

Free and binary rotation of polyatomic molecules*

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Abstract. A modification of the quantum-mechanical theory of rotation of polyatomic molecules (binary rotation) is proposed, which is based on the algebra and representations of the $SO(4)$ group and allows the introduction of the concept of parity, as in atomic spectroscopy. It is shown that, if an asymmetric top molecule performing binary rotation finds itself in a spatially inhomogeneous electric field, its rotational levels acquire the additional energy due to the quadrupole moment. The existence of the rotational states of polyatomic molecules that cannot transfer to the free rotation state is predicted. In particular, the spin isomers of a water molecule, which corresponds to such states, can have different absolute values of the adsorption energy due to the quadrupole interaction of the molecule with a surface. The difference in the adsorption energies allows one to explain qualitatively the behaviour of the ortho- and para-molecules of water upon their adsorption on the surface of solids in accordance with experimental data.

Keywords: polyatomic molecules, rotation of molecules, spin isomers.

1. Introduction

It is true that modern quantum electronics has its origin in radio spectroscopy—the science studying the radio-frequency spectra of molecules. Radio spectroscopy was developed in connection with the radio communication and radiolocation at short wavelengths, when it was found that signals could not propagate through the atmosphere in many cases because of absorption by polar gas molecules, which are always present in the atmosphere.

In this paper, a new variant of the quantum-mechanical theory of rotation of polyatomic molecules is proposed. The generally accepted version of the rotational motion of molecules is presented in monographs [1–3] and was not noticeably changed since its publication [4].

*The paper is dedicated to the memory of academician A.M. Prokhorov

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The free rotation model was successfully used to describe rotating polar molecules in a low-density gas phase. This model takes into account the interaction of the molecular rotation with the spin and quadrupole moments of nuclei in the molecule, with molecular vibrations, and with external electric and magnetic fields, when these fields can be assumed spatially homogeneous within the molecule. The correctness of the theory of free rotation of molecules is confirmed by many examples presented in monographs [1–3].

The model of binary rotation of molecules considered in this paper assumes that a molecule can rotate in the region of the action of spatially inhomogeneous electromagnetic fields when the molecular shape and its symmetry are important. In the free rotation model, the molecular shape plays no role because external fields are homogeneous, and the interaction of the molecule with them can be described with the help of dipole or magnetic moment vectors.

The symmetry of the molecular shape can be taken into account in the molecular rotation only if the rotation group acts as a group of transformations in the three-dimensional physical space [the $SO(3)$] group because the symmetry operations of the molecule (rotations, reflections, and inversion) are realised in this space. Because the $SU(2)$ quantum group in the free rotation model does not act in the three-dimensional space, it cannot be used to take the full molecular shape into account.

In this paper, the F subgroup of the $SO(4)$ group is found which acts on a three-dimensional sphere like the $SU(2)$ group, where the rotational wave functions of a polyatomic molecule are defined, and contains the $SO(3)$ subgroup. The construction of F is similar to the subgroup of the proper Lorentz group, if only rotations in the three-dimensional space are considered.

Strong and spatially inhomogeneous electromagnetic fields exist near the surface of a condensed phase and appear in collisions between molecules in gases. The concept of binary rotation is applicable to a molecule in the state of physical adsorption on the surface of a solid, when the molecule interacts with the surface via the potentials of the multipole expansion (in particular, due to the deformation of the electron shell), but without the formation of the electron shell shared by the molecule and surface particles.

The free rotation model for a polyatomic molecule has a specific feature, which is most distinctly manifested in the case of an asymmetric top: the rotational Hamiltonian is not invariant with respect to spatial inversion operation I and its eigenfunctions cannot be properly transformed under this operation [5]. For this reason, radiative dipole transitions between the rotational levels of the molecule with the equal

quantum numbers of the angular momentum are allowed, whereas they are forbidden in atomic spectra in accordance with the Laporte selection rule (parity selection rule).

If a molecule has a quadrupole moment, as, for example, a water molecule, and is located in a spatially inhomogeneous electric field, then the rotational levels acquire an additional energy in the case of binary rotation. The electrostatic energy of the quadrupole moment remains invariable upon the inversion of coordinates because the quadrupole moment contains the pair products of the coordinates of charges, and the derivative of the electric field with respect to the coordinate is even relative to inversion.

In this case, the theoretical analysis of the molecular properties involves the use of the SU(2) group in the case of free rotation and the SO(4) group in the case of binary rotation. The representations of the SO(4) group and its so(4) algebra were early used in the problem of a non-relativistic hydrogen atom [6, 7]. The binary rotation model allows one to observe analogies between rotations of polyatomic molecules and a hydrogen atom, in particular, the role of the Runge–Lentz vector.

There is another reason to analyse again the theoretical foundations of rotation of polyatomic molecules. This is the absence of the theoretical explanation of the recently discovered effect of spin-selective adsorption of water molecules on the surface of solids [8–10]. It was found that water para-molecules with the zero nuclear spin retain in the adsorbed state longer than water ortho-molecules with the nuclear spin equal to unity. However, nuclear forces, which act between the molecules and the surface, are too weak to produce a significant change in the adsorption energy of spin modifications. In this case, the rotation of molecules in the adsorbed state plays a dominant role because the molecular rotation is rigidly coupled with the nuclear spin due to the Pauli principle.

2. Algebra of the binary and free rotation operators

The algebra of operators and basis wave functions for binary molecular rotation can be constructed in two ways. The first method has been realised in Ref. [11] based on free rotation, while the second method, which directly uses the operators and representations of the SO(4) group, is realised in this paper.

The relation between binary and free rotations can be conveniently analysed using the so(4) algebra. The so(4) algebra is six-dimensional and consists of the operators

$$A_{mn} = x_n \frac{\partial}{\partial x_m} - x_m \frac{\partial}{\partial x_n},$$

where x_n, x_m are coordinates of the four-dimensional Euclidean space; $m, n = 1, 2, 3, 4$. The basis operators of the algebra should be chosen so that they can be divided into two sets, each containing three operators:

$$[A_{23}, A_{13}] = A_{21}, \quad [A_{13}, A_{21}] = A_{23}, \quad [A_{21}, A_{23}] = A_{13}$$

and

$$[A_{14}, A_{42}] = A_{21}, \quad [A_{42}, A_{43}] = A_{23}, \quad [A_{43}, A_{14}] = A_{13}.$$

The first three operators A_{21}, A_{23} , and A_{31} generate the so(3) subalgebra and correspond to the components of the angular momentum vector. Other three operators A_{14}, A_{42} , and A_{43} are the components of the Runge–Lentz vector, but they do not generate a subalgebra [7].

The operators A_{21}, A_{23} , and A_{13} are the operators of the angular momentum of binary rotation. The operators A_1, A_2, A_3 and B_1, B_2, B_3 of the angular momentum of free rotation are formed as the sum and difference of the operators from the first and second sets. In such a basis, the so(4) algebra is decomposed in the direct sum of two subalgebras, which are isomorphic to so(3) [12]:

$$A_1 = \frac{1}{2}(A_{23} + A_{14}), \quad A_2 = \frac{1}{2}(A_{13} + A_{42}), \quad A_3 = \frac{1}{2}(A_{21} + A_{43})$$

and

$$B_1 = \frac{1}{2}(A_{23} - A_{14}), \quad B_2 = \frac{1}{2}(A_{13} - A_{42}), \quad B_3 = \frac{1}{2}(A_{21} - A_{43}).$$

The operators A_1, A_2, A_3 and B_1, B_2, B_3 satisfy the commutation relations for angular momentum operators and commute with each other. These operators correspond to the components of the angular momentum in the laboratory (immobile) and molecular (rotating) coordinate systems, respectively.

It follows from the relations presented above that the binary rotation operators can be obtained from free rotation operators. If the operators in the laboratory and molecular coordinate systems are added, the part of the operators related to the Runge–Lentz vector disappears. This method for obtaining binary rotation operators can be used when the free rotation operators are represented by differential expressions in the terms of Euler angles, and the Wigner d-functions are used as wave functions [11].

The addition of the operators of the laboratory and molecular coordinates to obtain the binary rotation operators explains the origin of the term ‘binary rotation’, because the free rotation operators are related to infinitesimal rotations of the laboratory and molecular coordinate systems.

There exist three mutually commuting subgroups $\varepsilon_+(\mathbf{a})$, $\varepsilon_-(\mathbf{b})$ and $\varepsilon_+(\mathbf{a})\varepsilon_-(\mathbf{a}) = F$ of the SO(4) group, which correspond to the subalgebras A_1, A_2, A_3 and B_1, B_2, B_3 , as well as to the subalgebra A_{21}, A_{23}, A_{13} . Here, \mathbf{a}, \mathbf{b} are arbitrary three-dimensional vectors, which denote the elements of the subgroups. In the latter subgroup, transformations are performed successively [13].

3. Parity of binary and free rotation

The concept of two coordinate systems is always used in problems on the rotation of solids. The first reference system – laboratory coordinate system, is usually fixed to the environment, while the second one – the molecular coordinate system is coupled with a rotating solid. Let us now stop the rotation of the molecular system at some instant and fix the orientation of the molecular rectangular coordinate system (e'_1, e'_2, e'_3) with respect to the laboratory coordinate system (e_1, e_2, e_3), which coincided with the molecular system at the initial moment. The scalar products of the basis vectors of the two coordinate systems form the transition matrix Q from the laboratory to molecular system, which we call the direct rotation matrix

$$(e'_1, e'_2, e'_3) = (e_1, e_2, e_3)Q. \quad (1)$$

It is assumed in (1) that the laboratory system is the initial system and the molecular system is the final system. Vice versa, we can assume that the molecular system is the initial system and the laboratory system is final. Then,

$$(e_1, e_2, e_3) = (e'_1, e'_2, e'_3)Q^{-1}.$$

In this case, the position of a rotating body with respect to the environment did not change, the mutual orientation of the coordinate systems remained invariable, but the inverse matrix Q^{-1} appeared in the mathematical description instead of the matrix Q . The question of a choice of the rotation matrix (direct or inverse), of which of the coordinate systems should be treated as initial or final is beyond the scope of the situation described. If it is impossible to make a certain choice, the dualism related to the definition of the rotation matrix should be taken into account [14].

We will call the operation of the replacement of the direct Q matrix by the inverse Q^{-1} matrix the reversion operation R . Let us show that the operation R corresponds to the inversion operation I known in atomic and molecular spectroscopy. The Q matrix is an element of the $SO(3)$ group of the three-dimensional real orthogonal matrices. The inverse element is the transposed Q matrix.

The central object in the proof of the equivalence of the reversion and inversion operations is a three-dimensional sphere S_3 of unit radius in the four-dimensional Euclidean real space E_4 . In this case, first, the points of the sphere S_3 are in the one-to-one correspondence with the elements of the $SU(2)$ group [16], second, the sphere S_3 transforms to itself upon the transformations of the $SO(4)$ group, and, third, the representations of the $SU(2)$ and $SO(4)$ groups are constructed by using the functions and homogeneous harmonic polynomials on the sphere S_3 [15].

The unitary unimodular 2×2 matrix $g \in SU(2)$ is specified by two complex numbers u and v [16]:

$$g = \begin{vmatrix} u & v \\ -\bar{v} & \bar{u} \end{vmatrix} = \begin{vmatrix} x_4 + ix_3 & x_2 + ix_1 \\ -(x_2 - ix_1) & x_4 - ix_3 \end{vmatrix}, \quad (2)$$

$$|u|^2 + |v|^2 = 1, \quad x_4^2 + x_3^2 + x_2^2 + x_1^2 = 1,$$

where $x_4, x_3, x_2,$ and x_1 are coordinates in the E_4 space, the end of the radius vector with these coordinates lying on the sphere S_3 ; the bar denotes complex conjugation. The inverse matrix g^{-1} is obtained by conjugating the complex number u and changing the sign of the number v [17]:

$$g^{-1} = \begin{vmatrix} \bar{u} & -v \\ \bar{v} & u \end{vmatrix} = \begin{vmatrix} x_4 - ix_3 & -(x_2 + ix_1) \\ x_2 - ix_1 & x_4 + ix_3 \end{vmatrix}. \quad (3)$$

Matrix (3), containing the coordinates $x_4, x_3, x_2,$ and x_1 differs from matrix (2) in that the coordinates $x_1, x_2,$ and x_3 of the three-dimensional subspace E_3 have the opposite sign. Therefore, the reversion operation $R(g) = g^{-1}$ applied to the g matrix is equivalent to the reversion operation I in $E_3 \subset E_4$.

The transformation of the operators A_{mm} of the $so(4)$ algebra under the action of the reversion operation R provides the basis for the classification of free and binary rotation operators. This operation form, together with the identical operation, the group of two elements. The group has two irreducible one-dimensional representations: sym-

metric (even) and antisymmetric (odd). If the operator contains the coordinate x_4 , it is odd, if it contains only coordinates $x_3, x_2,$ and x_1 , it is even.

The operators, which are the linear combinations of the even and odd operators, for example, A_1, A_2, A_3 and B_1, B_2, B_3 , cannot be classified according to its parity because they cannot be transformed in the representations discussed above.

In the case of binary rotation, the components $A_{21}, A_{23},$ and A_{13} of the angular momentum operator are transformed in the symmetric representation. The rotational Hamiltonian composed of the components of the angular momentum is transformed in the same representation.

In the case of free rotation, the concept of parity does not exist. For example, the operators A_1, A_2, A_3 and B_1, B_2, B_3 are the components of the angular momentum, but they have no the parity quantum number.

4. Wave functions of free and binary rotation

The basis functions from which the eigenfunctions of the rotational Hamiltonian are constructed, belong to the spaces of irreducible representations of the $SO(4)$ group in the case of binary rotation and of the $SU(2)$ group in the case of free rotation. This section is devoted to analysis of the dependence of these functions on the reversion operation. We consider the relation between homogeneous harmonic polynomials [$SO(4)$ group] and the Wigner d-functions [$SU(2)$ group] because both classes of the functions are defined on the sphere S_3 .

The basis polynomials of the representation space of the $SO(4)$ group are specified by three integers $k_0 \geq k_1 \geq k_2$ [15]. The number k_0 defines the dimension $(k_0 + 1)^2$ of the representation space and the power k_0 of basis polynomials. The number k_1 is interpreted as the quantum number of the square of the angular momentum. The number k_2 can be positive or negative and is the quantum number of the projection of the angular momentum on the axis Oz of the orthogonal coordinate system in the subspace E_3 .

As an example, we consider the normalised basis polynomials of the $k_0 = 2$ representation of the $SO(4)$ group. The polynomials are written in the form of a linear combination making them the eigenfunctions of the operator A'_{21} . The polynomials are also the eigenfunctions of the square operator of the angular momentum $L^2 = A'^2_{21} + A'^2_{13} + A'^2_{23}$ and the inversion operator I . The prime means that the operators are Hermitian, i.e., of the form iA_{mm} . The fact that the polynomials are the eigenfunctions of the operators is reflected in their indices. The first index is k_0 , the second index is the quantum number of the square operator, and the third index is the quantum number of the operator A'_{21} :

$$\langle 222 \rangle = \sqrt{3}(x_2 + ix_1)^2, \quad \langle 211 \rangle = 2\sqrt{3}x_4(x_2 + ix_1),$$

$$\langle 221 \rangle = 2\sqrt{3}x_3(x_2 + ix_1), \quad \langle 210 \rangle = 2\sqrt{6}x_4x_3,$$

$$\langle 220 \rangle = \sqrt{2}(2x_3^2 - x_2^2 - x_1^2), \quad \langle 21-1 \rangle = 2\sqrt{3}x_4(x_2 - ix_1),$$

$$\langle 22-1 \rangle = 2\sqrt{3}x_3(x_2 - ix_1), \quad \langle 200 \rangle = 3x_4^2 - x_3^2 - x_2^2 - x_1^2,$$

$$\langle 22-2 \rangle = \sqrt{3}(x_2 - ix_1)^2.$$

It is important that one representation of the SO(4) group contains polynomials with different quantum numbers k_1 of the square operator of the angular momentum $k_0 \geq k_1 \geq 0$, which distinguishes them from the representations of the SO(3) and SU(2) groups. Each finite-dimensional representation of the SO(3) and SU(2) groups contains polynomials and functions only with one value of this quantum number.

The behaviour of the basis polynomials of the representations of the SO(4) group with respect to the reversion operation R is determined by the same rule as for the operators of the so(4) algebra. Note that polynomials with even values of k_1 are symmetric and with odd k_1 are antisymmetric with respect to the inversion operation I .

It is interesting to analyse the passage from the basis polynomials of the representations of the SO(4) group to the matrix elements of the representations of the SU(2) group by the example of the $k_0 = 2$ representation of the SO(4) group. The first condition is an equal number of basis polynomials in the $k_0 = 2$ representation of the SO(4) group and the d-functions in the weight j representation of the SU(2) group. Because the number of elements in the representation matrix of the SU(2) group is $(2j + 1)^2$, we have

$$(k_0 + 1)^2 = (2j + 1)^2, \quad j = \frac{1}{2}k_0.$$

Because in the case of free rotation, the representation weight j (the quantum number of the square of the angular momentum) is an integer, the expansion of basis polynomials in the d-functions can be performed only when k_0 is even. This means that binary rotation can pass to free rotation and back, when the first index k_0 of the representation of the SO(4) group is even. If k_0 is odd, the transition is forbidden. For this reason, the binary rotation states with odd k_0 are isolated from free rotation and exist independently. The first such representation with the minimal value $k_0 = 1$ is considered in section 7.

The explicit expressions for the d-functions in terms of polynomials in the case $j = 1$ can be obtained by comparing the matrix elements of the representation of weight $j = 1$, when they are expressed in terms of the complex numbers u and v , which in turn are expressed [see (2)] via the coordinates x_4, x_3, x_2 , and x_1 on the sphere S_3 :

$$\begin{vmatrix} d_{11} & d_{10} & d_{1-1} \\ d_{01} & d_{00} & d_{0-1} \\ d_{-11} & d_{-10} & d_{-1-1} \end{vmatrix} = \begin{vmatrix} \bar{u}^2 & -\sqrt{2}u\bar{v} & \bar{v}^2 \\ \sqrt{2}u\bar{v} & |u|^2 - |v|^2 & -\sqrt{2}u\bar{v} \\ v^2 & \sqrt{2}uv & u^2 \end{vmatrix} =$$

$$\begin{vmatrix} \psi + ic_1\langle 210 \rangle & -c_1((21-1) - i(22-1)) & c_2\langle 22-2 \rangle \\ c_1((211) - i(221)) & c_1^2\langle 200 \rangle + 2c_1c_2\langle 220 \rangle & -c_1((21-1) + i(22-1)) \\ c_2\langle 222 \rangle & c_1((211) + i(221)) & \psi - ic_1\langle 210 \rangle \end{vmatrix},$$

where $c_1 = 1/\sqrt{6}$; $c_2 = 1/\sqrt{3}$; $\psi = c_1^2\langle 200 \rangle - c_1c_2\langle 220 \rangle$.

The analysis of the matrix of the $j = 1$ representation shows that a part of the matrix elements are linear combinations of the even and odd basis polynomials. For this reason, the concept of parity does not exist for these functions. Because neither the free rotation operators A_k, B_k ($k = 1, 2, 3$) nor a greater part of the d-functions have parity, the concept of parity cannot be used in the case of free rotation of molecules.

The squares of the operators A and B are identical ($A^2 = B^2$),

$$A^2 = \frac{1}{4}(A_{23}^2 + A_{13}^2 + A_{21}^2) + \frac{1}{4}(A_{14}^2 + A_{42}^2 + A_{43}^2),$$

$$A_{23}A_{14} + A_{13}A_{43} + A_{21}A_{43} = 0.$$

Upon the action of the operators A^2 and B^2 on all the d-functions of the representation of the weight $j = 1$, the same factor $j(j+1)$ appears. In other words, the $(2j + 1)^2$ -fold degeneracy in the operators A^2 and B^2 appears. The d-functions can be distinguished with the help of the eigenvalues of the operators A_3 and B_3 , which commute with each other and the operators A^2 and B^2 :

$$A_3 = \frac{1}{2}(A_{21} + A_{43}), \quad B_3 = \frac{1}{2}(A_{21} - A_{43}).$$

The operators A_3 and B_3 are the projections of the angular momentum on the axes Oz and Oz' of the laboratory and molecular coordinate systems.

5. Hamiltonians of binary and free rotation

The rotational Hamiltonians of polyatomic molecules represent a linear combination of the components of the angular momentum with positive coefficients. The linear combination contains squared operators of the components. The coefficients of the linear combination, representing rotational constants, are inversely proportional to the principal inertia moments of a molecule. In the general case of an asymmetric top, all the three rotational constants are different. For example, in the case of binary rotation,

$$H = \chi_1 A_{23}'^2 + \chi_2 A_{13}'^2 + \chi_3 A_{12}'^2. \quad (4)$$

The components of the angular momenta can be related to the rotational constants by different methods [18]. Here we assign the operator A_{23} of rotation around the axis $O'x$ to the smallest inertia moment of the molecule (the greatest χ_1). The rotational constants χ_2 and χ_3 ($\chi_2 > \chi_3$) correspond to the two remaining operators.

In the case of binary rotation of symmetric top molecules, a complete set of commuting operators consists of the rotational Hamiltonian H , the angular momentum operator L^2 , the operator of projection on the molecular axis A_{21} , and the inversion (parity) operator I . If the top is asymmetric, the projection operator is excluded from a complete set.

In the case of free rotation, the operators B_1, B_2 , and B_3 should be substituted into (4) instead of the operators A_{23}, A_{13} , and A_{21} because these operators correspond to infinitesimal rotations around the axes of the molecular coordinate system.

Two sets of the angular momentum operators, which are involved in the problems of free rotation of molecules, appear due to the rotational invariance [19]. The rotational invariance is manifested, first, in the degeneracy of the rotational levels in the first lower index of the d-function and, second, in the description of the top rotation simultaneously by the operators A_k and B_k ($k = 1, 2, 3$). The rotational Hamiltonian H is constructed using operators B_k , while operators A_k determine the projections of the angular momentum on the axes of the laboratory coordinate system. The invariance of the Hamiltonian H with respect to rota-

tions means that the Hamiltonian commutes with any rotational operator in the laboratory system, including infinitesimal rotations, to which operators A_k correspond [20].

In the case of free rotation, a complete set of commuting operators, except the rotational Hamiltonian, consists of the square operators A^2 or B^2 of the angular momentum and two projection operators on the molecular (B_3) and laboratory (A_3) coordinate axes. If a top is asymmetric, the projection on the molecular quantisation axis is not preserved (the operator B_3 does not commute with the Hamiltonian H) and therefore is excluded from the complete set.

The eigenfunctions of the rotational Hamiltonian for asymmetric top molecules can be classified over the representations of the D_2 group. The classification is based on the invariance of the Hamiltonian (4) with respect to the operation of the D_2 group containing four elements [21]. The three elements of the group are interpreted as rotations through the angle π around the coordinate axes in the three-dimensional space, i.e., D_2 is a finite-dimensional subgroup of the $SU(2)$ group. The representations A , B_1 , B_2 , and B_3 of the commutative group are one-dimensional, and their number coincides with the number of elements of this group.

In the case of binary rotation, the D_2 group extends due to the reversion operation R , which is permutable with the rotational operators. Then D_2 group contains eight elements and the same number of one-dimensional representations A , B_1 , B_2 , B_3 , A' , B'_1 , B'_2 , B'_3 . The prime denotes the representations that are symmetric the operation R .

The eigenfunctions of the rotational Hamiltonian are the linear combinations of the basis functions. The results of comparison of binary and free rotations for the lower rotational levels of water molecules are presented in Table 1.

Table 1.

Level	Energy	Rotation			Rotational level energy / cm^{-1}	
		Binary	Free			
1_{10}	$\chi_1 + \chi_2$	$x_4 x_3$	$\langle B'_1 \rangle$	d_{n0}^1	$\langle B_1 \rangle$	42.4
1_{11}	$\chi_1 + \chi_3$	$x_4 x_2$	$\langle B'_2 \rangle$	$d_{n1}^1 + d_{n-1}^1$	$\langle B_2 \rangle$	37.1
1_{01}	$\chi_2 + \chi_3$	$x_4 x_1$	$\langle B'_3 \rangle$	$d_{n1}^1 - d_{n-1}^1$	$\langle B_3 \rangle$	23.8

In the first column of Table 1, the generally accepted notation of the rotational levels (and of the eigenfunctions of free rotation) are presented for an oblate asymmetric top [18], when the rotational constants $\chi_1 > \chi_2 > \chi_3$ correspond to the molecular coordinate axes $O'x$, $O'y$, and $O'z$. In the second and third columns, the eigenvalues (rotational level energies, which are common for binary and free rotation) and the proper polynomials (without the normalising factor) of the rotational Hamiltonian (4) are given. In the fourth column, the eigenfunctions of the Hamiltonian are presented (without the normalising factors) for the case of free rotation of molecules. The first subscript of the d-functions is related to one of the degenerate functions. The classification of the eigenfunctions of free rotation is performed in the representations of the D_2 group. In the last column, the rotational level energies are presented.

6. Quadrupole interaction of molecules in the case of binary rotation

A specific feature of binary rotation compared to free rotation is the appearance of the additional potential energy of the rotational levels of the molecule due to the

quadrupole moment when the molecule finds itself in a spatially inhomogeneous electric field. The energy of quadrupole interaction can be negative or positive, by increasing or decreasing, respectively, the potential energy of adsorption of molecule on the surface of a condensed medium.

Consider the quadrupole interaction between molecules during their binary rotations by the example of water molecules, because the quadrupole energy can substantially affect the process of separation of spin modifications.

The tensor Q_{ab} ($a, b = x, y, z$) of the quadrupole momentum of the molecule proves to be diagonal if the molecule has the spatial symmetry of the electron shell and the nuclear core. A simple model [22] for the calculation of a water molecule shows that the nondiagonal elements ($a \neq b$) of the tensor vanish, while the diagonal elements ($a = b$) are close to the experimental values [22] $Q_{xx} = 5.18 \times 10^{-26}$ esu cm^2 , $Q_{yy} = -5.73 \times 10^{-26}$ esu cm^2 , and $Q_{zz} = -6.56 \times 10^{-26}$ esu cm^2 .

The operator H_d of the interaction of a constant dipole moment of a molecule with an external electric field is constructed in the theory of rotation of polyatomic molecules as follows. The vector d of the dipole moment of the molecule is defined in the molecular coordinate system and the electric field vector E is defined in the laboratory coordinate system, so that the operator $H_d = Ed$ certainly contains the transformation matrix $SO(3, R)$ from one system to another. In rotational spectroscopy, this matrix is called the direction cosine matrix [18].

Numerous spectroscopic observations of free rotation of molecules show that the $SO(3, R)$ matrix, more exactly its elements a_{mm} , acting as operators, correctly describe the dipole interaction of the molecule with an external electric field [2, 3]. Here, we assume that, in the case of binary rotation, the quadrupole interaction of the molecule with an external field is also determined by the matrix elements of the $SO(3, R)$ matrix.

The operators of the quadrupole moment are determined by the decomposition of the symmetric part of the $SO(3, R)$ matrix into irreducible representations of the $SU(2)$ group of weights $j = 0$ and $j = 2$:

$$\begin{aligned}
 T_{00} &= a_{11} + a_{22} + a_{33} = 3x_4^2 - x_3^2 - x_2^2 - x_1^2, \\
 T_{+2} &= 1/2[(a_{11} - a_{22}) + i(a_{21} + a_{12})] = (x_1 + ix_2)^2, \\
 T_{+1} &= 1/2[(a_{31} + a_{13}) + i(a_{32} + a_{23})] = 2(x_1 + ix_2)x_3, \\
 T_0 &= 1/\sqrt{6}(2a_{33} - a_{11} - a_{22}) = 1/\sqrt{6}(2x_3^2 - x_2^2 - x_1^2), \\
 T_{-1} &= 1/2[-(a_{31} + a_{13}) + i(a_{32} + a_{23})] = 2(x_1 - ix_2)x_3, \\
 T_{-2} &= 1/2[(a_{11} - a_{22}) - i(a_{21} + a_{12})] = (x_1 - ix_2)^2.
 \end{aligned} \tag{5}$$

The matrix elements of the operator T_0 are calculated using the same rules as in the determining of the normalised factors for the basis polynomials. The coordinates are expressed in terms of the angular variables and integration is performed over the surface of the sphere S_3 [14].

Because only the diagonal components of the quadrupole moment tensor of a water molecule are nonzero, only the operator T_0 is used from all operators (5). The operator

T_0 is added to the Hamiltonian (4). The matrix elements of the operator T_0 are found from the proper polynomials of the rotational Hamiltonian. Because the operator T_0 is symmetric (type A), the initial and final polynomials entering the matrix element are identical and belong to the same rotational level of the molecule. Radiative transitions, which correspond to the operator T_0 , are not considered here.

Table 2 presents the matrix elements of the operator T_0 (the last column), which were calculated from the proper polynomials of the rotational levels from Table 1.

Table 2.

Level	Energy	Proper polynomial	Matrix element
$\langle 21 B'_1 \rangle$	$\chi_1 + \chi_2$	$2\sqrt{6}x_4x_3$	$-1/(2\sqrt{6})$
$\langle 21 B'_2 \rangle$	$\chi_1 + \chi_3$	$2\sqrt{6}x_4x_2$	$-1/(2\sqrt{6})$
$\langle 21 B'_3 \rangle$	$\chi_2 + \chi_3$	$2\sqrt{6}x_4x_1$	$1/\sqrt{6}$

The quantum numbers k_0 and k_1 and the type of representation in the D'_2 group are indicated as the indices of the proper polynomials (the first column). The proper polynomials of the Hamiltonian (4) presented in the third column have normalisation factors.

To estimate the quadrupole energy of a water molecule, we assume that the electric field near a solid is produced by a single electron and has the spherical symmetry. The quadrupole energy U of the molecule for $T_0 = 1$ is a function of the distance r from a nucleus producing the field

$$U = \frac{e}{r^3}(2Q_{zz} - Q_{yy} - Q_{xx}). \quad (6)$$

The quadrupole energy of a rotational level is obtained by multiplying (6) by $\langle T_0 \rangle$. The potential energy in the field of a negative charge $U > 0$, so that the rotational levels $\langle 21 B'_1 \rangle$ and $\langle 21 B'_2 \rangle$ acquire an addition to the adsorption energy, whereas the adsorption energy for the $\langle 21 B'_3 \rangle$ level becomes smaller. The value of this addition becomes equal to the rotational level energy at a distance of 8 Å from a charge on the surface.

7. Isolated lowest states in the case of binary rotation

It was pointed out in section 4 that polyatomic molecules have the binary states from which they cannot pass to the free rotational state. Such transitions are forbidden because the quantum number of the square of the angular momentum should be an integer.

The simplest possible state corresponds to the $k_0 = 1$ representation of the SO(4) group. The dimension of this representation is $(k_0 + 1)^2 = 4$ and it contains three basis polynomials with the quantum number $k_1 = 1$ and one polynomial with $k_1 = 0$:

$$\langle 11 B'_3 \rangle = 2x_1, \quad \langle 11 B'_1 \rangle = 2x_3, \quad \langle 11 B'_2 \rangle = 2x_2, \quad \langle 10 A \rangle = 2x_4.$$

Table 3 presents the parameters characterising a water molecule in the binary rotation state with $k_0 = 1$.

The energies of rotational levels coincide with those for a free molecule with the angular momentum $j = 0$ and $j = 1$, but the levels with $j = 1$ do not have the three-fold degeneracy inherent in free rotation.

Table 3.

Level	Energy	Rotational level energy /cm ⁻¹	Dipole moment component	Matrix element
$\langle 11 B'_1 \rangle$	$\chi_1 + \chi_2$	42.4	μ_z	$4/(3\sqrt{6})$
$\langle 11 B'_2 \rangle$	$\chi_1 + \chi_3$	37.1	μ_y	$-2/(3\sqrt{6})$
$\langle 11 B'_3 \rangle$	$\chi_2 + \chi_3$	23.8	μ_x	$-2/(3\sqrt{6})$
$\langle 10 A \rangle$	0	0	–	0

The last column of Table 3 contains the matrix element of the quadrupole interaction operator. All the four levels with $k_0 = 1$ are populated by water molecules at room temperature with the same probability (the level energy is much lower than kT). Therefore, a total addition to the energy of all the rotational levels caused by quadrupole interaction vanishes.

The rotational states can be classified according to their spin modifications, the $\langle 10 A \rangle$, $\langle 11 B'_2 \rangle$ states corresponding to para-water and the $\langle 11 B'_3 \rangle$, $\langle 11 B'_1 \rangle$ states corresponding to ortho-water. The classification of the polynomials to symmetric (para-water) and antisymmetric (ortho-water) is performed in accordance with the operation $R_{y\pi}$, which interchanges the coordinates x of protons (see Table 1). Para-molecules acquire the quadrupole addition to the potential adsorption energy due to the $\langle 11 B'_2 \rangle$ level, while the average adsorption energy for the $\langle 11 B'_3 \rangle$ and $\langle 11 B'_1 \rangle$ levels of water ortho-molecules becomes lower. This example shows that the quadrupole energy of rotational levels can change adsorption of water molecules in the way required to explain the effect of spin-selective adsorption.

8. Conclusions

We have considered above two approaches to the problem of rotation of polyatomic molecules. They can be treated as two representations (in terms of quantum mechanics), in which free and binary rotations have coincidences and differences. Some examples are presented below.

The eigenvalues of the rotational Hamiltonian coincide for the two representations, so that the rotational energy level diagram is the same for free and binary rotation. However, the behaviour of the eigenfunctions and proper polynomials is substantially different. In the case of free rotation, each rotational level, except the ground-state level, is degenerate. The multiplicity of the degeneracy is determined by the quantum number of the angular momentum. In the case of binary rotation, only one proper polynomial belongs to each rotational level, if one representation of the SO(4) group is sufficient for the solution of the problem. If two or several representations are used, then some rotational levels become degenerate, and the ground rotational state has the highest degeneracy.

The interaction of a molecule with an external electric field via the quadrupole moment imparts an additional energy of different signs to the rotational levels only in the case of binary rotation. The energy addition due to the quadrupole moment can be comparable to the rotational energy of the molecule.

The two representations of the rotation of a polyatomic molecule can be simply described as follows. In the case of free rotation, there exist two coordinate systems and the reversion operation, which transforms the rotational Hamiltonian and wave functions from one coordinate system to another. This transformation does not lead to any con-

servation law and therefore it is neglected in the common treatment of rotational motion. In the case of binary rotation, there exist one coordinate system and one Hamiltonian, which is invariant with respect to the reversion operation, so that the concept of parity can be introduced. The rotational energy of the molecule and the proper polynomials of the rotational Hamiltonian can be classified in the case of binary rotation in the same way as in atomic spectroscopy.

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