

MOLECULAR VIBRATIONAL SPECTRA IN THE SOLID STATE

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ABSTRACT

The site and factor group methods of interpreting solid state vibrational spectra are compared. As examples, K_2TiF_6 (which has one molecular unit in a unit cell) and K_2ZrF_6 (which has eight in a non-primitive unit cell) are considered. Benzenetricarbonylchromium enables a distinction between site and factor group methods. The modification of the latter needed to account for the spectra of $Cr(CO)_6$, $dienMo(CO)_3$ and $(C_6H_5)_3SnFe(C_5H_5)(CO)_2$ are discussed and the concept of a vibrational unit cell introduced.

In this paper I shall discuss some features of vibrational spectroscopy which are of importance in the understanding of the infra-red and Raman spectra of crystalline solids.

The simplest way of looking at a crystal, be it ionic or molecular, is to regard it as a giant molecule. This viewpoint correctly indicates the complexity of the vibrational problem—there are an enormous number of modes associated with each crystal. For, for example, the understanding of specific heat phenomena, it is necessary to have a fairly detailed knowledge of the energy distribution of these modes. However, if one is only interested in the interpretation of the infra-red and Raman spectra of solids a considerable simplification results. This arises as a consequence of the fact that, in either form of spectroscopy, the wavelength of the incident radiation is very much greater than the distances between molecules (or ions, but we confine our discussion to the molecular case). Consider two molecules in adjacent primitive unit cells, interrelated by a simple translation operation. The effect of the electric vector associated with the incident radiation in either infra-red or Raman spectroscopy will be essentially identical for both of the molecules. That is, to a very good level of approximation, only those vibrations in which all translationally-related molecules move in phase will be observed. Evidently, this generalization cannot be extended to molecules interrelated by other than a pure translation because such molecules will usually be oriented differently in space. This means that a phase difference between the vibrations of two such molecules is to be expected.

In a perfect crystal any two molecules are symmetry-related (ignoring the discontinuities imposed by the finite dimensions of the crystal) and so the number of operations of a space group is very large indeed. Fortunately, the fact that we are interested only in vibrations which are invariant with respect to the translational operations introduces a simplification. This is that we

need only consider the vibrations within a single primitive unit cell; what happens in all other unit cells follows. This is, effectively, the so-called 'Factor Group' approach. We factor out from the whole set of space group operations just those few which interrelate molecules within a unit cell. A word of caution—we work with *primitive* unit cells. For convenience, crystallographers may work with a non-primitive unit cell (face- or body-centred, for instance). In such cases the vibrational spectroscopist must not use the crystallographic unit cell.

The character table of a factor group will be isomorphous with that of one of the thirty-two crystallographic point groups. We shall give several examples of the relationship between factor and point groups later on.

A full factor group analysis can be very complicated—it would not be unusual to predict a hundred infra-red and Raman modes—as we shall see, the $3N-6$ rule for non-linear isolated molecules carries over to the solid state with little modification (N is now the number of atoms in a unit cell). However, provided that there is, effectively, no coupling between symmetry-related molecules in a unit cell it is possible to use the so-called site symmetry approach, resulting in a considerable simplification. The group of operations which characterize the site symmetry of a molecule in a crystal is always a sub-group of the point group to which the factor group is isomorphous. The internal vibration of the molecule can be classified according to its behaviour under the site group operations and the normal selection rules applied. It may then be found that modes which were degenerate in the isolated molecule transform independently and so appear as two peaks, rather than one, and that inactive modes become formally active.

While the site symmetry approach is an isolated molecule approach, the factor group approach is a collective molecule approach. Experimentally, the distinction may be one of instrumental resolution. At low resolution a spectrum may be interpretable in terms of site symmetry but for a spectrum run with more care, or on a machine with better resolution, the factor group method is required to explain fine splittings which become evident. Similarly, for any one molecule a factor group analysis may be needed for one set of vibrations whilst the site symmetry method is adequate for another set. Roughly, the more peripheral the vibrations, the more necessary is a factor group analysis. So, in the transition metal carbonyls, the M—C stretching region is usually amenable to a site group analysis but the C—O stretching region requires the use of a factor group treatment. Finally, the detailed theory of the effect indicates that factor group splittings will be observed only for vibrations which absorb strongly in the infra-red.

As an illustration of the factor group approach we shall consider in detail two species studied by Lane and Sharp¹. K_2TiF_6 crystallizes in the $P3m^1(D_{3d}^3)$ space group with one formula unit in each unit cell^{2, 3}. Because there is no multiple occupancy of the unit cell the factor and site group predictions are identical. The arrangement in the unit cell is shown in *Figure 1*. The classes of the factor group are in a 1:1 correspondence with those of the D_{3d} point group; the correspondence is:

D_{3d}^3	$\{E \tau\}$	$2\{C_3 \tau\}$	$3\{C_2\{i \tau\}$	$\{i \tau\}$	$2\{S_6 \tau\}$
D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$

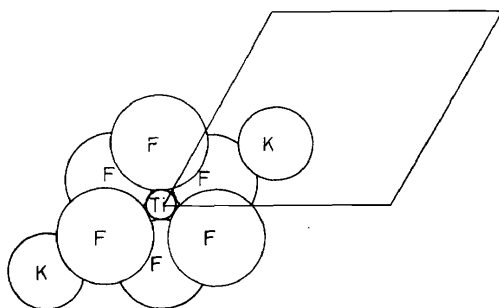
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$$D_{3d}^3 \text{ (contd)} \quad 3\{\sigma, g|\tau\}$$

$$D_{3d} \quad 3\sigma_d$$

Here τ denotes the set of all primitive translations. The unit cell operations

Figure 1.



corresponding to the factor group sets are shown in *Figure 2*, where it should be noted that what corresponds to a single unit cell operation above may appear as several fragments in the figure (in a different choice of primitive unit cell—and there is no unique choice—the fragmentation would be different. One must be careful to distinguish between a symmetry operation and the corresponding group operator).

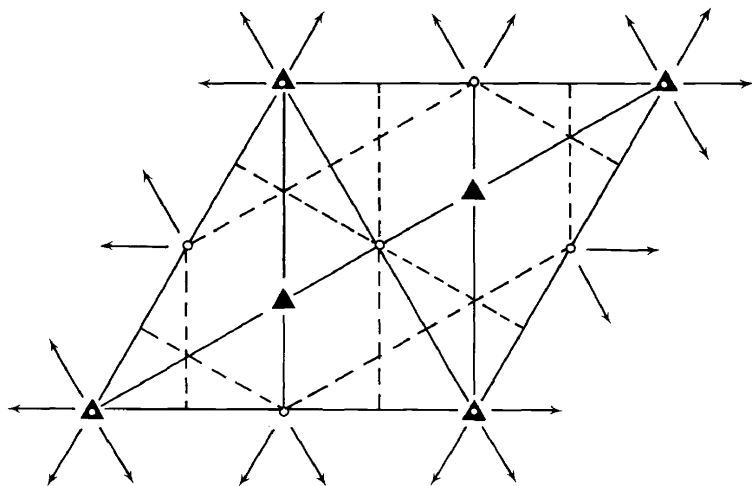


Figure 2.

It is now necessary to obtain the characters of the representations generated by the transformations of the atoms comprising a single unit cell. Strictly, the full factor group should be considered, but it is usually simpler to force all unit cell operations to pass through a common point by setting all non-primitive translation components of, and separations between, non-trivial symmetry operations to zero. In this way, for example, the three threefold rotation axes in the D_{3d}^3 unit cell (*Figure 2*) become coincident. The group

theoretical aspect of the molecular vibrations now reduces to a point-group problem. However, care must be taken when handling 'coincident', but distinct atoms. In the case of K_2TiF_6 , we obtain the modified unit cell shown schematically in *Figure 3*. It is now an elementary exercise to show that the

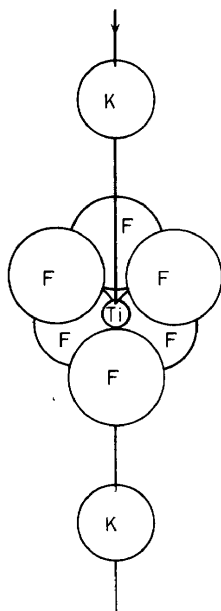


Figure 3.

27 (9×3) independent translations of the atoms in the unit cell transform to give the reducible representation:

$$\begin{array}{cccccc}
 \text{'E'} & 2\text{'C}_3\text{' } & 3\text{'C}_2\text{' } & \text{'i'} & 2\text{'S}_6\text{' } & 3\text{'}\sigma_d\text{' } \\
 27 & 0 & -1 & -3 & 0 & 5
 \end{array}$$

which has $3A_{1g} + A_{2g} + 4E_g + A_{1u} + 4A_{2u} + 5E_u$ irreducible components. Of these, $A_{2g} + E_g + A_{2u} + E_u$ correspond to *en masse* movement of the entire unit cell, rotations and translations. The translations, $A_{2u} + E_u$, will not be observed in the infra-red spectrum because the required translationally invariant combinations over all unit cells correspond to the translations of the entire crystal.

Of more importance are the movements of the three ions within the unit cell relative to one another, the modes having no resultant linear or angular momentum. The three ions have nine (3×3) degrees of translational freedom, three of which ($A_{2u} + E_u$) have already been discussed. The other six transform as $A_{1g} + E_g + A_{2u} + E_u$, are referred to as translatory lattice modes, and may be observed in the infra-red and Raman spectra. Evidently, if we regard the three ions as forming a single molecule, these 'lattice' modes may become internal molecular modes. The rotatory modes (only E_g in the present case since the three ions considered all lie on threefold axes of the

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unit cell and so do not subtend the A_{2g} representation) do not correlate with internal modes but with the rotations of the single molecule. Note that the rotation of the entire crystal is not a simple combination of unit cell rotations, neither is it a translationally invariant phenomenon.

There remain the fifteen internal modes of the $[\text{TiF}_6]^{2-}$ ion, $2A_{2g} + 2E_g + A_{1u} + 2A_{2u} + 3E_u$. Of these $2A_{1g} + 2E_g$ are Raman active and $2A_{2u} + 3E_u$ infra-red active. Correlation with the parent modes of the isolated (octahedral) ion :

$$\begin{aligned} O_h &\rightarrow D_{3d} \\ A_{1g} &\rightarrow A_{1g} \\ E_g &\rightarrow E_g \\ T_{2g} &\rightarrow A_{1g} + E_g \end{aligned}$$

indicates that all of the Raman-active modes in the crystal derive from Raman-allowed modes in O_h and so, presumably, will appear with similar intensities in the two environments. For the infra-red,

$$\begin{aligned} O_h &\rightarrow D_{3d} \\ T_{1u} &\rightarrow A_{2u} + E_u \end{aligned}$$

in contrast, only four of the five crystal fundamentals are expected to appear strongly.

The observed spectra are in agreement with these predictions¹. Detailed assignments require either single crystal infra-red and Raman analyses or,

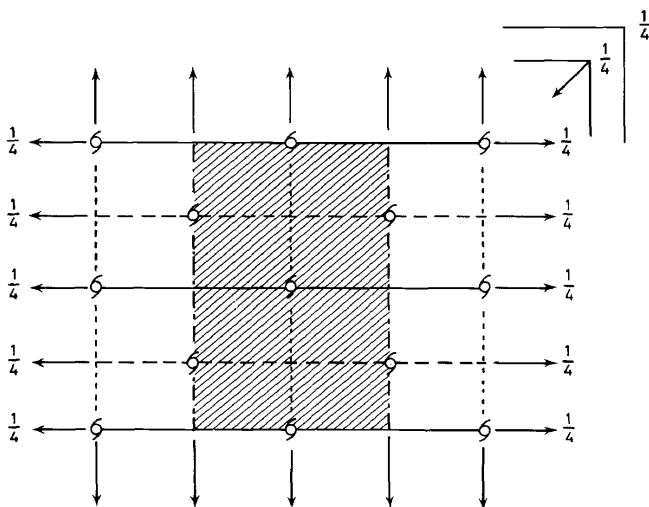


Figure 4. Unit cell operations of $Cmc m(D_{2h}^{17})$. The primitive unit cell is shaded.

in some cases for which the crystal structure is known, a detailed prediction of relative bond intensities may suffice. The single crystal methods are described in the literature⁴; we shall give a qualitative discussion of the use of infra-red intensities later. Raman intensities are more difficult and are considered elsewhere⁵.

A more difficult example is provided by K_2ZrF_6 . This has the space group $Cmcm (D_{2h}^{17})$ with four molecules in the unit cell⁶. This is a face-centred unit cell and the corresponding primitive unit cell contains only two molecules (Figure 4). As in the previous example, one may relate the factor group classes to those of the isomorphous point group (D_{2h}). Bode and Teufer⁶ found the following atomic coordinates in K_2ZrF_6 :

	x	y	z
2 × Zr generated from	0.00	0.05	0.25
4 × K generated from	0.00	0.35	0.00
4 × F(1) generated from	0.31	0.00	0.25
4 × F(2) generated from	0.19	0.21	0.25
4 × F(3) generated from	0.00	0.10	0.57

Treatment of these five sets separately and setting all non-primitive translations to zero leads to the atomic arrangements shown schematically in Figure 5. Working in the D_{2h} point group, the 54 (18×3) cartesian dis-

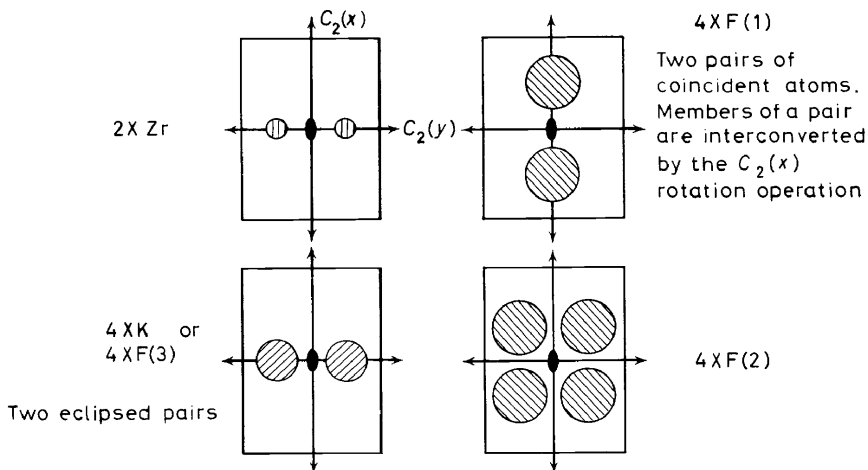


Figure 5. Atomic arrangements in K_2ZrF_6 .

placements of the atoms generate the direct sum $9A_g + 7B_{1g} + 4B_{2g} + 7B_{3g} + 4A_u + 7B_{1u} + 9B_{2u} + 7B_{3u}$. Of these, the six unit-cell motions transform as $B_{1g} + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$, and the fifteen lattice modes (including unit-cell rotatory modes) as $3A_g + 3B_{1g} + B_{2g} + 2B_{3g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$. The internal vibrations of the two $[ZrF_6]^{2-}$ ions transform as the difference between the first and the sum of the second and third direct sums (including the rotations, $B_{1g} + B_{2g} + B_{3g}$ once only). We thus conclude that the 36 internal motions transform as $6A_g + 4B_{1g} + 3B_{2g} + 5B_{3g} + 3A_u + 5B_{1u} + 6B_{2u} + 4B_{3u}$. It will be noticed that the components of this representation fall into pairs:

$$\begin{aligned}
 6A_g &- 6B_{2u} \\
 4B_{1g} &- 4B_{3u} \\
 3B_{2g} &- 3A_u \\
 5B_{3g} &- 5B_{1u}
 \end{aligned}$$

These pairs arise by virtue of the centre of symmetry in the unit cell. If the interactions between the two $[\text{ZrF}_6]^{2-}$ ions are all zero then, for example, each A_g vibration (observable in the Raman) occurs at the same position as B_{2u} (observable in the infra-red). This, again, indicates the connection between the site and factor group methods.

However, this is not a good example with which to test the applicability of the site and factor group approaches. This is because all of the solid-state modes correlate with modes which are either centrosymmetric or centro-antisymmetric in the O_h symmetry of the isolated $[\text{ZrF}_6]^{2-}$ anion. The resulting selection rules carry over relatively little modified into the solid state and ensure a non-coincidence of principal Raman and infra-red spectral features. All that is observable is a splitting of modes degenerate in O_h symmetry. This splitting could arise as a consequence of site symmetry or of factor group effects (or both); site effects most probably predominate.

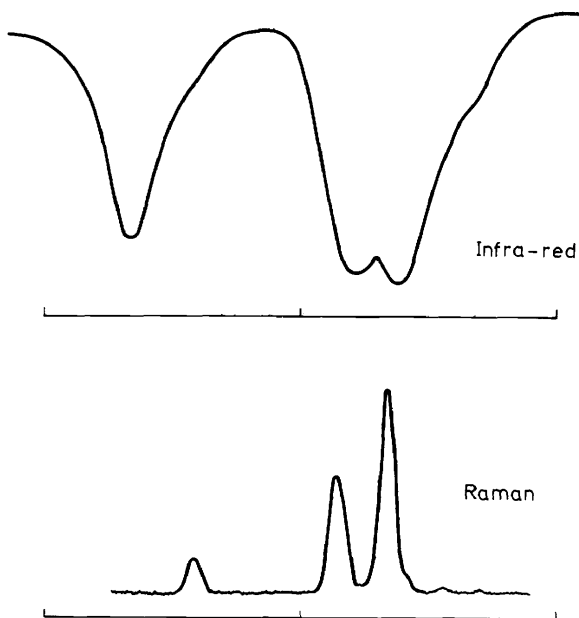


Figure 6

A simple, and unambiguous, example of factor group splitting is provided by benzenetricarbonylchromium. This crystallizes in the $P2_1/m$ (C_{2h}^2) space group with two molecules in the unit cell, interrelated by a centre of symmetry⁷. The site symmetry is C_s , so that it is predicted that three terminal CO stretching peaks will be observed in both Raman and infra-red spectra.

The site-symmetry model predicts they will be coincident, but the factor group predicts non-coincidence. Non-coincidence is observed⁸ (Figure 6).

In this example the full factor group predictions are realized, viz. three infra-red and three non-coincident, Raman peaks. More commonly, they are only partially realized (at least in the case of terminal CO stretching vibrations) and we now proceed to give three reasons for this. We shall consider only the factor group approach, usually comparing it with that appropriate to the isolated molecule. The site symmetry method, which represents an intermediate level of complexity, is not adequate for the cases we consider, namely, the vibrations of transition metal carbonyls in the 2000 cm^{-1} region.

MOLECULAR SYMMETRY

Hexacarbonylchromium has⁹, most probably, an orthorhombic unit cell, $Pnma$ (D_{2h}^{16}), with $Z = 4$. The factor group is isomorphous with D_{2h} and so ten infra-red ($4B_{1u} + 2B_{2u} + 4B_{3u}$) and twelve Raman ($4A_g + 2B_{1g} + 4B_{2g} + 2B_{3g}$) peaks are expected in the 2000 cm^{-1} region. However, the molecular symmetry is not far from O_h in the crystal and so it is reasonable to suppose that only those infra-red modes which correlate with T_{1u} and Raman modes

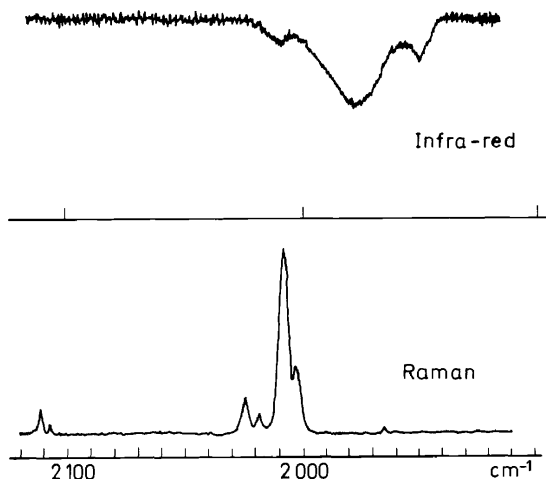


Figure 7

which correlate with A_{1g} or T_{2g} will be observed. It follows that, of the peaks predicted by the full factor group, only five infra-red and six Raman would be expected to be strong, in good agreement with experiment (Figure 7).

MOLECULAR ORIENTATION

When one uses the factor group approach one arrives at a list of irreducible representations which correspond to predicted infra-red and Raman peaks.

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A necessary (but not sufficient) condition that has to be fulfilled in order that these predictions are in accord with experiment is that the vibrating atoms are not arranged in space in such a way that the intensity of one or more of the vibrational bands is accidentally zero.

The vector corresponding to an infra-red active molecular vibration of a molecule occupying a general unit cell site is therefore assumed to have non-zero projections on to the three cartesian axes. If one of these projections is small, the corresponding factor group mode will appear weakly, if at all, in the solid state spectrum. This situation is somewhat aggravated by the relative magnitudes of the factor group splittings and the half-widths of vibrational bands—the latter are often the larger. This means that a weak peak may be present on the side of a larger peak and very difficult to locate. Cooling the sample sharpens vibrational bands and so facilitates the resolution of weak peaks but may also cause phase changes.

The existence of an accidental orientation phenomenon may find strong support from a full structural analysis. Conversely, its presence (and, particularly, its study using a single crystal and polarized radiation) can give information on molecular orientation in the absence of a complete structure analysis.

As an example we consider the molecule diethylenetriamine-tricarbonyl molybdenum [$P2_12_12_1 (D_2^4); Z = 4$]¹⁰. Of particular interest are the crystal modes corresponding to the totally symmetric C—O stretching mode of the Mo(CO)₃ unit. This unit has a symmetry which is very close to C₃. If, in the crystal, the totally symmetric CO stretching vector (to which we confine our discussion) lies along the 'threefold axis' then it also lies almost exactly in a plane parallel to the *ab* crystallographic plane. This is evident from a comparison of the Mo coordinates with those of the average of the three carbon and oxygen coordinates (Table I). It follows that the factor group mode

Table I. Comparison of Mo coordinates with the average of C and O coordinates in dien Mo(CO)₃. The vector characteristic of the A₁ vibration of the Mo(CO)₃ unit (in C_{3v} symmetry) is seen to lie approximately in the *xy* plane and to make approximately equal angles with the *x* and *y* axes.

Axis	Average of atomic coordinates		Mo coordinates	Difference between Mo coordinates and the average of	
	C	O		C	O
<i>x</i>	0.422	0.468	0.319	0.087	0.127
<i>y</i>	0.465	0.509	0.396	0.083	0.123
<i>z</i>	0.815	0.815	0.811	0.004	0.004

which corresponds to a dipole-moment change along the *c* axis will appear very weakly, if at all. Similar arguments lead to the prediction that the two other factor group modes will appear with similar intensities. The experimental data (Figure 8) are in excellent agreement with this. The case of what in the isolated molecules are the degenerate *E* modes is more complicated and is conveniently discussed in a different manner (*vide infra*).

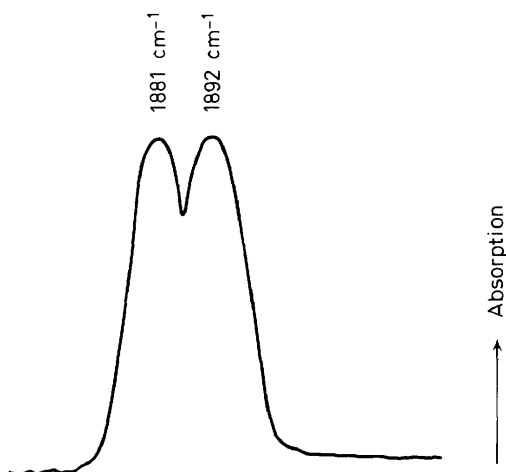


Figure 8

INTERMOLECULAR COUPLING

The distinction between a full factor group analysis and the site symmetry approach is that in the former all intermolecular interaction constants are non-zero whilst in the latter all are, effectively, zero. Evidently, the intermediate situation is also possible, some interaction constants being non-zero whilst others are zero. This situation, which is most prevalent in structures with large unit cells so that some interactions are between well separated units, will lead to spectra intermediate between those predicted by the factor group and site symmetry methods. There is no formal method which deals with this situation; often it is difficult to decide whether one is dealing with this intermediate situation or one in which accidental coincidences are present. In the terminal carbonyl region, for example, in which perhaps six (allegedly) non-coincident peaks occur in both Raman and infra-red spectra in a region approximately 100 cm^{-1} wide, the interpretation of coincidences can seldom be unambiguous.

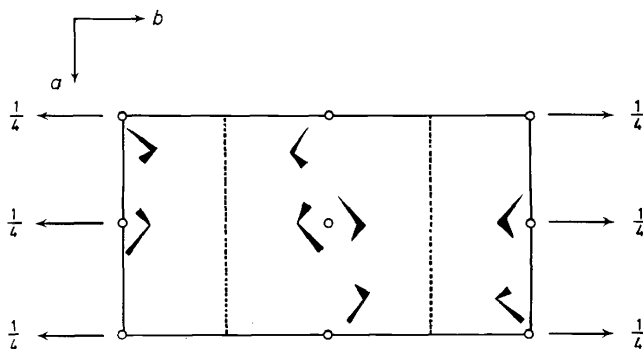


Figure 9

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An example which is reasonably clear-cut is provided by cyclopentadienyldicarbonyliron triphenyltin. A potentially complicating feature in this case is the presence of two non-symmetry-related molecules in the primitive unit cell. It transpires, however, that the distinction between the two units is unimportant for the interpretation of the vibrational spectra. A crystal structure analysis (space group $P2_1/c - C_{2h}^5$; $Z = 8$) reveals that the terminal carbonyl groups are located in two well separated parts of the unit cell (Figure 9)¹¹. A factor group analysis predicts four modes each of A_g , B_g , A_u and B_u symmetries in the 2000 cm^{-1} region. Just as for $[\text{ZrF}_6]^{2-}$, these

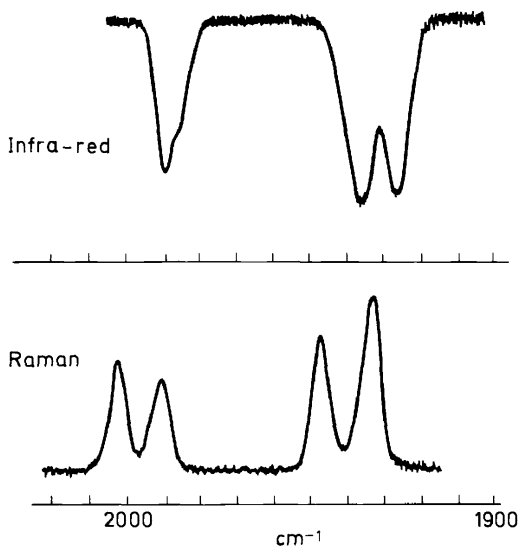


Figure 10

fall into two effective sets, distinguished as in-phase and out-of-phase coupling between the two carbonyl-containing volumes. If the interaction between these two volumes is small, a coincidence between the two sets will be observed. Experimentally, four infra-red and four non-coincident Raman peaks are observed (Figure 10), just as predicted for each set separately.

THE VIBRATIONAL UNIT CELL

It is evident from the discussion so far that sometimes a site symmetry approach is appropriate, sometimes a factor group and sometimes something intermediate. How may these be collectively rationalized?

It has been suggested that it may be useful to introduce the concept of a vibrational unit cell. Let us consider an example.

We have already considered the molecule diethylene triamine tricarbonylmolybdenum. Figure 11 is a photograph of a model of the unit cell in which only the $\text{Mo}(\text{CO})_3$ fragments are shown. The higher symmetry of the latter is evident [in Figure 11 are also shown new symmetry operations which interrelate $\text{Mo}(\text{CO})_3$ fragments but not whole molecules]. In fact, the space

group subtended by the $\text{Mo}(\text{CO})_3$ units is $Pnma$ (D_{2h}^{16}), to a very good approximation (cf. $P2_12_12_1$ for the entire molecule). The analysis of the vibrational spectrum in the 2000 cm^{-1} region is simple in $Pnma$ but, as we have seen, rather difficult in $P2_12_12_1$.

Similarly, the analysis of the spectrum of cyclopentadienyldicarbonyliron

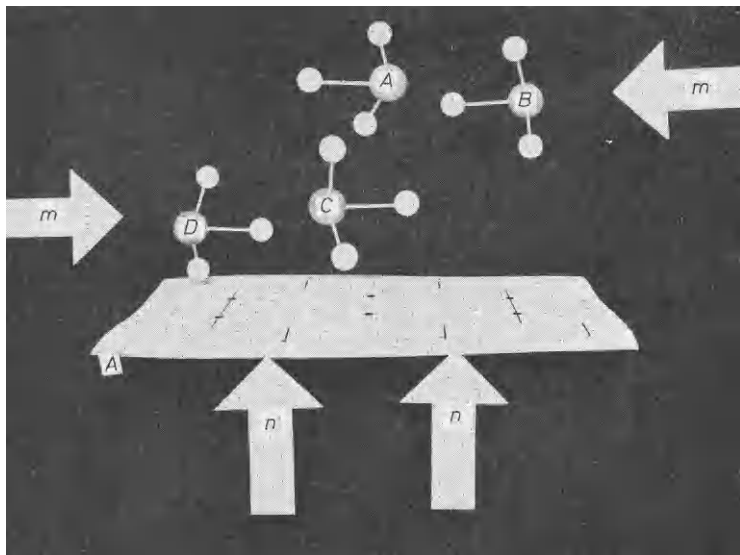


Figure 11

triphenyltin was facilitated by the recognition that the vibrational unit cell is only half of the crystallographic unit cell. The analysis is straightforward in a factor group isomorphic to the C_i space group. Further, different molecules may possess isomorphic vibrational unit cells even when they are not crystallographically isomorphic and this feature may enable a detailed analysis of their vibrational spectra¹².

A word of caution, however, is appropriate. First, a vibrational unit cell and vibrational space group of the type we have described apply to only part of the molecule. Different parts of the same molecule may require different vibrational unit cells. Secondly, with improved resolution or for single-crystal studies with polarized radiation, a full factor-group approach may become necessary.

It may well happen that the near-zero interaction constants are such that their neglect is not equivalent to working in a new vibrational space group. Such cases can only be dealt with by the full factor group method together with the recognition of 'accidental' degeneracies. A similar situation may arise when symmetry non-related interaction terms have, essentially, the same value.

On the other hand it is now clear that it is a potentially dangerous procedure to attempt to infer probable crystallographic space groups from

vibrational data unless these are unusually complete. With incomplete data even the crystal class may be incorrectly diagnosed!

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