽²⁷⁾ have made an extensive study of the infrared spectra of ammonium halide crystals. They found that there is a combination band between $\nu_4(F_2)$ and ν_6 (rotatory lattice vibration) as when the ammonium ion does not rotate freely in the crystal lattice.

If one of the Y atoms of an XY_4 molecule is replaced by a Z atom, the symmetry of the molecule is lowered. If two of the Y atoms are replaced, the symmetry is also lowered. The lowering of symmetry splits the degenerate vibrations and activates infrared inactive vibrations, thus, the number of infrared active vibration is increased to six in $2XY_3$ and to nine in $2XY_2$ molecules.

7.2 Square-planar XY_4 molecules, the figure 4.8 shows the seven normal modes of vibration of square planar XY_4 molecules.

The vibration ν_3 , ν_6 , ν_7 are infrared active.

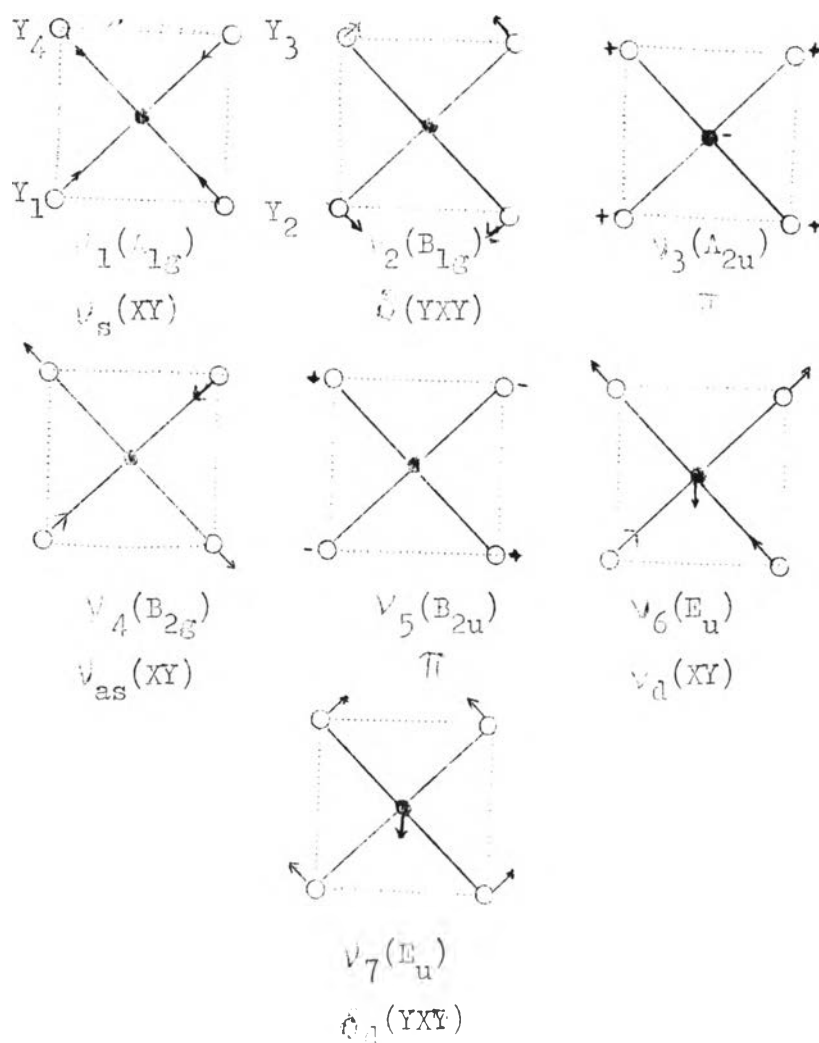


Fig. 4.8 Normal modes of vibration of square-planar XY_4 (27)

8) More than five-atom molecules such as XY_5 , XY_6 , XY_7 etc.

(8.1) An XY_5 molecule may be a trigonal bipyramid or a tetragonal pyramid. If it is trigonal bipyramidal, five of the eight normal vibrations are infrared active (A_2 and E). If it is tetragonal pyramidal, only six (A_1 and E) are infrared active, the vibrations mode are shown in Fig.4.9

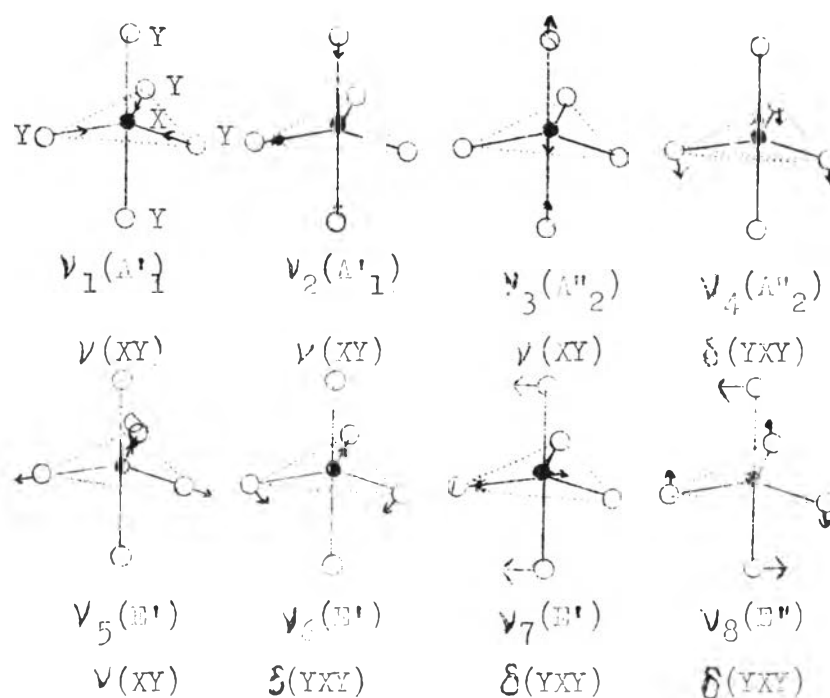


Fig. 4.9 Normal modes of vibration of trigonal bipyramidal XY_5 molecules⁽²⁷⁾

It is interesting to note that in the gaseous and liquid states phosphorous pentachloride (PCl_5) exists as a trigonal bipyramidal molecule, whereas in the crystalline state it has an ionic structure consisting of $(PCl)^+$ $(PCl_6)^{-}$ units.

(8.2) Octahedral XY_6 molecules.

The six normal modes of vibration of an octahedral XY_6 molecules are shown in Fig.4.10.

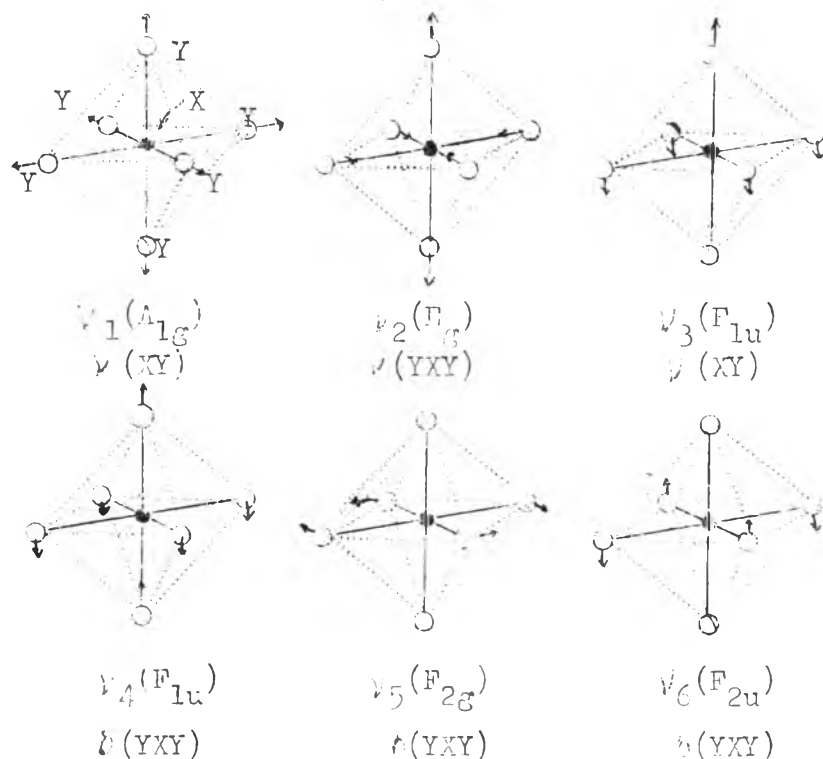


Fig. 4.10 Normal modes of vibration of octahedral XY_6 molecules (27)

Only ν_3 and ν_4 are infrared active, the molecule K_2F_6 is definitely distorted from the regular octahedral configuration. If it has octahedral (O_h) symmetry, it should expect one K_2F stretching (F_{1u}) band between 650 and 500 cm^{-1} . However, three bands were observed at 612 (strong) 565 (shoulder), and 520 (medium) cm^{-1} . The result suggests that its symmetry is definitely lower than O_h (octahedral).

(8.3) XY_7 molecules

Molecules of this type are very rare, if it is pentagonal bipyramidal, five vibrations should be infrared active. In the IF_7 molecule, these vibrational spectra of 676 (A_2), 368 (A_2), 547 (E_1), 426 (E_1) and 250 (E_1) cm^{-1} are obtained, so the structure of IF_7 is pentagonal bipyramidal. The same conclusion has been obtained by nuclear magnetic resonance and electron diffraction studies on this molecule.