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Additional information on J. Chem. Phys.

Motions of Molecules in Condensed Systems: I. Selection Rules, Relative Intensities, and Orientation Effects for Raman and Infra-Red Spectra

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(Received August 30, 1945)

A method is described that permits deduction of selection rules for Raman and infra-red spectra of crystals from a knowledge of just the space group designation and the population of the unit cell. When implemented by an appendix to this article showing, in a convenient arrangement, the distribution of point symmetries within space groups the method can be applied by a user familiar with point group manipulation but having no special knowledge of space groups. There are no selection rules operating in the liquid state. Some tentative qualitative conclusions are drawn concerning the relative intensities of certain kinds of components appearing in spectra of condensed systems. Sharpened selection rules are expected, and have been observed by others, to operate for single crystals containing non-rotating molecules when these are given special orientations in the light path. These special orientations and the appropriate selection rules can be predicted from information mentioned above along with inspection of the external form of a crystal. All procedures have a desirable advantage of simplicity over prior ones directed toward the same ends.

INTRODUCTION

DETAILED studies, both experimental and theoretical, of the motions of isolated molecules have yielded a vast dividend of valuable accurate information about gaseous substances. This information not only has immediate physical significance but also, when combined with powerful tools of statistical mechanics, contains many chemical implications. The store of substances which may be regarded conveniently as vapors is becoming rapidly exhausted while generally reliable procedures for dealing similarly with substances in condensed states remain to be developed. Theoretical problems which must be overcome in this connection are severely complicated and are not likely to be solved without the aid of simplifying idealizations. The possibilities in this direction are numerous while an intelligent assessment of their merits is hampered by an insufficiency of experimental information in several categories, especially concerning the details of molecular motions in condensed systems.

The most direct experimental route to knowledge of molecular motions in any situation is through the spectra they produce. The interpretation of spectra demands certain concomitant theoretical machinery. This communication will be devoted to the development of some principles appropriate for condensed phases, that will be applied subsequently in separate reports to the interpretation of experimental investigations.

SELECTION RULES FOR CRYSTALS

Well-known procedures[1] permit the deduction of selection rules for vibration-rotation spectra of isolated symmetric molecules. To review them briefly, the mutual potential energy of a collection of interacting atoms will reflect the symmetry of their equilibrium configuration. This symmetry can be described by means of a *group* of physical operations. The term *group* is used here in a specialized mathematical sense and implies many consequences that follow logically from the restrictive definition. For instance, associated with the group is a set of irreducible representations which may be visualized as non-equivalent examples of the given symmetry. These are limited in number and have the property that all other examples of the same symmetry can be constructed from combinations of the irreducible ones. Thus, the potential energy of a distribution of interacting points can be analyzed into a sum of independent contributions. Each contribution is associated with some one of the irreducible representations of the group describing the symmetry of the equilibrium con-

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[1] For details see J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys. **8**, 317 (1936); L. Tisza, Zeits. f. Physik **82**, 48 (1933).

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figuration. Each contribution to the analyzed potential energy determines a set of fundamental modes of motion. The totality of fundamental modes is the composite sum extended over all irreducible representations. Finally, the collection of points in motion will possess a transitory electric moment and a transitory polarizability. These properties furnish two mechanisms for exchange of energy with a radiation field and so give rise to infra-red and Raman spectra, respectively. These properties also reflect the symmetry of the equilibrium configuration and therefore can be analyzed into components associated with the irreducible representations. Only those modes of motion will be concerned in the corresponding spectra that appear in irreducible representations along with components of the transitory electric moment or transitory polarizability. Selection rules deduced in this way from the symmetry of an isolated molecular configuration find application in the analysis of spectra of dilute vapors where the condition of isolation is achieved. However, they are inappropriate for the analysis of spectra of condensed phases.

It is evident from the foregoing discussion that selection rules can be deduced in the same way for any situation where it is possible to specify and analyze the symmetry of a suitable configuration of interacting points. Recognizing this opportunity, Bhagavantam and Venkatarayudu[2] have taken the lead in developing methods to permit deduction of selection rules for molecular crystals. They propose that all of the spectroscopically important *frequencies* can be discovered and classified by examination of the isolated crystallographic unit cell. This proposal is almost certainly correct, not only for the reasons advanced by its authors but also in the light of experimental findings. The unit cell is then regarded as an example of the **space group** appropriate for the crystal lattice; a point is deemed invariant under any operation that carries it either into itself or into the identical point in another unit cell but not so under an operation that carries it into an equivalent point in its own or another unit cell. The logic of this last convention, considered in relation to the potential energy of the complete crystal, is not altogether satisfactory under close scrutiny.

This theoretical machinery for crystals has been tested against a number of experimental cases.[2,3] In practice it is found that the method introduces and emphasizes distinctions that are without meaning in relation to available experimental techniques. The results require further assessment and interpretation on this account so that the method is often cumbersome and sometimes even tedious to apply. The rhombic modification of crystalline sulfur furnishes an extreme example. The unit cell contains 16 molecules of S_8 and exhibits 384 distinct modes of motion whereas the Raman spectrum consists of only 10 lines.[4] This discrepancy is not the result of exceedingly strict selection rules but instead is caused by the circumstance that the 384 modes can be collected into sets such that the theoretically distinguishable frequencies in any one set are indistinguishable in practice. In a molecular crystal it is convenient to consider separately two types of motions: (1) lattice modes, which are approximately the motions of rigid molecules and (2) molecular modes, which are approximately the distortions of molecules whose centers of mass and principal axes of inertia are at rest. For sulfur, 288 molecular modes are distributed among 14 sets, each set having a representative frequency not sensibly different from one of the 14 fundamental frequencies of an isolated S_8 molecule. The members of a given set correspond to different ways of coupling the motions of 16 molecules when all are moving with the same frequency. In principle the coupling will yield 16 new frequencies but in practice the distinctions are not apparent. Similar considerations apply to lattice modes although in this category the opportunities should be better for practical resolution of the distinctions. Even so, in the example under discussion, only 2 somewhat broadened lines can be attributed to 48 modes arising out of restricted rotation of molecules contained in the unit cell. The lattice modes of translatory origin have low frequencies along with low intensities and so are not likely to be observed. In general the organization of modes

[2] S. Bhagavantam and T. Venkatarayudu, Proc. Ind. Acad. Sci. **9A**, 224 (1939); S. Bhagavantam, Proc. Ind. Acad. Sci. **13A**, 543 (1941).

[3] See review by G. Glockler: Rev. Mod. Phys. **15**, 111 (1943).

[4] R. Norris, Proc. Ind. Acad. Sci. **13A**, 291 (1941).

into sets can be accomplished more or less readily; when this has been done it still remains to examine the different selection rules for the members of a set in order to arrive at a representative selection rule for the common frequency. In summary it may be said that this ingenious procedure leaves something to be desired, both logically and practically speaking.

This writer prefers to employ another plan of attack. The idealization adopted is the one so strongly implied in experimental findings; i.e., to treat the motions of one molecule moving in a potential field reflecting the symmetry of the surrounding crystal. This permits the use of *point* symmetry rather than **space** symmetry and attributes a more logical quality of invariance to the potential energy of the complete crystal under the appropriate symmetry operations. The treatment yields at once a suitable number of *frequencies* with appropriate selection rules. Of course, the corresponding motions are fictitious in principle but so are those attributed by the other procedure to an isolated unit cell. If one is forced to adopt an idealization there is little to be gained by making it unduly elaborate. Furthermore, there is good reason to believe that the picture of molecular modes derived from examination of one molecule may be more accurate than the one derived from examination of the unit cell; coupling between molecular motions in different molecules is extremely weak, *ex post facto*.

A prerequisite to the treatment of any molecular crystal is a suitable knowledge of the crystal structure. This is provided by a detailed pattern of the unit cell, when one is available, but most often when found in convenient summaries consists merely of the **space group** designation along with the number of molecules per unit cell. It is highly expedient to have theoretical machinery designed to manufacture the desired results from the latter form of raw materials since these are so comparatively easy to procure. Such a formalism can be developed to operate in the great majority, if not all cases. If it is found to fail occasionally, the shortcoming will be apparent at once and resort can then be had to the information contained in a detailed pattern of the unit cell.

In order to make clear the basis for the formalism it is convenient to recall at this time a few well-founded principles of crystallography.[5] Crystals can be assigned, on the basis of their external symmetries, among 32 classes, each class being identified with a collection of symmetry elements and a unique *point group* of operations concerned with them. Each *point group* generates a characteristic number of **space groups**, descriptive of the internal crystal structure, when its operations are combined in various numbers and various ways with the primitive translations that carry one lattice point into another. An arbitrarily chosen point in the crystal is a member of a set of equivalent points, all contained within the same unit cell. The set can be generated by applying in turn the operations of the **space group** to the chosen point. In general, the number of equivalent points per set is equal to the number of operations in the **space group**. However, if a point is situated on one of the symmetry elements and if the operations of the **space group** concerned with that element are not composite translations, then the point remains invariant under these operations. Consequently, such a point belongs to a set having population less than the number of operations in the **space group**. Although usually called otherwise, such a point will be designated henceforth as a *site*. In general, a unit cell exhibits several different kinds of sites and sometimes several distinct sets of the same kind. As a further consequence of its definition a site is necessarily the affix for a point group, the *site group*, which is a sub-group of the **space group**. Thus, an infinite crystal (the limit is always appropriate in practice) has the point symmetry of a *site group* about each and every site.

The center of mass of a molecule is invariant under the operations of the associated *molecular group* and its equilibrium position in the crystal will be called the *affix* of this group. It is a well-substantiated rule[5] of crystallography that the affixes of symmetrical molecules are usually situated on sites. In order that this be so it is necessary that the *site group* be a sub-group of the *molecular group*. Thus, the complete potential energy of a crystal when considered from the affix

[5] For detailed development see R. W. G. Wyckoff, *The Analytical Expression of the Results of the Theory of Space Groups* (Carnegie Institution of Washington, 1930), second edition.

of any of its constituent molecules always has the symmetry of the appropriate *site group*. When the site group has been identified the selection rules can be deduced in the usual way for its irreducible representations. Furthermore, since the occupant of the site is a valid example of its symmetry the motions of one molecule can be assigned to the irreducible representations without regard for the motions of the rest of the crystal. Since this procedure accounts for a suitable number of *frequencies* no further elaboration is required. Of course, one retains the reservation that each motion of the one molecule is coupled to some degree with the motions of the rest of the crystal that are associated with the same irreducible representation of the *site group*. The relation between motions of an isolated molecule and those of one in the crystal can be established readily by comparing character tables for the *molecular group* and the *site group*.

The deduction of selection rules for a molecular crystal can be accomplished as outlined above, whenever the *site groups* have been identified. An acceptable *site group* must be a sub-group of both the **space group** and the *molecular group*. When the latter two groups are compared only a few common sub-groups will emerge and sometimes only one. In the latter case the choice is unequivocal and the *site group* is unambiguously identified. When more than one acceptable *site group* emerges, a further elimination is possible on the basis of the number of molecules contained in the unit cell. The molecular affixes must occupy a complete set of sites and the number per set varies with the order of the *site group*. When applying this criterion it is necessary to take into account the possible multiplicity of identical sets of sites, for several such sets may be in use. In most cases the foregoing considerations will suffice, but ambiguous situations are possible. These arise infrequently; when they do it is perhaps safest to refer to a map of the unit cell. In order to employ the easy procedure indicated in this paragraph it is necessary to have at hand a tabulation of the *site groups* contained in each **space group**, the numbers of equivalent sites per set, and the multiplicities of sets. This information can always be found in works on crystallography, but not arranged conveniently for the present purpose. Therefore, in order to implement

the procedure to the fullest possible extent, the requisite material has been compiled in a convenient form and appears as an appendix to this article.

An analysis of the spectra of calcite and aragonite will be undertaken now as an illustration of the procedure. Calcite is a representation of the **space group** D_{3d}^6 with two molecules per unit cell. Consultation of the appendix shows that this population can be accommodated only on *site groups* D_3 and C_{3i}. The first is a sub-group of the *molecular group* D_{3h} for carbonate ion whereas the second is not. On the other hand the second is suited to the point symmetry of calcium ion. Hence carbonate ion is surely on site D_3 and calcium ion on site C_{3i}. Resorting next to the usual analysis of group characters[1] one finds that the three lattice modes of translatory origin associated with calcium ion are forbidden in the Raman spectrum but permitted in the infra-red spectrum. Similarly one finds that carbonate ion yields four molecular frequencies, one permitted only in the Raman spectrum, another permitted only in the infra-red spectrum, and two others permitted in both spectra. In addition it yields one lattice frequency of translatory origin and one of rotatory origin active in both spectra along with one frequency of each type active only in the infra-red spectrum. The conclusions concerning molecular frequencies are in complete harmony with experimental observations while the ones concerning lattice frequencies are not violated although fewer than the expected number of frequencies are observed.[2a] The contrasting conclusions for aragonite follow readily from the knowledge that this crystal is a representation of the **space group** V_h^{16} with four molecules per unit cell. Reference to the appendix places calcium ion on site C_i and carbonate ion on site C_s. The lattice modes attributable to calcium ion are once again forbidden in the Raman spectrum but permitted in the infra-red spectrum. However, six molecular frequencies are now permitted to appear in both spectra. The two extra frequencies arise from removal of a degeneracy prevailing in both the free carbonate ion and calcite; if the splitting is not resolved only four frequencies will be observed. The lattice modes attributable to carbonate ion are now six in number and are permitted to appear in both spectra. Once more,

these conclusions are in harmony with experimental data.[2] Essentially the same predictions can be made, but less conveniently, by the method employing **space groups**.

The only failure of the easy procedure, encountered thus far by the writer in the course of examination of a substantial number of crystals, occurs with rhombic sulfur. A representation of the **space group** V_h^{24}, the unit cell, contains sixteen molecules. Referring to the appendix one finds that this population can be accommodated equally well on two sets of eight sites each with symmetry V or on one set of sites with symmetry C_2. Further discussion will be omitted except to mention that the analysis now involves only 24 instead of 384 modes.

In general, the *site group* will be of lower order than the *molecular group* although this is not necessarily the case. When true, the selection rules for the crystal will be less strict than those for the isolated molecule with the result that the crystal will possess a richer spectrum than the vapor. For *site groups* C_2, C_s, and C_3, it can be said without further examination that no selection rules will operate.

An interesting aberration develops in the case of ammonium chloride. The ammonium ion occupies a site having point symmetry O_h which is of higher order than the *molecular group* T_d. From this circumstance one must infer that the ion interacts with the rest of the crystal as though it were a point, a view which is entirely consistent with the prevalent conception that the ion is able to rotate freely in this crystal. Special selection rules will apply.

LIQUIDS

Turning now to the other common condensed state, *there will be no selection rules operating in the liquid phase*. This conclusion follows at once from the conception of the liquid state as one of disorder. The short range order in a liquid does not connote symmetry. Convincing proof will be presented in a separate communication describing an experimental study of liquid and solid benzene. For the present, attention is directed toward the observation[6] that the infra-red spectrum of

pentaerythritol, $C(CH_2OH)_4$, in solution exhibits a characteristic absorption band in a certain neighborhood whereas a comparable amount of solid in the light path is transparent at the same place while exhibiting other regions of absorption in common with the solution. Molecules of pentaerythritol[7] occupy sites S_4 in the crystal. This group has four irreducible representations and one of them, totally symmetric, containing six frequencies is forbidden to contribute to the infra-red spectrum. The case does not afford unequivocal proof of the general absence of selection rules for liquids. It can be argued that hydrogen bonds stabilize a symmetrical form in the crystal whereas the molecule, isolated from others of its own kind, might exhibit several configurations of approximately equivalent energy and no net symmetry. This alternative seems unlikely when attention is given to the observation[8] that pentaerythritol halogenohydrins have point symmetry S_4 in the vapor phase.

RELATIVE INTENSITIES

Although selection rules forbid certain modes of motion from contributing to a given spectrum they do not guarantee that contributions from the others will always be observed. It is outside the scope of currently workable theory to predict quantitatively the relative intensities in different regions of a spectrum. Nevertheless, cogent arguments can be directed at some aspects of this problem for a substance which follows the dominant pattern of behavior. Certain modes of motion develop spectroscopic activity in a condensed phase but do not contribute to the spectrum of the vapor. The intensity of this newly acquired activity depends upon the degree of interaction between the molecule and its surroundings. In a similar manner, for those modes of motion that are permitted to contribute to both spectra, the intensities depend as well upon the interactions residing within the molecule. In any condensed system where it is legitimate to speak of a collection of molecules the latter class of interactions must be considerably stronger than the former one. Hence, the contribution to the spectrum of a condensed phase, by a mode that

[6] Private communication from Dr. Daniel Norman, New England Spectrochemical Laboratories, Medway, Massachusetts.

[7] F. J. Llewellyn, E. G. Cox, and T. H. Goodwin, J. Chem. Soc. 882 (1937).

[8] H. de Laszlo, Comptes rendus **198**, 2235 (1934).

is active in the spectrum of the isolated molecule, will certainly be more intense than the contribution from a mode that becomes active only after condensation. Thus, the customary practice seems quite legitimate whereby the most intense frequencies are selected from the spectrum of a liquid for assignment to fundamentals permitted by the selection rules for the isolated molecule. At the same time, the interactions causing condensation are substantial, and it is an established fact that new contributions of appreciable intensity do appear in the spectrum of the condensed phase. Furthermore, the interactions become more powerful in a crystal than in a liquid so that some general increase of intensity might be expected to accompany solidification. This increase, when observed, will be most noticeable for fundamentals that develop activity only after entering the condensed phase. Components of the spectrum permitted also in the vapor will exhibit merely a small increment in a basic level of intensity; combinations that develop only after entering the condensed phase will be comparatively weak so that the increase of intensity will not be striking; the newly developed fundamentals will have medium intensity and their growth will seem more spectacular. Lattice modes of rotatory origin can develop high intensities,[3,4] whereas those of translatory origin may be strong in the infra-red spectra of ionic crystals but are probably weak otherwise.

ORIENTATION EFFECTS

The selection rules deduced for crystals by procedures described here are sometimes susceptible to further refinement for special conditions of observation. In addition to the usual alterations of a Raman spectrum resulting from the use of polarized light there are entirely new possibilities that have no counterpart in spectra of fluids. When a fluid is irradiated, its randomly oriented molecules present all possible aspects to the radiation. Consequently, the electric vector of the light can enter all suitable irreducible representations of the molecules in the course of a sufficiently large number of molecular encounters. However, in a large single crystal all molecules not rotating freely have similar orientations so that a beam of parallel light encounters much the same aspect of all molecules in its path. In some

cases, depending upon the nature of the *site groups* involved, a direction of approach can be selected so that no component of the electric vector will appear in one of the suitable irreducible representations of sites that are occupied. Then, only two of the components of transitory electric moment and only three of the elements of transitory polarizability will be energized. For some *site groups* it is possible in addition to select a plane of polarization for the incident light so as to exclude its components at the same time from another irreducible representation. Then, only one component of the transitory electric moment and one element of the transitory polarizability will be energized. The correspondingly sharpened selection rules and the directions of approach and planes of polarization for which they operate can be deduced easily from inspection of the external form of the crystal (provided that it is not pseudomorphous) and knowledge of the *site groups* that are in use. The irreducible representations of a *site group* that can be penetrated by a vector representing the radiation field will be the ones containing components of the transitory electric moment. The orientations of these components relative to the elements of symmetry of the *site group* can be established by inspecting the table of group characters. However, the elements of symmetry contained in the *site group* must be identical with those contained in the *crystallographic point group* and hence they can be located relative to the faces of the crystal by inspecting its external form. To predict the effect produced in the Raman spectrum is likewise easy. Each element of polarizability is associated with two, not necessarily distinct components of the electric vector of the radiation field. When two irreducible representations, not necessarily distinct but each containing a component of the electric vector, are combined in a direct product[1] the resulting irreducible representation will contain the associated element of polarizability. If either of the components is absent for a particular orientation of the crystal then the associated element of polarizability will be inoperable. The manipulation of group characters required for this analysis is exactly the same one used to predict selection rules for combinations and overtones and would be undertaken in any event. The totally symmetric irreducible representation

of a *site group* will often contain the three diagonal elements of the polarizability tensor. Then this representation will contribute to the spectrum for all orientations of the single crystal. This persistence notwithstanding it is evident that relative intensities observed in spectra of single crystals will be highly sensitive to orientation. The validity of this conclusion is well established in fact.[3,4,9,10] The entire subject has received elaborate theoretical treatment.[3,11] It is interesting to note that a crystal containing freely rotating ions should not show the expected effects of orientation. This suggests a valuable tool for study of some second-order phase transitions.

FREQUENCY ASSIGNMENTS

Finally it will be remarked that the most fruitful approach, when feasible, to the identification of vibration frequencies for a symmetrical molecule will start with the spectra of the vapor, proceed to the spectra of the solid, and conclude with the spectra of the liquid. In favorable cases a complete assignment of frequencies can be made in this way without having any resort to data for isotopic molecules.

APPENDIX

Availabilities and Symmetries of Sites in the 230 Space Groups[5]

The standard symbol for the space group will be found below in boldface type. Following it are a series of symbols describing the various sites. The description for a site consists of the standard point group symbol preceded by the number of distinct sets of this kind and followed in parentheses by the number of equivalent sites per set. The numbers are appended only when they differ from unity. Thus, the entry $C_4^1: 2C_4, C_2(2)$ signifies that the space group C_4^1 contains 2 distinct sets of sites having point symmetry C_4 with one site per set and 1 set of sites having point symmetry C_2 with two equivalent sites per set. If the symbol for a space group is absent this means that it contains no sites.

$C_i^1: 8C_i$; $C_s^1: 2C_s$; $C_s^3: C_s(2)$; $C_2^1: 4C_2$; $C_2^3: 2C_2(2)$; $C_{2h}^1: 8C_{2h}, 4C_2(2), 2C_s(2)$; $C_{2h}^2: 4C_i(2), C_s(2)$;

[9] S. Bhagavantam, Proc. Ind. Acad. Sci. 11A, 62 (1940).
[10] R. B. Barnes, Phys. Rev. 39, 562 (1932).
[11] J. Cabannes, Comptes rendus 211, 625, 750 (1940).

$C_{2h}^3: 4C_{2h}(2), 2C_i(4), 2C_2(4), C_s(4)$; $C_{2h}^4: 4C_i(2), 2C_2(2)$; $C_{2h}^5: 4C_i(2)$; $C_{2h}^6: 4C_i(4), C_2(4)$; $C_{2v}^1: 4C_{2v}, 4C_s(2)$; $C_{2v}^2: 2C_s(2)$; $C_{2v}^3: 4C_2(2)$; $C_{2v}^4: 2C_2(2), C_s(2)$; $C_{2v}^6: 2C_2(2)$; $C_{2v}^7: C_s(2)$; $C_{2v}^8: 2C_2(2)$; $C_{2v}^{10}: 2C_2(2)$; $C_{2v}^{11}: 2C_{2v}(2), C_2(4), 2C_s(4)$; $C_{2v}^{12}: C_s(4)$; $C_{2v}^{13}: 3C_2(4)$; $C_{2v}^{14}: 2C_{2v}(2), 3C_s(4)$; $C_{2v}^{15}: 2C_2(4), C_s(4)$; $C_{2v}^{16}: C_2(4), C_s(4)$; $C_{2v}^{17}: C_2(4)$; $C_{2v}^{18}: C_{2v}(4), C_2(8), 2C_s(8)$; $C_{2v}^{19}: C_2(8)$; $C_{2v}^{20}: 2C_{2v}(2), 2C_s(4)$; $C_{2v}^{21}: 2C_2(4)$; $C_{2v}^{22}: C_2(4), C_s(4)$; $V^1: 8V, 12C_2(2)$; $V^2: 4C_2(2)$; $V^3: 2C_2(2)$; $V^5: 2C_2(4)$; $V^6: 4V(2), 7C_2(4)$; $V^7: 4V(4), 6C_2(8)$; $V^8: 4V(2), 6C_2(4)$; $V^9: 3C_2(4)$; $V_h^1: 8V_h, 12C_{2v}(2), 6C_s(4)$; $V_h^2: 4V(2), 2C_i(4), 6C_2(4)$; $V_h^3: 4C_{2h}(2), 4V(2), 8C_2(4), C_s(4)$; $V_h^4: 4V(2), 2C_i(4), 6C_2(4)$; $V_h^5: 4C_{2h}(2), 2C_{2v}(2), 2C_2(4), 3C_s(4)$; $V_h^6: 2C_i(4), 2C_2(4)$; $V_h^7: 4C_{2h}(2), 3C_2(4), C_s(4)$; $V_h^8: 2C_i(4), 3C_2(4)$; $V_h^9: 4C_{2h}(2), 2C_2(4), 2C_s(4)$; $V_h^{10}: 2C_i(4), 2C_2(4)$; $V_h^{11}: 2C_i(4), C_2(4), C_s(4)$; $V_h^{12}: 4C_{2h}(2), 2C_2(4), C_s(4)$; $V_h^{13}: 2C_{2v}(2), 2C_i(4), 2C_s(4)$; $V_h^{14}: 2C_i(4), C_2(4)$; $V_h^{15}: 2C_i(4)$; $V_h^{16}: 2C_i(4), C_s(4)$; $V_h^{17}: 2C_{2h}(4), C_{2v}(4), C_i(8), C_2(8), 2C_s(8)$; $V_h^{18}: 2C_{2h}(4), C_i(8), 2C_2(8), C_s(8)$; $V_h^{19}: 4V_h(2), 2C_{2h}(4), 6C_{2v}(4), C_2(8), 4C_s(8)$; $V_h^{20}: 2V(4), 4C_{2h}(4), 5C_2(8), C_s(8)$; $V_h^{21}: 2V(4), 4C_{2h}(4), C_{2v}(4), 5C_2(8), 2C_s(8)$; $V_h^{22}: 2V(4), 2C_i(8), 4C_2(8)$; $V_h^{23}: 2V_h(4), 3C_{2h}(8), V(8), 3C_{2v}(8), 3C_2(16), 3C_s(16)$; $V_h^{24}: 2V(8), 2C_i(16), 3C_2(16)$; $V_h^{25}: 4V_h(2), 6C_{2v}(4), C_i(8), 3C_s(8)$; $V_h^{26}: 2V(4), 2C_{2h}(4), C_i(8), 4C_2(8), C_s(8)$; $V_h^{27}: 2C_i(8), 3C_2(8)$; $V_h^{28}: 4C_{2h}(4), C_{2v}(4), 2C_2(8), 2C_s(8)$; $S_4^1: 4S_4, 3C_2(2)$; $S_4^2: 4S_4(2), 2C_2(4)$; $V_d^1: 4V_d, 2V(2), 2C_{2v}(2), 5C_2(4), C_s(4)$; $V_d^2: 4V(2), 2S_4(2), 7C_2(4)$; $V_d^3: 2S_4(2), C_{2v}(2), C_2(4), C_s(4)$; $V_d^4: 2S_4(2), 2C_2(4)$; $V_d^5: 4V_d(2), 3C_{2v}(4), 2C_2(8), 2C_s(8)$; $V_d^6: 2V(4), 2S_4(4), 5C_2(8)$; $V_d^7: 2S_4(4), 2V(4), 4C_2(8)$; $V_d^8: 2S_4(4), 2V(4), 4C_2(8)$; $V_d^9: 4V_d(4), 2C_{2v}(8), 2C_2(16), C_s(16)$; $V_d^{10}: 2S_4(8), 2V(8), 4C_2(16)$; $V_d^{11}: 2V_d(2), V(4), S_4(4), C_{2v}(4), 3C_2(8), C_s(8)$; $V_d^{12}: 2S_4(4), 2C_2(8)$; $C_4^1: 2C_4, C_2(2)$; $C_4^3: 3C_2(2)$; $C_4^5: C_4(2), C_2(4)$; $C_4^6: C_2(4)$; $C_{4h}^1: 4C_{4h}, 2C_{2h}(2), 2C_4(2), C_2(4), 2C_s(4)$; $C_{4h}^2: 4C_{2h}(2), 2S_4(2), 3C_2(4), C_s(4)$; $C_{4h}^3: 2S_4(2), C_4(2), 2C_i(4), C_2(4)$; $C_{4h}^4: 2S_4(2), 2C_i(4), 2C_2(4)$; $C_{4h}^5: 2C_{4h}(2), C_{2h}(4), S_4(4), C_4(4), C_i(8), C_2(8), C_s(8)$; $C_{4h}^6: 2S_4(4), 2C_i(8), C_2(8)$; $C_{4v}^1: 2C_{4v}, C_{2v}(2), 3C_s(4)$; $C_{4v}^2: C_4(2), C_{2v}(2), C_s(4)$; $C_{4v}^3: 2C_{2v}(2), C_2(4), C_s(4)$; $C_{4v}^4: C_{2v}(2), C_2(4), C_s(4)$; $C_{4v}^5: 2C_4(2), C_2(4)$; $C_{4v}^6: C_4(2), C_2(4)$; $C_{4v}^7: 3C_{2v}(2), 2C_s(4)$; $C_{4v}^8: 2C_2(4)$; $C_{4v}^9: C_{4v}(2), C_{2v}(4), 2C_s(8)$; $C_{4v}^{10}: C_4(4), C_{2v}(4), C_s(8)$; $C_{4v}^{11}: C_{2v}(4),$

$C_s(8)$; $\mathbf{C}_{4v}{}^{12}$: $C_2(8)$; $\mathbf{D}_4{}^1$: $4D_4$, $2V(2)$, $2C_4(2)$, $7C_2(4)$; $\mathbf{D}_4{}^2$: $2V(2)$, $C_4(2)$, $3C_2(4)$; $\mathbf{D}_4{}^3$: $3C_2(4)$; $\mathbf{D}_4{}^4$: $C_2(4)$; $\mathbf{D}_4{}^5$: $6V(2)$, $9C_2(4)$; $\mathbf{D}_4{}^6$: $2V(2)$, $4C_2(4)$; $\mathbf{D}_4{}^7$: $3C_2(4)$; $\mathbf{D}_4{}^8$: $C_2(4)$; $\mathbf{D}_4{}^9$: $2D_4(2)$, $2V(4)$, $C_4(4)$, $5C_2(8)$; $\mathbf{D}_4{}^{10}$: $2V(4)$, $4C_2(8)$; $\mathbf{D}_{4h}{}^1$: $4D_{4h}$, $2V_h(2)$, $2C_{4v}(2)$, $7C_{2v}(4)$, $5C_s(8)$; $\mathbf{D}_{4h}{}^2$: $2D_4(2)$, $2C_{4h}(2)$, $V(4)$, $C_{2h}(4)$, $2C_4(4)$, $4C_2(8)$, $C_s(8)$; $\mathbf{D}_{4h}{}^3$: $2D_4(2)$, $2V_d(2)$, $2C_{2h}(4)$, $C_4(4)$, $C_{2v}(4)$, $4C_2(8)$, $C_s(8)$; $\mathbf{D}_{4h}{}^4$: $2D_4(2)$, $V(4)$, $S_4(4)$, $C_4(4)$, $C_i(8)$, $4C_2(8)$; $\mathbf{D}_{4h}{}^5$: $2C_{4h}(2)$, $2V_h(2)$, $C_4(4)$, $3C_{2v}(4)$, $3C_s(8)$; $\mathbf{D}_{4h}{}^6$: $2C_{4h}(2)$, $C_{2h}(4)$, $V(4)$, $C_4(4)$, $2C_2(8)$, $C_s(8)$; $\mathbf{D}_{4h}{}^7$: $2V_d(2)$, $C_{4v}(2)$, $2C_{2h}(4)$, $C_{2v}(4)$, $2C_2(8)$, $2C_s(8)$; $\mathbf{D}_{4h}{}^8$: $V(4)$, $S_4(4)$, $C_4(4)$, $C_i(8)$, $2C_2(8)$; $\mathbf{D}_{4h}{}^9$: $4V_h(2)$, $2V_d(2)$, $7C_{2v}(4)$, $C_2(8)$, $3C_s(8)$; $\mathbf{D}_{4h}{}^{10}$: $2V_d(2)$, $2V_h(2)$, $V(4)$, $C_{2h}(4)$, $4C_{2v}(4)$, $3C_2(8)$, $2C_s(8)$; $\mathbf{D}_{4h}{}^{11}$: $3V(4)$, $S_4(4)$, $C_i(8)$, $5C_2(8)$; $\mathbf{D}_{4h}{}^{12}$: $2V_d(2)$, $2V(4)$, $2C_{2h}(4)$, $C_{2v}(4)$, $5C_2(8)$, $C_s(8)$; $\mathbf{D}_{4h}{}^{13}$: $2C_{2h}(4)$, $S_4(4)$, $V(4)$, $3C_2(8)$, $C_s(8)$; $\mathbf{D}_{4h}{}^{14}$: $2V_h(2)$, $C_{2h}(4)$, $S_4(4)$, $3C_{2v}(4)$, $C_2(8)$, $2C_s(8)$; $\mathbf{D}_{4h}{}^{15}$: $2V_d(2)$, $2C_{2v}(4)$, $C_i(8)$, $C_2(8)$, $C_s(8)$; $\mathbf{D}_{4h}{}^{16}$: $V(4)$, $S_4(4)$, $2C_{2h}(4)$, $C_{2v}(4)$, $3C_2(8)$, $C_s(8)$; $\mathbf{D}_{4h}{}^{17}$: $2D_{4h}(2)$, $V_h(4)$, $V_d(4)$, $C_{4v}(4)$, $C_{2h}(8)$, $4C_{2v}(8)$, $C_2(16)$, $3C_s(16)$; $\mathbf{D}_{4h}{}^{18}$: $D_4(4)$, $V_d(4)$, $C_{4h}(4)$, $V_h(4)$, $C_{2h}(8)$, $C_4(8)$, $2C_{2v}(8)$, $2C_2(16)$, $2C_s(16)$; $\mathbf{D}_{4h}{}^{19}$: $2V_d(4)$, $2C_{2h}(8)$, $C_{2v}(8)$, $2C_2(16)$, $C_s(16)$; $\mathbf{D}_{4h}{}^{20}$: $V(8)$, $S_4(8)$, $C_i(16)$, $3C_2(16)$; $\mathbf{T}^1$: $2T$, $2V(3)$, $C_3(4)$, $4C_2(6)$; $\mathbf{T}^2$: $4T(4)$, $C_3(16)$, $2C_2(24)$; $\mathbf{T}^3$: $T(2)$, $V(6)$, $C_3(8)$, $2C_2(12)$; $\mathbf{T}^4$: $C_3(4)$; $\mathbf{T}^5$: $C_3(8)$, $C_2(12)$; $\mathbf{T}_h{}^1$: $2T_h$, $2V_h(3)$, $4C_{2v}(6)$, $C_3(8)$, $2C_s(12)$; $\mathbf{T}_h{}^2$: $T(2)$, $2C_{3i}(4)$, $V(6)$, $C_3(8)$, $2C_2(12)$; $\mathbf{T}_h{}^3$: $2T_h(4)$, $T(8)$, $C_{2h}(24)$, $C_{2v}(24)$, $C_3(32)$, $C_2(48)$, $C_s(48)$; $\mathbf{T}_h{}^4$: $2T(8)$, $2C_{3i}(16)$, $C_3(32)$, $C_2(48)$; $\mathbf{T}_h{}^5$: $T_h(2)$, $V_h(6)$, $C_{3i}(8)$, $2C_{2v}(12)$, $C_3(16)$, $C_s(24)$; $\mathbf{T}_h{}^6$: $2C_{3i}(4)$, $C_3(8)$; $\mathbf{T}_h{}^7$: $2C_{3i}(8)$, $C_3(16)$, $C_2(24)$; $\mathbf{T}_d{}^1$: $2T_d$, $2V_d(3)$, $C_{3v}(4)$, $2C_{2v}(6)$, $C_2(12)$, $C_s(12)$; $\mathbf{T}_d{}^2$: $4T_d(4)$, $C_{3v}(16)$, $2C_{2v}(24)$, $C_s(48)$; $\mathbf{T}_d{}^3$: $T_d(2)$, $V_d(6)$, $C_{3v}(8)$, $S_4(12)$, $C_{2v}(12)$, $C_2(24)$, $C_s(24)$; $\mathbf{T}_d{}^4$: $T(2)$, $V(6)$, $2S_4(6)$, $C_3(8)$, $3C_2(12)$; $\mathbf{T}_d{}^5$: $2T(8)$, $2S_4(24)$, $C_3(32)$, $2C_2(48)$; $\mathbf{T}_d{}^6$: $2S_4(12)$, $C_3(16)$, $C_2(24)$; $\mathbf{O}^1$: $2O$, $2D_4(3)$, $2C_4(6)$, $C_3(8)$, $3C_2(12)$; $\mathbf{O}^2$: $T(2)$, $2D_3(4)$, $3V(6)$, $C_3(8)$, $5C_2(12)$; $\mathbf{O}^3$: $2O(4)$, $T(8)$, $V(24)$, $C_4(24)$, $C_3(32)$, $3C_2(48)$; $\mathbf{O}^4$: $2T(8)$, $2D_3(16)$, $C_3(32)$, $2C_2(48)$; $\mathbf{O}^5$: $O(2)$, $D_4(6)$, $D_3(8)$, $V(12)$, $C_4(12)$, $C_3(16)$, $3C_2(24)$; $\mathbf{O}^6$: $2D_3(4)$, $C_3(8)$, $C_2(12)$; $\mathbf{O}^7$: $2D_3(4)$, $C_3(8)$, $C_2(12)$; $\mathbf{O}^8$: $2D_3(8)$, $2V(12)$, $C_3(16)$, $3C_2(24)$; $\mathbf{O}_h{}^1$: $2O_h$, $2D_{4h}(3)$, $2C_{4v}(6)$, $C_{3v}(8)$, $3C_{2v}(12)$, $3C_s(24)$; $\mathbf{O}_h{}^2$: $O(2)$, $D_4(6)$, $C_{3i}(8)$, $S_4(12)$, $C_4(12)$, $C_3(16)$, $2C_2(24)$; $\mathbf{O}_h{}^3$: $T_h(2)$, $V_h(6)$, $2V_d(6)$, $D_3(8)$, $3C_{2v}(12)$, $C_3(16)$, $C_2(24)$, $C_s(24)$; $\mathbf{O}_h{}^4$: $T_d(2)$, $2D_{3d}(4)$, $V_d(6)$, $C_{3v}(8)$, $V(12)$, $C_{2v}(12)$, $2C_2(24)$, $C_s(24)$; $\mathbf{O}_h{}^5$: $2O_h(4)$, $T_d(8)$, $V_h(24)$, $C_{4v}(24)$, $C_{3v}(32)$, $3C_{2v}(48)$, $2C_s(96)$; $\mathbf{O}_h{}^6$: $O(8)$, $T_h(8)$, $V_d(24)$, $C_{4h}(24)$, $C_{2v}(48)$, $C_4(48)$, $C_3(64)$, $C_2(96)$, $C_s(96)$; $\mathbf{O}_h{}^7$: $2T_d(8)$, $2D_{3d}(16)$, $C_{3v}(32)$, $C_{2v}(48)$, $C_s(96)$, $C_2(96)$; $\mathbf{O}_h{}^8$: $T(16)$, $D_3(32)$, $C_{3i}(32)$, $S_4(48)$, $C_3(64)$, $2C_2(96)$; $\mathbf{O}_h{}^9$: $O_h(2)$, $D_{4h}(6)$, $D_{3d}(8)$, $V_d(12)$, $C_{4v}(12)$, $C_{3v}(16)$, $2C_{2v}(24)$, $C_2(48)$, $2C_s(48)$; $\mathbf{O}_h{}^{10}$: $C_{3i}(16)$, $D_3(16)$, $V(24)$, $S_4(24)$, $C_3(32)$, $2C_2(48)$; $\mathbf{C}_3{}^1$: $3C_3$; $\mathbf{C}_3{}^4$: C_3; $\mathbf{C}_{3i}{}^1$: $2C_{3i}$, $2C_3(2)$, $2C_i(3)$; $\mathbf{C}_{3i}{}^2$: $2C_{3i}$, $C_3(2)$, $2C_i(3)$; $\mathbf{C}_{3v}{}^1$: $3C_{3v}$, $C_s(3)$; $\mathbf{C}_{3v}{}^2$: C_{3v}, $C_3(2)$, $C_s(3)$; $\mathbf{C}_{3v}{}^3$: $3C_3(2)$; $\mathbf{C}_{3v}{}^4$: $2C_3(2)$; $\mathbf{C}_{3v}{}^5$: C_{3v}, $C_s(3)$; $\mathbf{C}_{3v}{}^6$: $C_3(2)$; $\mathbf{D}_3{}^1$: $6D_3$, $3C_3(2)$, $2C_2(3)$; $\mathbf{D}_3{}^2$: $2D_3$, $2C_3(2)$, $2C_2(3)$; $\mathbf{D}_3{}^3$: $2C_2(3)$; $\mathbf{D}_3{}^4$: $2C_2(3)$; $\mathbf{D}_3{}^5$: $2C_2(3)$; $\mathbf{D}_3{}^6$: $2C_2(3)$; $\mathbf{D}_3{}^7$: $2D_3$, $C_3(2)$, $2C_2(3)$; $\mathbf{D}_{3d}{}^1$: $2D_{3d}$, $2D_3(2)$, $C_{3v}(2)$, $2C_{2h}(3)$, $C_3(4)$, $2C_2(6)$, $C_s(6)$; $\mathbf{D}_{3d}{}^2$: $3D_3(2)$, $C_{3i}(2)$, $2C_3(4)$, $C_i(6)$, $C_2(6)$; $\mathbf{D}_{3d}{}^3$: $2D_{3d}$, $2C_{3v}(2)$, $2C_{2h}(3)$, $2C_2(6)$, $C_s(6)$; $\mathbf{D}_{3d}{}^4$: $D_3(2)$, $C_{3i}(2)$, $2C_3(4)$, $C_i(6)$, $C_2(6)$; $\mathbf{D}_{3d}{}^5$: $2D_{3d}$, $C_{3v}(2)$, $2C_{2h}(3)$, $2C_2(6)$, $C_s(6)$; $\mathbf{D}_{3d}{}^6$: $D_3(2)$, $C_{3i}(2)$, $C_3(4)$, $C_i(6)$, $C_2(6)$; $\mathbf{C}_{3h}{}^1$: $6C_{3h}$, $3C_3(2)$, $2C_s(3)$; $\mathbf{D}_{3h}{}^1$: $6D_{3h}$, $3C_{3v}(2)$, $2C_{2v}(3)$, $3C_s(6)$; $\mathbf{D}_{3h}{}^2$: $3D_3(2)$, $3C_{3h}(2)$, $3C_3(4)$, $C_2(6)$, $C_s(6)$; $\mathbf{D}_{3h}{}^3$: $2D_{3h}$, $2C_{3h}(2)$, $C_{3v}(2)$, $2C_{2v}(3)$, $C_3(4)$, $3C_s(6)$; $\mathbf{D}_{3h}{}^4$: $D_3(2)$, $3C_{3h}(2)$, $2C_3(4)$, $C_2(6)$, $C_s(6)$; $\mathbf{C}_6{}^1$: C_6, $C_3(2)$, $C_2(3)$; $\mathbf{C}_6{}^4$: $2C_2(3)$; $\mathbf{C}_6{}^5$: $2C_2(3)$; $\mathbf{C}_6{}^6$: $2C_3(2)$; $\mathbf{C}_{6v}{}^1$: C_{6v}, $C_{3v}(2)$, $C_{2v}(3)$, $2C_s(6)$; $\mathbf{C}_{6v}{}^2$: $C_6(2)$, $C_3(4)$, $C_2(6)$; $\mathbf{C}_{6v}{}^3$: $C_{3v}(2)$, $C_3(4)$, $C_s(6)$; $\mathbf{C}_{6v}{}^4$: $2C_{3v}(2)$, $C_s(6)$; $\mathbf{C}_{6h}{}^1$: $2C_{6h}$, $2C_{3h}(2)$, $C_6(2)$, $2C_{2h}(3)$, $C_3(4)$, $C_2(6)$, $2C_s(6)$; $\mathbf{C}_{6h}{}^2$: $3C_{3h}(2)$, $C_{3i}(2)$, $2C_3(4)$, $C_i(6)$, $C_s(6)$; $\mathbf{D}_6{}^1$: $2D_6$, $2D_3(2)$, $C_6(2)$, $2V(3)$, $C_3(4)$, $5C_2(6)$; $\mathbf{D}_6{}^2$: $2C_2(6)$; $\mathbf{D}_6{}^3$: $2C_2(6)$; $\mathbf{D}_6{}^4$: $4V(3)$, $6C_2(6)$; $\mathbf{D}_6{}^5$: $4V(3)$, $6C_2(6)$; $\mathbf{D}_6{}^6$: $4D_3(2)$, $2C_3(4)$, $2C_2(6)$; $\mathbf{D}_{6h}{}^1$: $2D_{6h}$, $2D_{3h}(2)$, $C_{6v}(2)$, $2V_h(3)$, $C_{3v}(4)$, $5C_{2v}(6)$, $4C_s(12)$; $\mathbf{D}_{6h}{}^2$: $D_6(2)$, $C_{6h}(2)$, $D_3(4)$, $C_{3h}(4)$, $C_6(4)$, $V(6)$, $C_{2h}(6)$, $C_3(8)$, $3C_2(12)$, $C_s(12)$; $\mathbf{D}_{6h}{}^3$: $D_{3h}(2)$, $D_{3d}(2)$, $C_{3h}(4)$, $D_3(4)$, $C_{3v}(4)$, $C_{2h}(6)$, $C_{2v}(6)$, $C_3(8)$, $C_2(12)$, $2C_s(12)$; $\mathbf{D}_{6h}{}^4$: $D_{3d}(2)$, $3D_{3h}(2)$, $2C_{3v}(4)$, $C_{2h}(6)$, $C_{2v}(6)$, $C_2(12)$, $2C_s(12)$.