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CLASSIFICATION OF ENERGY STATES IN LINEAR MOLECULES

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A new system of classifying the energy states in molecules is proposed which is simpler and more universal than the existing one. Application of this system to linear molecules makes it possible to treat the latter in the same manner as and together with nonlinear ones.

Studies concerning the symmetry of molecular states are a traditional object of high-resolution molecular spectroscopy. A bibliography on this subject and a description of existing methods can be found in several monographs [1, 2]. Many problems relating to the symmetry of molecular states are, however, far from being completely solved. A convincing example of this is the situation with classification of energy states in linear molecules. At the present time these molecules are necessarily put into a separate class and the system of classifying their energy states looks most unwieldy as well as artificial [3]. Here a new, simpler, and more universal method of classifying the molecular states will be proposed. Application of this system makes it possible to treat linear molecules in the same manner as and together with nonlinear ones. In constructing this system the authors have paid special attention to the physical interpretation of the proposed relation between symmetry groups in various models used for describing the molecular states.

The symmetry in the rigorous problem of stationary states in a spatially isolated molecule is related to the symmetry space and time as well as to symmetry with respect to transpositions of identical particles. An exact solution to this problem is not possible to obtain, as a rule, so that it becomes necessary to use methods of the perturbation theory. As the zeroth approximation one usually selects a model where: A) hyperfine interactions associated with the nuclear spin have been disregarded, B) the nonadiabatic interaction between the motion of electrons and that of nuclei in a molecule has been disregarded (Born—Oppenheimer approximation), and C) the motion of nuclei in a molecule is split into mutually independent vibrational motion and rotational motion, which one describes with the aid of the "harmonic oscillator" model and the "rigid top" model, respectively. In order to end up with a correct classification on the basis of such an approximate solution, it is necessary to determine the relation between the symmetry of this solution and that of the exact one. For convenience and simplicity, we will first demonstrate our approach to the solution of this problem on a specific example of a nonlinear molecule, namely the planar BF_3 molecule of the "symmetric top" kind. Then, without any modifications we will extend this approach to linear molecules.

The transpositional symmetry group of nuclei in the BF_3 molecule is π_3, associated with transpositions of the three fluorine nuclei.* Inasmuch as fluorine nuclei are fermions, any complete wave function of this molecule must be transformable with respect to an irreducible representation $[1^3]$ of the π_3 group. When hyperfine interactions associated with the nuclear spin are negligible, then the complete wave function of this stationary molecule can be represented in the form [2]

$$\psi(x,\, s,\, X,\, \sigma) = \frac{1}{\sqrt{f_\lambda}} \sum_r \Phi_r^{[\lambda]}(x,\, s,\, X) \chi_{\tilde{r}}^{\widetilde{[\lambda]}}(\sigma).$$ (1)

Here $x,\, s$ are space and spin coordinates of electrons; $X,\, \sigma$, space and spin coordinates of nuclei; f_λ, dimensionality of the irreducible representation $[\lambda]$ of the π_3 group, $\Phi^{[\lambda]}(x, s, X)$, coordinate wave function which transforms according to the representation $[\lambda]$; $\chi^{\widetilde{[\lambda]}}(\sigma)$ spin wave function which transforms according to the representation $[\lambda]$, the conjugate of representation $[\tilde{\lambda}]$; $r,\, \tilde{r}$, indices in Young's table for representations $[\lambda]$ and $[\tilde{\lambda}]$, respectively. Since the spin of a fluorine nucleus is $\frac{1}{2}$, the dimensionality of the spin space is 2 and only two (out of three) Young spin schemes are allowed:

$$[\tilde{\lambda}_s]:\quad [3],\, [21].$$ (2)

To these schemes correspond, respectively, the values $3/2$ and $1/2^\dagger$ of the total spin of fluorine nuclei and the Young coordinate schemes

$$[\lambda_c]:\quad [1^3],\, [21].$$ (3)

In the Born–Oppenheimer approximation one regards the motion of electrons as taking place in the potential field produced by stationary nuclei. The electron wave functions Φ_{el} (x, s, X) and the electron energy terms $E_{el}(X)$ are found here to depend on the positions of the nuclei as well as on relevant parameters. One then considers the motion of nuclei in the $E_{el}(X)$ potential field. Accordingly, the coordinate wave function can be described by the expression

$$\Phi(x, s, X) = \Phi_{el}(x, s, X)\Phi_{nu}(X).$$ (4)

In connection with a given electron state one introduces the equilibrium configuration of nuclei concept, which corresponds to their equilibrium positions. The spatial symmetry of this equilibrium configuration determines the symmetry of the force field relative to the motion of electrons attending small displacements of nuclei from their equilibrium state as well as relative to these small displacements of nuclei. The corresponding symmetry group is called the point symmetry group of the molecule. Elements of this group act only on the space coordinates of nuclei. For the BF_3 molecule, (its equilibrium configuration shown in Fig. 1), the point symmetry group is D_3h. Near the equilibrium configuration one can write instead of expression (4)

$$\Phi(x, s, X) = \Phi_{el}(x, s, X_0)\Phi_{nu}(X),$$ (5)

where X_0 are the space coordinates of nuclei in their equilibrium configuration. It is important to emphasize that the physical concept about the existence of a nuclear equilibrium configuration with a definite symmetry has only been introduced in connection with the Born–Oppenheimer approximation. Accordingly, the point symmetry group of a molecule contains much information about the symmetry of the force field, information which is missing in the symmetry group of transpositions of identical nuclei. This aspect is an important consideration in determining the equivalent transformations in the point symmetry group of a molecule on the one hand and in the transposition group on the other, inasmuch as it leads to the following requirement. Those nuclei configurations which result from small displacements of nuclei from their equilibrium positions differ from one another only with respect to the force field and, consequently, are all identified from the standpoint of the transposition group. For this reason, one can always compare the transformations according to the trans-

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*The notation for all symmetry groups occurring in this article, as well as for their classes and irreducible representations, is also that used in [2, 4].

†For particles with the spin $\frac{1}{2}$ only one value of the total spin moment corresponds to each Young spin scheme. For particles with spin 1 or larger there is no such correspondence [2].
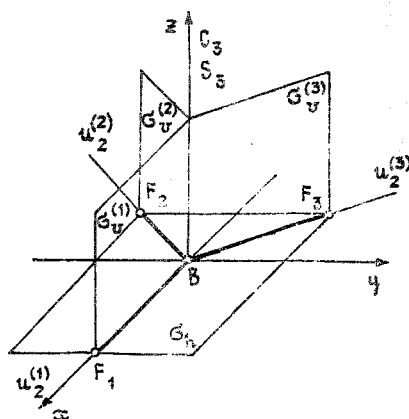
Fig. 1. Equilibrium config-
uration in the BF₃ molecule
with the D₃ₕ point symmetry
group.

position group and the point group respectively on the basis of their effect on the equilib-
rium configuration of nuclei. Accordingly, the point group of a molecule can evidently have
even more elements than the transpositions of identical nuclei group. It is essential here,
however, that to each element in the point group of a molecule one can place in correspondence
an element in the transpositions of identical nuclei group, although different elements in
the point group can correspond here to the same element in the transpositions group. The
converse is not true. Therefore, in the general case the point group of a molecule can be
homomorphously mapped as a subgroup of the transpositions of identical nuclei group of a mole-
cule.*

Using this set of concepts, we obtain the following correspondence between classes of
the transpositions of identical nuclei group and classes of the point group for the BF₃
molecule:

Classes π_3	$\{1^3\}$	$\{1^3\}$	$\{3\}$	$\{3\}$	$\{12\}$	$\{12\}$
Classes D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3U_2$	$3\sigma_v$

(6)

i.e., we have homomorphously mapped the D₃ₕ group into the π₃ group. Moreover, only those
multiplets will be allowed which behave identically with respect to elements in the point
group homomorphously mapped into the same element in the transition group, namely

Irreducible rep-resentations π_3	[3]	$[1^3]$	—	...	[21]	—
Irreducible rep-resentations D_{3h}	A_1'	A_2'	A_1''	A_2''	E'	E''

(7)

Considering that multiplet A'₁ corresponds to a forbidden Young coordinate scheme, we finally
have the allowed multiplets

$$4A_2', \quad 2E',$$ (8)

where the numerals before the symbols designating these multiplets denote the statistical
weight of the latter in the nucleus, according to the corresponding values of the total spin
of fluorine nuclei.

Until now we have assumed that a molecule has one equilibrium configuration. In reality,
however, there can be several such configurations. When transition from one configuration
to another is accompanied by a restructurization of the nuclear system, then it occurs across
a potential barrier. The BF₃ molecule has two equilibrium configurations, both energetically
equivalent with a high degree of accuracy. The existence of another configuration has to do
with the invariance of the Hamiltonian operator for this molecule with respect to inversion

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*Not so according to [2], where the point group of a molecule is homomorphous with a subgroup of
the transpositions of identical nuclei group of the same molecule.

of space coordinates of all particles,* when some of the relativistic interactions have been disregarded. Consequently, the allowed multiplets are

$$4A_2'^{(+)}, \ 4A_2'^{(-)}; \ \ 2E'^{(+)}, \ 2E'^{(-)}, \tag{9}$$

where the signs (+) and (−) correspond to the behavior of the coordinate wave function following an inversion transformation of the space coordinates of all particles with respect to the center of mass of the molecule.

Transformation of Inversion

According to the definition in [6], the transformation of inversion will change the sign of Cartesian space coordinates of all particles,† i.e.,

$$\hat{i}x = -x, \quad \hat{i}X = -X. \tag{10}$$

Wave functions having a definite symmetry with respect to such a transformation can be described by the expression

$$\Phi^{(\pm)}(x, s, X) \sim \Phi_{el}(x, s, X_0)\Phi_{nu}(X) \pm \Phi_{el}(-x, s, -X_0)\Phi_{nu}(-X). \tag{11}$$

We note that information about the change of equilibrium structure is contained in the electron wave function. The nuclear wave function describes only small deviations from the equilibrium position.

In the case of small displacements of nuclei from their equilibrium positions their motion can be split into mutually independent vibrational motion and rotational motion [7]. This is usually done by extracting the "purely rotational motion" and associating it with rotation of a movable system of coordinates fixed relative to the equilibrium configuration of the molecule. In the zeroth approximation the models of a harmonic oscillator and a rigid top are used for describing vibrational and rotational motion. Accordingly, the nuclear wave function in the movable system of coordinates becomes

$$\Phi_{nu}(X) = \Phi_{vib}(Q)\Phi_{rot}(\theta), \tag{12}$$

where Q is the set of $3N - 6$ normal vibration coordinates (N denoting the number of nuclei in the molecule) and θ is the set of three Euler angles.‡ The "purely rotational motion" symmetry group is called the rotational symmetry group of a molecule. Elements in this group act only on the Euler angles, i.e., on the spatial position of the molecules as a whole. The rotational symmetry group of the BF_3 molecule is D_∞. It is very typical that an approximate model always rests on a definite physical concept. It therefore always contains additional qualitative information about a given system. In our case this information pertains to introducing the concept of an inertial ellipsoid associated with the equilibrium configuration of the molecule.

There arises the question as to how the position of the movable system of coordinates changes, also how the electron coordinates and the vibration coordinates change relative to this movable system of coordinates, when an inversion transformation is performed on the molecule. The answer to this question is ambiguous, which, for instance, explains why various different rules of transformation are applied to the rotational wave function for an inversion. For a better understanding of this ambiguity, let us rewrite the right-hand side of expression (11) in the movable system of coordinates as

$$\Phi^{(\pm)}(x, s, X) \sim \Phi_{el}(\tilde{x}, s, \tilde{X}_0)\Phi_{vib}(Q)\Phi_{rot}(\theta) \pm \Phi_{el}(\tilde{x}', s, \tilde{X}'_0)\Phi_{vib}(Q')\Phi_{rot}(\theta'), \tag{13}$$

where $\tilde{x}$, $\tilde{X}_0$ are space coordinates of electrons and of equilibrium positions occupied by nuclei in the movable system of coordinates. The set of coordinates $(\tilde{x}, \tilde{X}_0, Q, \theta)$ defines the spatial disposition of nuclei and electrons in the molecule prior to inversion and the set of coordinates $(\tilde{x}', \tilde{X}'_0, Q', \theta')$ defines it after transformation. The ambiguity has to do with the absence of any constraints (other than those dictated by convenience) on selecting for

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*Following the procedure in [6], we regard the operation of inversion as not being defined in the spin space, contrary to the procedure in [1], where the invariance of the spin of a particle with respect to the operation of inversion follows from the axiality of this vector.
†This can be done either by correspondingly changing the spatial positions of particles or by reversing the directions of all coordinate axes. We will do it by the first method.
‡In the case of a linear molecule there is one more vibration coordinate and rotation of the molecule is described in a manner analogous to motion of a point on a sphere.

the movable system of coordinates the kind of change which will occur as a result of an inversion transformation, i.e., on the selection of the Euler angles θ'. We believe that, at least for classification purposes, it is most convenient to select

$$\theta' = \theta \quad \text{or} \quad \hat{i}\theta = \theta. \tag{14}$$

This leads to the transformation rule for rotational wave functions as proposed by J. T. Hougen [8], namely

$$\hat{i}\Phi_{\text{rot}}(\theta) = \Phi_{\text{rot}}(\theta). \tag{15}$$

As to the changes of the remaining coordinates, these can be expressed in the very natural form*

$$\hat{i}\widetilde{x} = -\widetilde{x}, \quad \hat{i}\widetilde{X}_0 = -\widetilde{X}_0, \quad \hat{i}Q = -Q. \tag{16}$$

This rule will also be used here later on.

Let us briefly review some other choices for the change in the position of the movable system of coordinates, i.e., for $\theta' - \theta$. Their gist is to compensate, by rotation of this system of coordinates

$$\widetilde{X}_0' = \widetilde{X}_0 \quad \text{or} \quad \hat{i}\widetilde{X}_0 = \widetilde{X}_0, \tag{17}$$

the changes of equilibrium positions of nuclei in the system which occur as a result of the inversion transformation. In three-dimensional space it is obviously impossible to replace inversion of a three-dimensional structure with the transformation of rotation, inasmuch as inversion, unlike rotation, constitutes an improper transformation. Therefore, requirement (17) can be satisfied only for molecules with a linear or a planar equilibrium configuration. The transformation rule for rotational wave functions is then

$$\hat{i}\Phi_{\text{rot}}(\theta) = (-1)^J \Phi_{\text{rot}}(\theta), \tag{18}$$

in the case of linear molecules and

$$\hat{i}\Phi_{\text{rot}}(\theta) = (-1)^{k_c} \Phi_{\text{rot}}(\theta), \tag{19}$$

in the case of planar molecules, with J denoting the quantum number of the total moment of momentum; the meaning of index k_c becomes evident as the rotational energy term is written in the form $J_{k-1,k+1} \equiv J_{k_\alpha, k_c}$. The transformation rules (18) and (19) have been used before [1, 6, 9]. It must be immediately emphasized here that satisfying the requirement (17) will lead to a rather intricate and unnatural transformation rule for inversion of almost any other characteristic of the molecule (electron and vibration coordinates, dipole moment, etc.) in the movable system of coordinates; this rule also depends on the kind of molecule.

As has been noted earlier, it is not possible to satisfy requirement (17) for a molecule with a three-dimensional equilibrium structure. In this case the choice $\theta' - \theta$ can be used for altering the transformation pattern when the molecular configuration in the movable system of coordinates undergoes inversion. Upon rotation of the movable system of coordinates through the angle π, for instance, the inversion transformation will appear as a reflection in a plane perpendicular to the axis of rotation.

The evidence presented in this chapter indicates clearly that, from the standpoint of the inversion transformation, only the behavior of the coordinate function has a physical meaning and the behavior of its parts is of a tentative nature.

Classification of the Vibrational—Rotational States

in a BF₃ Molecule

We thus have a classification of the coordinate wave function for the BF_3 molecule (i.e., allowed multiplets) according to the $D_{3h} \times C_i$ group, with elements of D_{3h} acting on the space coordinates of nuclei and elements of the C_i group acting on the space coordinates of nuclei as well as of electrons. We must know next with which electron, vibration, and rotation functions in the zeroth approximation allowed multiplets can be built. No difficulties arise here as far as electron and vibration functions are concerned, inasmuch as they can be classified according to the D_{3h} group. In the electron ground state and in a vibrational state

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*We use the same notation for the inversion operator acting in the configurational space of the system and for the inversion operator acting in the functional space of system states.

TABLE 1. Table of Correlations for the BF$_3$ Molecule between Rotational Representations of the D$_\infty$ Group and Rotational—Inversional Representations of the D$_{3h}$ × C$_i$ Group. Coupling between Groups D$_\infty$ and D$_{3h}$ × C$_i$ is Effected through Their Common Rotational Nuclear Subgroup D$_6$

D_∞	D_6	$D_{3h} \times C_i$
A_1	A_1	$A_1'^{(+)}, \quad A_1''^{(-)}$
A_2	A_2	$A_2'^{(+)}, \quad A_2''^{(-)}$
E_1	E_1	$E''^{(+)}, \quad E'^{(-)}$
E_2	E_2	$E'^{(+)}, \quad E''^{(-)}$
E_3	$B_1 + B_2$	$A_1''^{(+)}, \quad A_1'^{(-)} + A_2''^{(+)}, \quad A_2'^{(-)}$
E_4	E_2	$E'^{(+)}, \quad E''^{(-)}$
E_5	E_1	$E''^{(+)}, \quad E'^{(-)}$
E_6	$A_1 + A_2$	$A_1'^{(+)}, \quad A_1''^{(-)} + A_2'^{(+)}, \quad A_2''^{(-)}$
. . .	. . . .	. . . . . .

of the BF$_3$ molecule, for instance, $\Phi_{el}(\widetilde{x}, s, \widetilde{X}_0)$ and $\Phi_{vib}(Q)$ transform according to the single representation of this group.

The situation is much more complicated in the case of the rotation function, which belongs in the D$_\infty$ group. In order to overcome this difficulty, it is necessary to find the elements in the D$_\infty$ group whose projections on the motion of nuclei have analogs of motion of nuclei in the D$_{3h}$ group. For this one must consider the nuclear subgroup D$_{3h}$ × C$_i$, namely

$$R_0 \Longrightarrow (E)_{D_{3h}} (E)_{el}, \quad R_3 \Longrightarrow (C_3)_{D_{3h}} (C_3)_{el}, \quad R_2 \Longrightarrow (U_2)_{D_{3h}} (U_2)_{el},$$

$$R_2 \Longrightarrow i(\sigma_h)_{D_{3h}} (\sigma_h)_{el}, \quad R_6 \Longrightarrow i(S_3)_{D_{3h}} (S_3)_{el}, \tag{20}$$

$$R_2 \Longrightarrow i(\sigma_v)_{D_{3h}} (\sigma_v)_{el}.$$

Here R are elements in the D$_\infty$ group; ( )$_{D3h}$, elements in the point group; and ( )$_{el}$, elements which act on the electron coordinates. The last three elements in (20) must be taken into account, because they too couple the given kinds of motion. One must also remember, however, that here the sign associated with the inversion transformation refers to the coordinate function. Therefore, coupling the groups D$_\infty$ and D$_{3h}$ × C$_i$ through their common subgroup D$_6$ will yield a correlation between the rotational representations of the D$_\infty$ group and the rotational—inversional representations of the D$_{3h}$ × C$_i$ group shown in Table 1, where a representation of D$_{3h}$ refers to the rotation function and a representation of C$_i$ refers to a multiplet. Such a coupling between representations can be explained by a lack of a specific inversional degree of freedom, inversional motion being effected through the regular degrees of freedom in a molecule. Consequently, the classification system can be tentatively stipulated as

$$(\Gamma_{multiplet})_{D_{3h} \times C_i} \leftarrow (\Gamma_{el})_{D_{3h}} (\Gamma_{vib})_{D_{3h}} (\Gamma_{rot\text{-}inv})_{D_{3h} \times C_i}, \tag{21}$$

with Γ denoting an irreducible representation. Only those combinations on the right-hand side of (21) are possible which lead to allowed multiplets.

As an example, in Figs. 2 and 3 is shown the classification of rotational states in the BF$_3$ molecule respectively in the vibrational ground state and in the vibrational excited state $v_4 = 1$ for the electron ground state. It appears trivial that in terms of the Born—Oppenheimer approximation there are rather many splits of energy levels coinciding in the "harmonic oscillator" and the "rigid top" approximation. We would like to point out, however,
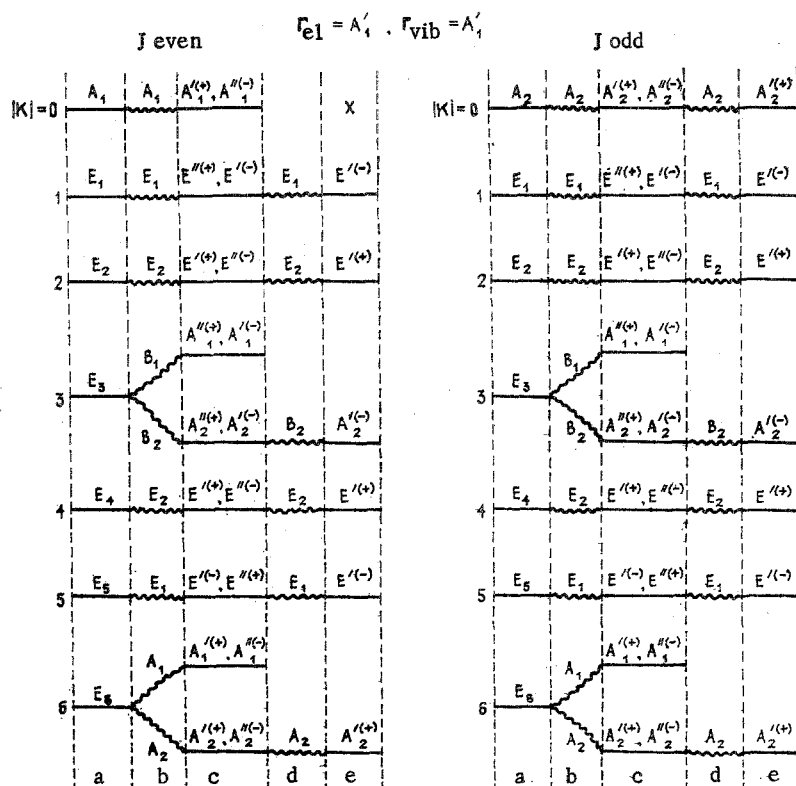
$$\Gamma_{el} = A'_1 \ . \ \Gamma_{vib} = A'_1$$

J even   J odd

Fig. 2. Classification of rotational states in the BF$_3$ molecule in the vibrational and electron ground state: a) irreducible representations of the D$_\infty$ group according to which the rotation functions are transformed in the "rigid top" approximation; b) irreducible representations of the rotational nuclear subgroup D$_3$ according to the which irreducible rotational representations of the D$_\infty$ group and rotational—inversional representations of the D$_{3h}$ × C$_i$ group are coupled; c) rotational—inversional representations of the D$_{3h}$ × C$_i$ group (representation of the point group refers to the rotation function and representation of the C$_i$ group refers to a multiplet); d) irreducible representations of the rotational nuclear subgroup D$_6$ corresponding to coordinate wave functions or multiplets; e) irreducible representations of the D$_{3h}$ × C$_i$ group according to which multiplets are transformed.

that levels coinciding in the zeroth approximation, which correspond to multiplets $\Gamma^{(+)}$ and $\Gamma^{(-)}$, do not necessarily split only as a result of inversional interaction. When these multiplets are formed by a process different with respect to representation of the nuclear rotational subgroup, then they will also split as a result of vibrational—rotational interaction. With the orders of these interactions known, therefore, it is possible to qualitatively represent the splitting pattern.

In concluding this chapter, we consider the problem of selection rules for molecular energy transitions caused by an electromagnetic field. We will consider electric-dipole transitions only.* Obviously, the dipole moment of a molecule should not change due to transposition of identical nuclei. It therefore will be transformed according to the Young scheme [3] of the π_3 group. Taking into account correspondence (7), we find that only representation A'$_1$ is allowed for the dipole moment. Taking into account the behavior of the dipole moment with respect to the inversion transformation, we write the allowed representation as A$_1$'$^{(-)}$. Accordingly, the electric-dipole selection rules can be represented as

$$A'^{(+)}_2 \longleftrightarrow A'^{(-)}_2, \qquad E'^{(+)} \longleftrightarrow E'^{(-)}, \tag{22}$$

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*This is not because of any principle involved here, inasmuch as a similar analysis can be easily performed for any multipole moment whatsoever.

and they are obeyed by any electric-dipole transitions in the Born—Oppenheimer approximation, including also so-called forbidden [10] (forbidden in the zeroth approximation) electric-dipole transition.

With this we conclude our discussion pertaining to classification of energy states in the BF_3 molecule. Our ideology of classification will be now applied directly, without changes, to linear molecules.

Classification of Vibrational—Rotational States in Linear Molecules

Linear molecules can have only two point symmetry groups: $C_{\infty v}$ and $D_{\infty h}$. Let us first consider those with the $C_{\infty v}$ symmetry group. Such molecules can, without loss of generality, be regarded as corresponding to the π_1 transposition group.* Using the earlier described method of determining equivalent transformations in the transposition group of a molecule on the one hand and in the point group of that molecule on the other, we obtain the following correspondence between their classes:

Classes τ_1	{1}	{1}	{1}
Classes $C_{\infty v}$	E	$2C_\varphi$	σ_v

(23)

We have thus homomorphously mapped the infinite point group of a molecule into its transposition group consisting of one element.

Using this homomorphism, we obtain the following correspondence between irreducible representations of these groups:

Irreducible representation π_1	[1]	—	—	...	—	...
Irreducible representation $C_{\infty v}$	A_1	A_2	E_1	...	E_n	...

(24)

According to this correspondence, only one multiplet A_1 is allowed for a linear molecule with the $C_{\infty v}$ point group. Taking into account the behavior of a multiplet with respect to the inversion transformation, we have

$$A_1^{(+)}, \quad A_1^{(-)}.$$

(25)

As has been already mentioned, rigid rotation of a linear molecule can be described in a manner analogous to motion of a point on a sphere. The symmetry group of such a rotational motion is the rotational group R_3 of three-dimensional space.† Coupling the groups R_3 and $C_{\infty v} \times C_i$ through their common rotational nuclear subgroup D_∞, we obtain the correlation between rotational representations of the R_3 group and rotational—inversional representations of the $C_{\infty v} \times C_i$ group shown in Table 2. Analogous to the system (21) is the following tentative representation of the classification system:

$$(\Gamma_{\text{multiplet}})_{C_{\infty v} \times C_i} \leftarrow (\Gamma_{\text{el}})_{C_{\infty v}} (\Gamma_{\text{vib}})_{C_{\infty v}} (\Gamma_{\text{rot-inv}})_{C_{\infty v} \times C_i}.$$

(26)

Naturally, only those combinations on the right-hand side of (26) are possible which lead to allowed multiplets. As an example, in Fig. 4 is shown the classification of rotational states in an asymmetric linear triatomic molecule in the vibrational ground state and in the vibrational excited states $v_2 = 1, 2$ for the case of an electron state completely symmetric with respect to the $C_{\infty v}$ group. We would like to point out two items. First of all, the well-known absence of states with $J < |l|$ (l denoting the quantum number of the vibrational

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*The fact of the matter is that, although such molecules can also have identical nuclei, there are no transformations in the $C_{\infty v}$ point group which correspond to transpositions of these nuclei.

†The energy of rotational levels in a linear molecule is correspondingly, in the zeroth approximation, $E_{\text{rot}} \sim J(J + 1)$.
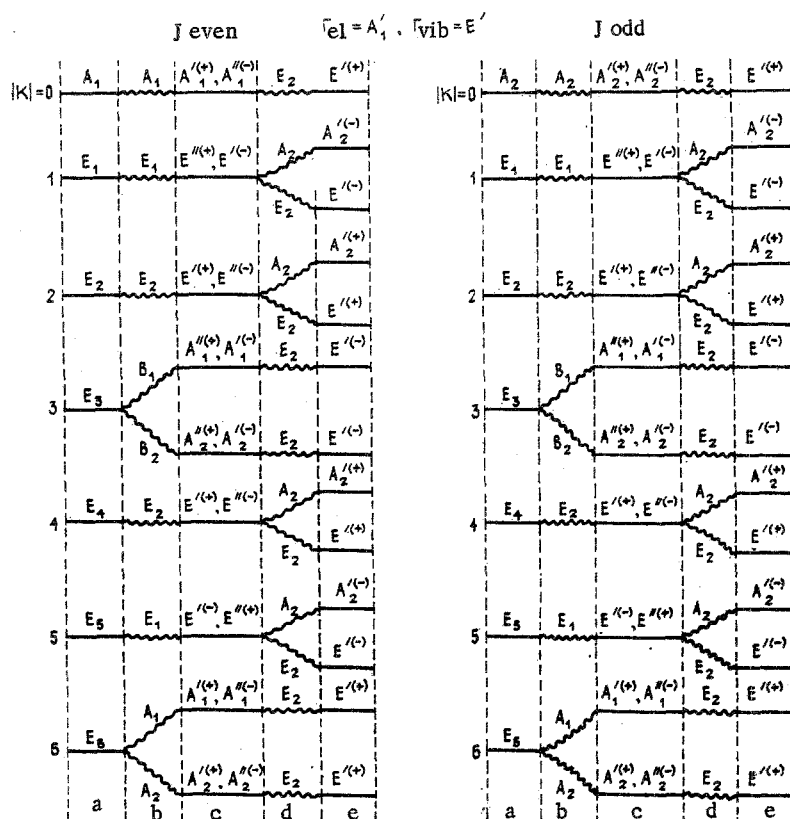
Fig. 3. Classification of rotational states in the BF₃ molecule in the vibrational excited state $v_4 = 1$ for the electron ground state. Notation is the same as in Fig. 2.

Table 2. Correlation Table for a Linear Molecule with the $C_{\infty V}$ Point Group between Rotational Representations of the R_3 Group and Rotational—Inversional Representations of the $C_{\infty V} \times C_i$ Group. Coupling of the Groups R_3 and $C_{\infty V} \times C_i$ Is Effected through Their Common Rotational Nuclear Subgroup D_∞

R_3	D_∞	$C_{\infty v} \times C_i$
$J = 0$	A_1	$A_1^{(+)}, \quad A_2^{(-)}$
1	$A_2 + E_1$	$A_2^{(+)}, \quad A_1^{(-)} + E_1^{(\pm)}$
2	$A_1 + E_1 + E_2$	$A_1^{(+)}, \quad A_2^{(-)} + E_1^{(\pm)} + E_2^{(\pm)}$
3	$A_2 + E_1 + E_2 + E_3$	$A_2^{(+)}, \quad A_1^{(-)} + E_1^{(\pm)} + E_2^{(\pm)} + E_3^{(\pm)}$
. . .	. . . .	. . . . . .

moment of the molecule) is explainable as a consequence of the properties of symmetry alone. Secondly, levels coinciding in the approximation of a harmonic oscillator and a rigid top split as a result of vibrational—rotational interaction. This is reflected in the classification insofar as the processes of formation of multiplets corresponding to these levels differ with respect to representations of the rotational subgroup D_∞.

Following the same procedure as for the BF₃ molecule, we find that the dipole moment of a linear molecule with the $C_{\infty V}$ point group symmetry is transformed according to representation $A_1^{(-)}$. Therefore, the electric-dipole selection rules can be written as
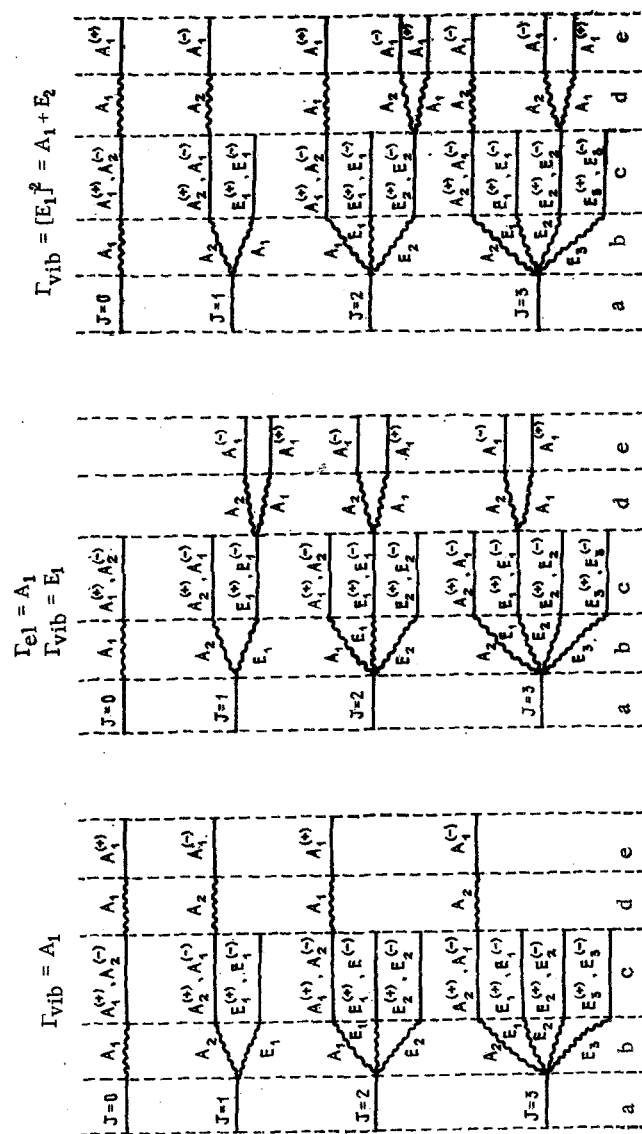
Fig. 4. Classification of rotational states in a linear triatomic molecule with the $C_{\infty v}$ point symmetry group in the vibrational ground state and in the vibrational excited states $v_2 = 1, 2$ for the case of an electron state in this molecule completely symmetric with respect to the $C_{\infty v}$ group. Notation the same as in Fig. 2.

$$A_1^{(+)} \longleftrightarrow A_1^{(-)}. \tag{27}$$

Let us next consider linear molecules with the $D_{\infty h}$ point symmetry group. This group is interesting because it includes the operation of inversion of the coordinates of nuclei. As will become evident subsequently, this does not give rise to any difficulties and the entire ideology of classification remains unchanged. So as to be more specific, we will demonstrate it on the $C^{16}O_2$ molecule. The transposition of identical nuclei group for this molecule is π_2. Since the spin of a ^{16}O nucleus is zero, the dimensionality of the spin space is 1 and only one (out of two) Young spin schemes is allowed: $[\lambda_{spin}] = [2]$. Naturally, to this scheme corresponds a zero total spin of oxygen nuclei and the analogous Young coordinate scheme $[\lambda_{coord}] = [2]$. Using the method of determining equivalent transformations in the transposition group on the one hand and in the point group on the other, we obtain the following correspondence between classes and irreducible representations π_2 and $D_{\infty h}$:

Classes π_2	$\{1^2\}$	$\{1^2\}$	$\{2\}$	$\{2\}$	$\{2\}$	$\{1^2\}$
Classes $D_{\infty h}$	E	$2C_\varphi$	U_2	I	$2IC_\varphi$	IU_2

$\tag{28}$

Irreducible representations π_2	$[2]$	—	—	$[1^2]$	—	—	...
Irreducible representations $D_{\infty h}$	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_{1g}	E_{1u}	...

$\tag{29}$

Consequently, for a linear molecule with the $D_{\infty h}$ point symmetry group two multiplets are possible: A_{1g} and A_{2u}. Only one of them is retained for the $C^{16}O_2$ molecule, namely A_{1g} corresponding to the Young coordinate scheme $[2]$. Taking into account the behavior with respect to the inversion transformation, we finally obtain the allowed multiplets

$$A_{1g}^{(+)}, \quad A_{1g}^{(-)}. \tag{30}$$

Operation i inverts the coordinates of all particles in the molecule, i.e., of nuclei and electrons, while operation I of the point group inverts only the coordinates of nuclei. They are different operations and they commute with each other. Because of this we can organize the $D_{\infty h} \times C_i$ group. Coupling the R_3 symmetry group of rigid rotational motion in a linear molecule and the $D_{\infty h} \times C_i$ group through their common rotational nuclear subgroup, we obtain the correlation between rotational representations of the R_3 group and rotational–inversional representation of the $D_{\infty h} \times C_i$ group shown in Table 3. Accordingly, the classification system is constructed in a manner analogous to (21) or (26) and can be tentatively represented as

$$(\Gamma_{multiplet})^{D_{\infty h} \times C_i} \leftarrow (\Gamma_{el})_{D_{\infty h}} (\Gamma_{vib})_{D_{\infty h}} (\Gamma_{rot\text{-}inv})_{D_{\infty h} \times C_i}. \tag{31}$$

The subgroup common to the rotational nuclear group R_3 and the $D_{\infty h} \times C_i$ group is, in fact, D_∞. Since each D_∞ class in the $D_{\infty h} \times C_i$ group appears twice, namely,

$$E \text{ and } Ii, \qquad 2C_\varphi \text{ and } 2C_\varphi Ii, \qquad U_2 \text{ and } U_2 Ii, \tag{32}$$

there must exist the correspondence

$$g \longleftrightarrow +, \qquad u \longleftrightarrow -, \tag{33}$$

where indices "g" and "u" refer to the rotational term and indices "+" and "−" refer to the multiplet. This property is common to all molecules whose point group includes inversion of the coordinates of nuclei. As an example, in Fig. 5 is shown the classification of rotational states in the $C^{16}O_2$ molecule in the vibrational ground state and in the vibrational excited states $v_2 = 1, 2$ for the electron ground state.

It is easy to find that the dipole moment of a linear molecule with the $D_{\infty h}$ group will be transformed according to representation $A_{1g}^{(-)}$. Therefore, the electric-dipole selection
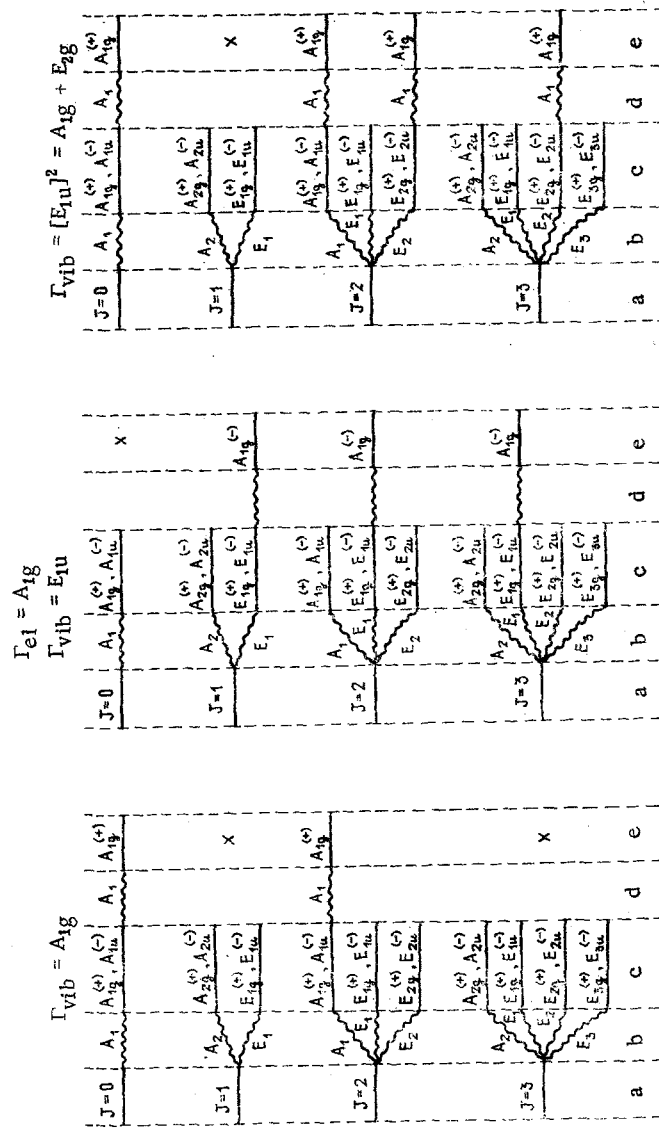
Fig. 5. Classification of rotational states in the linear $C^{16}O_2$ molecule in the vibrational ground state and in the vibrational excited states $v_2 = 1, 2$ for the electron ground state in the molecule. Notation is the same as in Fig. 2.

TABLE 3. Correlation Table for the Linear $C^{16}O_2$ Molecule between Rotational Representations of the R_3 Group and Rotational—Inversional Representations of the $D_{\infty h} \times C_i$ Group. Coupling of the Groups R_3 and $D_{\infty h} \times C_i$ is Effected through Their Common Rotational Nuclear Subgroup D_∞

R_3	D_∞	$D_{\infty h} \times C_i$
$J = 0$	A_1	$A_{1g}^{(+)}$, $A_{1u}^{(-)}$
1	$A_2 + E_1$	$A_{2g}^{(+)}$, $A_{2u}^{(-)} + E_{1g}^{(+)}$, $E_{1u}^{(-)}$
2	$A_1 + E_1 + E_2$	$A_{1g}^{(+)}$, $A_{1u}^{(-)} + E_{1g}^{(+)}$, $E_{1u}^{(-)} + E_{2g}^{(+)}$, $E_{2u}^{(-)}$
3	$A_2 + E_1 + E_2 + E_3$	$A_{2g}^{(+)}$, $A_{2u}^{(-)} + E_{1g}^{(+)}$, $E_{1u}^{(-)} + E_{2g}^{(+)}$, $E_{2u}^{(-)} + E_{3g}^{(+)}$, $E_{3u}^{(-)}$
...	......	....

rules can be written as

$$A_{1g}^{(+)} \longleftrightarrow A_{1g}^{(-)}, \qquad A_{2u}^{(+)} \longleftrightarrow A_{2u}^{(-)}. \tag{34}$$

We note that a consequence of correspondence (33) is the well-known exclusion [10] of purely rotational dipole transitions in the Born—Oppenheimer approximation for any molecules whose point group includes an element of inversion.

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