The Degeneracy, Selection Rules, and Other Properties of the Normal Vibrations of Certain Polyatomic Molecules

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The number, degeneracies, and symmetries of the normal modes of vibration are given for molecules in which several atoms are bonded to a central atom. Ninety-nine symmetries, including all possible structures with three to seven atoms and the more important structures of eight and nine atoms are listed in tables. The selection rules for the Raman and infrared spectra are included as well as the polarization properties of the Raman lines and the rotational structure of the vibrational bands. In a number of more important cases figures are given showing the normal modes of vibration. Many examples of molecules which are believed to possess certain of the structures are included in the tables, together with references to experimental papers dealing with them.

In drawing structural conclusions from observed Raman and infrared spectra, it is necessary to know the number of normal frequencies of vibration and the selection rules which characterize the various possible configurations of atoms. The theory of the number and degeneracy of the normal vibrations of symmetric molecules, first developed by Brester,1 was very concisely expressed by Wigner,2 using group theory, while the selection rules for the Raman and infrared have been discussed by Placzek,3 Tisza4 and others.

In order to provide a tabular presentation of the important results of these theories for a special class of molecules, so arranged that they may be used without any knowledge of group theory, the degeneracies, number of permitted Raman and infrared fundamentals, and the polarization properties of the Raman lines have been calculated for molecules in which two or more atoms (which may be identical or different) are attached to a single central atom. The treatment is intended to be complete up to six attached atoms; that is, every possible symmetry for such molecules is listed, even those which are not very reasonable physically. For molecules with seven and eight outer atoms, only a few of the more reasonable structures are given, since there are very few molecules of these classes known and a very large number of possible symmetries.

The group-theoretical method used to find the number and degeneracies of the normal vibrations was described in a previous paper,4 where it was used to obtain the normal coordinates and frequency formulas for benzene. The selection rules have also been obtained by the application of group theory4 and the results checked wherever possible with the table given by Placzek.3 (The following divergences from his results were found: p. 81 of the English translation,6 point group \( S_{pu} \), line labelled \( B_1 \), fifth column, read "all zero but \( C_{xy} \)"; line labelled \( B_2 \), fifth column, "all zero but \( C_{xx} = -C_{yy} \); line labelled \( C \), fifth column, \( \text{"all zero but } C_{xy} = C_{ii} = 0 \); line labelled \( D \), sixth column, \( C_{xx} = -C_{yy}, C_{ii} = 0 \."

In using these results in connection with experimentally observed spectra, it is necessary to take certain precautions. Thus the number of Raman lines found may not coincide with that theoretically required for two reasons: first, lines which are not forbidden by symmetry restrictions may still be so weak that they do not appear under ordinary conditions, and second, overtones and combinations may occur in special cases. The latter difficulty is one which is rather frequently observed in spite of the fact that overtones and combinations should be much less important in Raman spectra than in infrared spectra. Another phenomenon which sometimes

1 C. J. Brester, Kristallsymmetrie und Reststrahlen, Utrecht, 1923; Zeits. f. Physik 24, 324 (1924).
4 L. Tisza, Zeits. f. Physik 82, 48 (1933).
occurs, for example in \( \text{CO}_2 \) and \( \text{CCl}_4 \), and which causes deviations from the simple selection rules, is quantum-mechanical resonance between certain of the energy states of the molecule due to accidental coincidence or approximate coincidence of the levels corresponding to different types of vibration. This effect usually allows otherwise forbidden lines to appear in the spectrum, but it is probably not very common.

**Explanation of Tables**

The results are given in separate tables, arranged according to the number of atoms in the molecule. Thus Table I lists triatomic molecules of the type \( \text{AB}_2 \) and \( \text{ABB}' \), Table II includes \( \text{AB}_3 \), \( \text{AB}_2 \text{B}' \), and \( \text{ABB}' \text{B}'' \), etc. A is not equivalent by symmetry to any of the B's (although it may be an atom of the same element, as for example in \( \text{N} - \text{N} - \text{O} \)).

The numbering, given in the first column of the tables, is designed to indicate the number and character of the attached atoms. The figure in front of the dot gives the total number of attached atoms while the figures following the dot indicate the numbers of symmetrically related atoms. Thus 6.6 means that the molecule is \( \text{AB}_6 \) in which all six B atoms are equivalent from a symmetry standpoint. 6.42 refers to \( \text{AB}_4 \text{B}_2 \), etc. When there are several molecules of the same type but of different symmetries, they are distinguished by using a, b, c, etc. The name, given in the second column, is meant to be descriptive enough to characterize the structure if possible, but in addition the coordinates of the atoms are given under the discussion of each type. The notation R and L following the name of a structure indicates that right and left-handed forms are possible.

The column labelled I gives the point-group symmetry of the structure, the symbols being those of Schönflies, which represent the axes, planes and other elements of symmetry possessed by the molecule. The column headed II tells whether the molecule is a linear rotator L, a spherical top Sp (which has three equal moments of inertia), a symmetric top S (with one distinct and two equal moments of inertia), or an asymmetric top A (which has three unequal moments of inertia).

The columns labelled \( \nu_1 \), \( \nu_2 \), \( \nu_3 \) contain the number of singly, doubly, and triply degenerate normal frequencies of vibration. Only molecules with cubic point-group symmetries can have triply degenerate frequencies. Under R is listed the number of fundamental frequencies of vibration which are allowed to appear in the Raman spectrum, although a line so permitted may be of very small intensity. Following this number, in parentheses, is the number of these Raman fundamentals which have the special depolarization \( \rho = \frac{2}{3} \), when plane polarized incident light is used. \( \rho \) is the ratio of the intensities of the perpendicular and parallel components of the scattered light. For unpolarized incident light this becomes \( \rho = \frac{6}{7} \).

Under I.R. is given the number of fundamental frequencies which are active in the infrared absorption spectra, the figures in parentheses being the number of these bands which are of the \( || \) type if the molecule is a symmetric top. Finally, the last column tabulates the symmetries of the possible normal vibrations, the degrees of the factors into which the secular equation for the normal coordinate problem may be factored by the use of the symmetry of the molecule, the degeneracies of these vibrations, and the ones which are active in the Raman and infrared spectra. To illustrate: 2R, 0, 2\( \beta \), 1\( \alpha \), 2\( \beta \) after 4.4d means that there are two frequencies with the symmetry of \( \Gamma_1 \) or \( \alpha_1 \), the first irreducible representation of the point-group \( V_d \), none with symmetry \( \Gamma_3 \) or \( \alpha_2 \), two with \( \Gamma_3 \) or \( \beta_2 \), one with \( \Gamma_4 \) or \( \beta_1 \), and two doubly degenerate frequencies with symmetry \( \Gamma_5 \) or \( \beta_3 \), the degeneracy being indicated by the subscript. The meaning of the term "irreducible representation" is explained in the paper on benzene already referred to. The order \( \Gamma_1 \), \( \Gamma_2 \), etc. is that used by Wigner in his tabulation of the irreducible representations of the crystallographic point groups. Several point groups which do not occur in crystallography were used: namely \( D_{\infty h} \), \( C_{\infty v} \), \( D_{\infty h} \), \( C_{\infty v} \), \( C_{2h} \), \( C_{2v} \), \( C_{2h} \), \( C_{2v} \), and \( D_{4d} \), the characters for their irreducible representations being taken from the general tables given by Tisza.

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The numbers with superscript R indicate the frequencies which are active in the Raman spectrum while a superscript I on a number means that this frequency is infrared active. The numbers themselves, besides the significance given to them above, also represent the degrees of the factors of the factored secular equation. For the linear molecules, to which Wigner's tables do not apply, the notation of Tisza is used for the irreducible representations.

**DISCUSSION OF RESULTS**

In the discussion of individual cases which is given below, the number and name of the structure is followed by the Cartesian coordinates of the different atoms, with A always at the origin. u, v, w represent parameters which are not fixed by the symmetry, while the letter o has been printed instead of zero. These were mostly taken from a tabulation by Nowacki of the equivalent positions for the point-groups. (Two slight misprints were found in this paper; namely, in Table III, p. 28, after Ds=bV (4) the second line should read \( |xz|/xz|\bar{x}x|/xz| \) (C₄ν). After D₅d (6) (b) the second line should read \( |xoz|/xoz|0|xz|/xoz| \) (C₅ν).) Wherever possible examples are given of molecules which have been found or which might be supposed to belong to the given type. In a number of examples which seem likely to be of importance and which, so far as I know, have not been previously treated, figures are given showing the normal vibrations, derived from the symmetry restrictions yielded by the group theory. The order used in the diagrams is the same as that in the last column of the tables. Only one representative of a set of degenerate vibrations is shown. An example is Fig. 2 which shows the normal vibrations for 5.32a, the trigonal bipyramid model of \( \text{AB}_3\text{B}_2^+ \). The last column of Table IV reads: 2\( ^{\prime}\), 0, 3\( ^{\prime}\); 0, 2, 1\( ^{\prime}\). Therefore the first two motions of Fig. 2, labelled \( \nu_1 \) and \( \nu_2 \), belong to \( \Gamma_3 \) or \( \Gamma'_1 \), the first irreducible representation of Wigner’s table for \( \text{Dah}_5 \), and since 2\( ^{\prime}\) has the superscript R, they are Raman active. The next three motions, \( \nu_3 \), \( \nu_4 \), \( \nu_5 \) belong to \( \Gamma_1 \) or \( \Gamma'_1 \). They are active in both the Raman and infrared spectra and are doubly degenerate; i.e., for each of them there exists another similar motion with the same frequency, differing only in spatial orientation of the directions of motion. The primes on the \( \nu \)'s indicate that to obtain the three true normal vibrations these three motions enclosed in the square brackets must be compounded with proportions determined by the force constants.

Many of the simpler structures listed in Tables I–VII have been previously studied, and although it is impracticable to give all the references it is hoped that those listed will enable the others to be found.

I am very much indebted to Professor Linus Pauling for many valuable suggestions in connection with this paper.

**Table I. Molecules with three atoms.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>I</th>
<th>II</th>
<th>( p_1 )</th>
<th>( p_2 )</th>
<th>R</th>
<th>L.R.</th>
<th>Irreducible representations</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2a</td>
<td>Symmetrical collinear</td>
<td>Dab</td>
<td>L</td>
<td>2</td>
<td>1</td>
<td>1(0)</td>
<td>2</td>
<td>( A_{1g}, A_{2g}, E_{1g}(2) )</td>
</tr>
<tr>
<td>2.2b</td>
<td>Symmetrical bent</td>
<td>Cev</td>
<td>A</td>
<td>3</td>
<td>1</td>
<td>3(0)</td>
<td>3</td>
<td>( A_{1g}, A_{2g}, E_{1g}(2) )</td>
</tr>
<tr>
<td>2.11a</td>
<td>Unsymmetrical collinear</td>
<td>Cnv</td>
<td>L</td>
<td>2</td>
<td>1</td>
<td>3(0)</td>
<td>3</td>
<td>( A_{1g}, A_{2g}, E_{1g}(2) )</td>
</tr>
<tr>
<td>2.11b</td>
<td>Unsymmetrical bent</td>
<td>Cuv</td>
<td>A</td>
<td>3</td>
<td>1</td>
<td>3(0)</td>
<td>3</td>
<td>( A_{1g}, A_{2g}, E_{1g}(2) )</td>
</tr>
</tbody>
</table>

**Molecules with Three Atoms**

| 2.2a  | Symmetrical collinear       | B : oow, (oow. CO\(_2\), \( 1^{10} \) CS\(_2\), \( 1^{12} \) Normal coordinates. | \( 1^{10} \) Normal coordinates. |
|       |                             |     |     |           |           |        |                       |                                                  |
| 2.2b  | Symmetrical bent            |     |     |           |           |        |                       |                                                  |

9 W. Nowacki, Zeits. f. Kristallographie (A) 86, 19 (1933).
12 G. Placzek, reference 6, p. 88.
Molecules with Four Atoms

3.3a. Plane equilateral triangle. B : (ovo) $\left(\frac{1}{2}\sqrt{3}v, -\frac{1}{2}v, o\right)\left(-\frac{1}{2}\sqrt{3}v, -\frac{1}{2}v, o\right)$. \(\text{CO}_2\). Normal coordinates.\(^{17, 18}\)

3.3b. Regular pyramid. B : (o, v, w) $\left(\frac{1}{2}\sqrt{3}v, -\frac{1}{2}v, w\right)\left(-\frac{1}{2}\sqrt{3}v, -\frac{1}{2}v, w\right)$. \(\text{NH}_3\), \(\text{AsCl}_3\).\(^{17, 20}\) Normal coordinates.\(^{17}\)

3.3b1. Linear. B : uow, B' : uow'. \(\text{PCl}_3\), \(\text{AsF}_3\), etc.\(^{21}\) Normal coordinates.\(^{17}\)

3.21a. Plane isosceles triangle. B : uov, vwo. \(\text{TeCl}_3\).\(^{17, 22}\)

3.21b. Plane scalene triangle. B : uov. \(\text{CH}_3\text{Cl}\), \(\text{CH}_3\text{Br}\) etc.\(^{23}\)

Molecules with Five Atoms

4.4a. Regular tetrahedron. B : www, wwww, wwww. \(\text{CCl}_4\), \(\text{CBr}_4\), \(\text{SiCl}_4\) etc. Normal coordinates.\(^{25, 26}\)

4.4b. Plane square. B : woo, owo, wwo, oww. \(\text{PtCl}_4\), \(\text{PdCl}_4\).\(^{27}\)

4.4c. Pyramid with square base. B : wov, oww, wov, oww. \(\text{SCl}_4\), \(\text{TeCl}_4\). Normal coordinates.\(^{27}\)

4.4d. Tetragonal sphenoid. B : wwww, wwwv, wwwv, wwwv.\(^{28}\)

4.4e. Plane rectangle. B : uvo, uvo, uvo.\(^{29}\)

4.4f. Orthorhombic sphenoid. B : uww, uww, uww, uww.\(^{30}\)

4.4g. Pyramid with rectangular base. B : uww, uww, uww, uww.\(^{31}\)

4.31. Trigonal pyramid.

4.4f. Orthorhombic sphenoid.

4.4g. Pyramid with rectangular base.

\(\text{H}_2\text{CO}\).\(^{32}\) Approximate normal coordinates.\(^{22, 23}\)

4.31a. Plane scalene triangle. B : uov. B' : uov'. \(\text{H}_2\text{H}_2\text{CO}\).

4.31c. Pyramid with scalene base. B : uow. B' : u'v'w'. \(\text{u'}\text{v'}\text{w'}\).
4.22a. Linear. B : oow, oow'. B' : oow', oow'.
CH₂O₂.²⁹
If the two B' atoms are placed above A with 2B below, this structure is a distorted tetrahedron. CH₂Cl₂, 30 CF₂Cl₂.³¹
4.22f. Pyramid with trapezoidal base. B : uvw, ñvw. B' : u'v'w', ñ'v'w'.
4.22g. Monoclinic sphenoid. B : uvw, ñvw. B' : u'w', ñ'w'. If B and B' are on same side of A this is a pyramid with a parallelogram for a base.
CH₂CO.

TABLE IV. Molecules with six atoms.

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>I</th>
<th>II</th>
<th>R</th>
<th>I.R.</th>
<th>Irreducible representations</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5a</td>
<td>Plane pentagon.</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>3(2)</td>
</tr>
<tr>
<td>5.5b</td>
<td>Pentagonal pyramid.</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>7(5)</td>
</tr>
<tr>
<td>5.5c</td>
<td>Square pyramid.</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>9(6)</td>
</tr>
<tr>
<td>5.5d</td>
<td>Rectangular pyramid.</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>12(8)</td>
</tr>
<tr>
<td>5.5e</td>
<td>Trigonal bipyramid.</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>6(4)</td>
</tr>
<tr>
<td>5.5f</td>
<td>Plane.</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>8(4)</td>
</tr>
<tr>
<td>5.5g</td>
<td>Triangular bipyramid.</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>12(7)</td>
</tr>
<tr>
<td>5.5h</td>
<td>Trapezoidal pyramid.</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>12(7)</td>
</tr>
<tr>
<td>5.5i</td>
<td>General (R+L).</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>12(6)</td>
</tr>
<tr>
<td>5.5j</td>
<td>Linear.</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>12(3)</td>
</tr>
<tr>
<td>5.5k</td>
<td>General</td>
<td>Da₅</td>
<td>S</td>
<td>2</td>
<td>5</td>
<td>12(0)</td>
</tr>
</tbody>
</table>

5.5a. Plane pentagon. B : (o, v, o)(av, bv, o)(cv, -dv, o)(cv, -dv, o)(-av, bv, o). Here a = sin 72°, b = cos 72°, c = sin 36°, d = cos 36°.
5.5b. Pentagonal pyramid. B : (o, v, w)(av, bv, w)(cv, -dv, w)(-cv, -dv, w)(-av, bv, w).
5.41a. Square pyramid. B : uow, ñow, ñow, ñow. B' : oow'. PF₅Cl₂. Modes of vibration, Fig. 1. Bracketed motions must be combined to give true modes.
5.32a. Trigonal bipyramid. B : (o, v, o)(½3v, -½v, o)(-½3v, -½v, o). B' : (oow')(oow'). PF₃Cl₂. Modes of vibration, Fig. 2. Bracketed motions must be combined to give true modes.
5.31a. Polar trigonal bipyramid. B : oow', oow'. B'' : (oow''). PF₃Cl₂, CH₃CN.

**Molecules with Six Atoms**

**Fig. 1.** Modes of vibration of 5.41a, square pyramid. Bracketed motions must be combined to give true modes.

**Fig. 2.** Modes of vibration of 5.32a, trigonal bipyramid. Bracketed motions must be combined to give true modes.
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B'' : oow''

B' : ov'w' , ûv'w'. B'' : oow''

5.221c. Trapezoidal pyramid. B : uuv, uuv.
B' : u'v'w' , u'v'w'. B'' : u'v'w''.

5.221d. B : uuv, ûuw. B' : u'v'w' , ûv'w'.

Table V. Molecules with seven atoms.

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>I</th>
<th>II</th>
<th>p1</th>
<th>p2</th>
<th>p3</th>
<th>R</th>
<th>I.R.</th>
<th>Irreducible representations</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.6a</td>
<td>Regular octahedron</td>
<td>D6h</td>
<td>Sp</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>5(3)</td>
<td>2</td>
<td>18 , 0, 1, 1, 2, 2, 0 ; 0, 0, 0, 1, 2, 2, 3, 3, 3, 3</td>
</tr>
<tr>
<td>6.6b</td>
<td>Regular octahedron</td>
<td>D6h</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>3(1)</td>
<td>6</td>
<td>18 , 0, 0, 1, 2, 2, 0 ; 0, 0, 1, 1, 2, 2</td>
</tr>
<tr>
<td>6.6c</td>
<td>Hexagonal pyramid</td>
<td>D6h</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>(7,5)</td>
<td>4(2)</td>
<td>2</td>
<td>281, 0, 0, 2, 1, 2, 2, 3, 3, 3, 3</td>
</tr>
<tr>
<td>6.6d</td>
<td>Trigonal prism</td>
<td>D3d</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>7(5)</td>
<td>4(2)</td>
<td>2</td>
<td>281, 0, 0, 2, 1, 2, 2, 3, 3, 3, 3</td>
</tr>
<tr>
<td>6.6e</td>
<td>Trigonal prism</td>
<td>D3d</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>7(5)</td>
<td>1(1)</td>
<td>2</td>
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<tr>
<td>6.6f</td>
<td>Trigonal prism</td>
<td>D3d</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>7(5)</td>
<td>1(1)</td>
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<tr>
<td>6.6g</td>
<td>Twisted trigonal prism</td>
<td>D3d</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>(4,2)</td>
<td>5(2)</td>
<td>5</td>
<td>281, 0, 0, 2, 1, 2, 2, 3, 3, 3, 3</td>
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<tr>
<td>6.6h</td>
<td>Twisted trigonal prism</td>
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<td>(4,2)</td>
<td>5(2)</td>
<td>5</td>
<td>281, 0, 0, 2, 1, 2, 2, 3, 3, 3, 3</td>
</tr>
<tr>
<td>6.6i</td>
<td>Twisted trigonal prism</td>
<td>D3d</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>(4,2)</td>
<td>5(2)</td>
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<td>5(2)</td>
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<tr>
<td>6.6k</td>
<td>General</td>
<td>D3d</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>(4,2)</td>
<td>5(2)</td>
<td>5</td>
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<td>S</td>
<td>5</td>
<td>5</td>
<td>(4,2)</td>
<td>5(2)</td>
<td>5</td>
<td>281, 0, 0, 2, 1, 2, 2, 3, 3, 3, 3</td>
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<tr>
<td>6.6m</td>
<td>General</td>
<td>D3d</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>(4,2)</td>
<td>5(2)</td>
<td>5</td>
<td>281, 0, 0, 2, 1, 2, 2, 3, 3, 3, 3</td>
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<tr>
<td>6.6n</td>
<td>General</td>
<td>D3d</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>(4,2)</td>
<td>5(2)</td>
<td>5</td>
<td>281, 0, 0, 2, 1, 2, 2, 3, 3, 3, 3</td>
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<tr>
<td>6.6o</td>
<td>General</td>
<td>D3d</td>
<td>S</td>
<td>5</td>
<td>5</td>
<td>(4,2)</td>
<td>5(2)</td>
<td>5</td>
<td>281, 0, 0, 2, 1, 2, 2, 3, 3, 3, 3</td>
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<td>6.6p</td>
<td>General</td>
<td>D3d</td>
<td>S</td>
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<td>S</td>
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<td>S</td>
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<td>5(2)</td>
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<td>S</td>
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<td>5</td>
<td>(4,2)</td>
<td>5(2)</td>
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<td>S</td>
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<td>5(2)</td>
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<td>S</td>
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<td>5(2)</td>
<td>5</td>
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</tr>
<tr>
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<td>S</td>
<td>5</td>
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<td>(4,2)</td>
<td>5(2)</td>
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<td>S</td>
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<td>5</td>
<td>(4,2)</td>
<td>5(2)</td>
<td>5</td>
<td>281, 0, 0, 2, 1, 2, 2, 3, 3, 3, 3</td>
</tr>
</tbody>
</table>

Molecules with Seven Atoms

6.6a. Regular octahedron. B : uoo, ûoo, ouo, oou, ouo, ouo. SF6, SF6, SF6, SF6. Modes of vibration, Fig. 3. Normal frequencies.

6.6b. Regular octahedron. B : (o, v, o)(1/3√3v, 1/3v, o)(1/3√3v, 1/3v, o)(1/3√3v, 1/3v, o)(1/3√3v, 1/3v, o).

6.6c. Hexagonal pyramid. B : (owv)(1/3√3v, 1/3v, w)(1/3√3v, 1/3v, w, o, o, v, w)(1/3√3v, 1/3v, w, o, o, v, w, w)(1/3√3v, 1/3v, w, o, o, v, w).

6.6d. Trigonal prism. B : (o, v, w)(1/3√3v, 1/3v, w)(1/3√3v, 1/3v, w, w)(1/3√3v, 1/3v, w, w, o, o, v, w, w)(1/3√3v, 1/3v, w, w, o, o, v, w, w).

6.6e. Trigonal prism. B : (u, v, o)(u, v, o)(1/3√3v + 1/3u, 1/3v + 1/3u, o)(1/3√3v + 1/3u, 1/3v + 1/3u, o).

Fig. 3. Modes of vibration of 6.6a, regular octahedron.
6.6g. Twisted trigonal prism. \( \mathbf{B} : (u, v, w)(uv, w)(\sqrt{3}v + 3w, \pm \sqrt{3}v, w)(\sqrt{3}v - 3u, -\sqrt{3}v - 3w, w) \). 
6.6h. Trigonal hexagonal pyramid. \( \mathbf{B} : (u, v, w)(u, v, w)(\sqrt{3}v + 3u, -\sqrt{3}v - 3w, w)(\sqrt{3}v - 3u, -\sqrt{3}v - 3w, w) \).
6.51a. Pentagonal pyramid. \( \mathbf{B} : (o, v, w)(av, bv, w)(-cv, -dv, w)(-av, bv, w) \).

3.222a. Linear. \( \mathbf{B} : ooo, oow. \mathbf{B}': oow', oow'. \)
3.222b. Orthorhombic octahedron. \( \mathbf{B} : uoo, uoo. \mathbf{B}': o'v'o, oo'o. \mathbf{B}'' : oow', oow'. \)
3.222c. Trapezoidal bipyramid. \( \mathbf{B} : uow, oow. \mathbf{B}': u'ow', uu'w'. \mathbf{B}'' : oow', oow'. \)
3.222d. Plane. \( \mathbf{B} : uv, uvo. \mathbf{B}': u'v'o, uu'o. \mathbf{B}'' : u'v'o, uu'o. \)
3.222e. Monoclinic octahedron. \( \mathbf{B} : uoo, uoo. \mathbf{B}': u'oo', u'oo'. \mathbf{B}'' : oow', oow'. \)
3.222f. Triangular prism. \( \mathbf{B} : uvw, uvw. \mathbf{B}': u''v'w', uu'w'. \mathbf{B}'' : u'v'w', u'v'w'. \)
3.222g. Monoclinic octahedron. \( \mathbf{B} : uvw, uvw. \mathbf{B}': u''v'w', uu'w'. \mathbf{B}'' : u'v'w', u'v'w'. \)
3.222h. Triclinic octahedron. \( \mathbf{B} : uvw, uvw. \mathbf{B}': u''v'w', uu'w'. \mathbf{B}'' : u'v'w', u'v'w'. \)
3.2211. Orthorhombic octahedron. \( \mathbf{B} : uow, oow. \mathbf{B}': oow', oow'. \mathbf{B}'' : oow', oow'. \)
3.2211b. Heptahedron. \( \mathbf{B} : uvw, uvw. \mathbf{B}': u''v'w', uu'w'. \mathbf{B}'' : u'v'w', u'v'w'. \)
3.2211c. Monoclinic octahedron. \( \mathbf{B} : uvw, uvw. \mathbf{B}': u''v'w', uu'w'. \mathbf{B}'' : u'v'w', u'v'w'. \)
3.22111a. Linear. \( \mathbf{B}^{(i)} : oo'o. \mathbf{B}^{(ii)} : oow'. \mathbf{B}^{(iii)} : uow'. \mathbf{B}^{(iv)} : uow'. \)
3.22111b. Plane. \( \mathbf{B}^{(i)} : uow'. \mathbf{B}^{(ii)} : uow'. \mathbf{B}^{(iii)} : oow'. \mathbf{B}^{(iv)} : oow'. \)

**Table VI. Molecules with eight atoms.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>I</th>
<th>H</th>
<th>( p_i )</th>
<th>( p_2 )</th>
<th>R</th>
<th>I.R.</th>
<th>Irreducible representations</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.7a</td>
<td>Plane heptagon</td>
<td>D_{7h}</td>
<td>S</td>
<td>2</td>
<td>8</td>
<td>(2)</td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>7.7b</td>
<td>Heptagonal pyramid</td>
<td>D_{7h}</td>
<td>S</td>
<td>2</td>
<td>8</td>
<td>(5)</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td>7.52a</td>
<td>Pentagonal bipyramid</td>
<td>D_{5h}</td>
<td>S</td>
<td>4</td>
<td>6</td>
<td>(1)</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td>7.33a</td>
<td>Truncated trigonal bipyramid</td>
<td>C_{4v}</td>
<td>S</td>
<td>6</td>
<td>11(6)</td>
<td>(11)</td>
<td>(5)</td>
<td></td>
</tr>
</tbody>
</table>

**Molecules with Eight Atoms**

Only the type AB_7 is treated completely; the other structures listed were chosen because they seem the most probable physically. \( \mathbf{D}_7 \) presumably belongs to one of the classes below.

**7.7a. Plane heptagon.** \( \mathbf{B} : (o, v, w)(h, k, o)(jv, k, o)(ev, f, o)(-ev, f, o)(-jv, k, o)(-g, h, o). \)

**7.7b. Heptagonal pyramid.** \( \mathbf{B} : (o, v, w)(g, h, o)(j, k, o)(-g, h, o). \)
NORMAL VIBRATIONS OF POLYATOMIC MOLECULES

w)(jv, kv, w)(ev, fv, w)(-ev, kv, w)(-gv, hv, w). g, h, j, k, e, f as in 7.7a.

B' : (ooov')(ooov').

7.33a, b. B : (o, v, w)(\(\frac{1}{2}\sqrt{3}v\), -\(\frac{1}{2}\sqrt{3}v\), w)(-\(\frac{1}{2}\sqrt{3}v\), -\(\frac{1}{2}\sqrt{3}v\), w).
B' : (o, v', w')(\(\frac{1}{2}\sqrt{3}v'\), -\(\frac{1}{2}\sqrt{3}v'\), w')
(-\(\frac{1}{2}\sqrt{3}v'\), -\(\frac{1}{2}\sqrt{3}v'\), w'). B'' : oow''.


TABLE VII. Molecules with nine atoms.

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>I</th>
<th>II</th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>R</th>
<th>I.R.</th>
<th>Irreducible representations</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.8a</td>
<td>Cube</td>
<td>Oh</td>
<td>Sp</td>
<td>2</td>
<td>2</td>
<td>4(3)</td>
<td>2</td>
<td>1(\Gamma_0), 1(\Gamma_1), 2(\Gamma_2), 0; 0, 1, 1, 1, 1, 2, 2, 2.</td>
</tr>
<tr>
<td>8.8b</td>
<td>Plane octagon</td>
<td>D4h</td>
<td>S</td>
<td>5</td>
<td>8</td>
<td>7(5)</td>
<td>4(2)</td>
<td>2(\Gamma_0), 0, 1, 1, 1, 2, 2, 3, 3, 3, 3.</td>
</tr>
<tr>
<td>8.8c</td>
<td>Octahedral pyramid</td>
<td>C2v</td>
<td>S</td>
<td>5</td>
<td>8</td>
<td>7(5)</td>
<td>5(2)</td>
<td>2(\Gamma_0), 1, 1, 1, 1, 2, 2, 3, 3.</td>
</tr>
<tr>
<td>8.8d</td>
<td>Archimedian anti-prism</td>
<td>D4h</td>
<td>S</td>
<td>11</td>
<td>5</td>
<td>7(5)</td>
<td>5(1)</td>
<td>2(\Gamma_0), 1, 1, 1, 1, 2, 2, 3, 3.</td>
</tr>
<tr>
<td>8.8e</td>
<td>Plane tetragonal octagon</td>
<td>D4h</td>
<td>S</td>
<td>11</td>
<td>5</td>
<td>7(5)</td>
<td>5(2)</td>
<td>2(\Gamma_0), 1, 1, 1, 1, 2, 2, 3, 3.</td>
</tr>
<tr>
<td>8.8f</td>
<td>Tetragonal parallelopiped</td>
<td>D4h</td>
<td>S</td>
<td>11</td>
<td>5</td>
<td>7(5)</td>
<td>5(1)</td>
<td>2(\Gamma_0), 1, 1, 1, 1, 2, 2, 3, 3.</td>
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<tr>
<td>8.8g</td>
<td>Twisted cube</td>
<td>C4v</td>
<td>S</td>
<td>11</td>
<td>5</td>
<td>14(11)</td>
<td>7(2)</td>
<td>2(\Gamma_0), 2, 2, 2, 2, 3, 3, 3, 3.</td>
</tr>
<tr>
<td>8.8h</td>
<td>Tetragonal pyramid</td>
<td>C2v</td>
<td>S</td>
<td>11</td>
<td>5</td>
<td>14(11)</td>
<td>7(2)</td>
<td>2(\Gamma_0), 2, 2, 2, 2, 3, 3, 3, 3.</td>
</tr>
<tr>
<td>8.8i</td>
<td>Twisted tetragonal parallelopiped</td>
<td>V4</td>
<td>S</td>
<td>11</td>
<td>5</td>
<td>14(11)</td>
<td>7(2)</td>
<td>2(\Gamma_0), 2, 2, 2, 2, 3, 3, 3, 3.</td>
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<td>8.8j</td>
<td>Rectangular parallelopiped</td>
<td>V4</td>
<td>A</td>
<td>21</td>
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<td>9(6)</td>
<td>9</td>
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</tr>
</tbody>
</table>

Molecules with Nine Atoms

Only the type AB\(_3\) is considered. OsF\(_3\)\(^{33}\) is said to belong to 8.8a or 8.8d.


8.8b. Plane octagon. B : (o, v, o)(mv, mv, o)(v, o, o)(mv, -mv, o)(v, o, o)(mv, -mv, o)(v, o, o)(mv, -mv, o). m = \(\frac{1}{2}\sqrt{2}\).

8.8c. Octahedral pyramid. B : (o, v, w)(mv, mv, w)(v, o, w)(mv, -mv, w)(o, v, w)(-mv, -mv, w). m = \(\frac{1}{2}\sqrt{2}\).

8.8d. Archimedian anti-prism. B : (uuw)(uuw)(pu, o, w)(o, pü, w)(pü, o, w)(o, pu, w). p = \(\sqrt{2}\).

8.8e. Plane tetragonal octagon. B : uvo, ūvo, ūvo, ūvo, ūvo, ūvo, ūvo, ūvo, ūvo.


8.8g. Twisted cube. B : uvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw.

8.8h. Tetragonal octagonal pyramid. B : uvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw.

8.8i. Twisted tetragonal parallelopiped. B : uvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw.

8.8j. Rectangular parallelopiped. B : uvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw, ūvw.

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\(^{33}\)H. Braune and S. Knöke, Naturwiss. 21, 349 (1933).