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RE-155

ROTATIONAL ENERGY LEVELS OF ASYMMETRIC TOP MOLECULES PART I: DISCUSSION OF THE THEORY

March 1962

Grumman
RESEARCH DEPARTMENT

GRUMMAN AIRCRAFT ENGINEERING CORPORATION
BETHPAGE NEW YORK

Grumman Aircraft Engineering Corporation

Research Department

Research Report RE-155

ROTATIONAL ENERGY LEVELS OF ASYMMETRIC TOP MOLECULES PART I: DISCUSSION OF THE THEORY

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ABSTRACT

The theory of rotational energy levels of symmetric and asymmetric top molecules is outlined herein. An expression is derived for the energy levels of symmetric tops, and the difficulties of finding exact energy values for asymmetric tops are discussed.

A table of reduced energies, from which the rotational energy levels of any asymmetric top molecule can be simply calculated to seven significant figures is given for values of rotational quantum number J from 1 to 5, and values of the asymmetry parameter κ from 0 to 1 in steps of 0.001. This table is useful in the accurate prediction of frequencies of rotational transitions, chiefly in the microwave region. It can also be used to determine the atomic configurations of molecules and the effects of interaction of rotational states with vibrational and electronic states. Molecules with energy level schemes suitable for design of maser devices to amplify frequencies in the infrared, millimeter, or microwave regions, can be selected by means of this table.

The table appears as Part II of this report.

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INTRODUCTION

The table published herein has been prepared, in connection with the Molecular Physics Project of Grumman's Research Department, as part of a broad study of rotational and vibrational energy levels of several classes of organic gas molecules. This table makes it possible to calculate with unprecedented accuracy the rotational energy levels of any asymmetric top molecule, provided that the molecular structure is known. Conversely, from experimental determination of the energy levels, such quantities as the moments of inertia, bond lengths, and bond angles of a given molecule can be determined very accurately.

Studies of the infrared and microwave spectra of some asymmetric top molecules, now in progress at Grumman, are expected to yield fundamental information about the configuration of these molecules and their rotational and vibrational stationary energy states. With this information, it should be possible to devise a means of overpopulating the higher energy levels and stimulating emission of radiation in the infrared, millimeter, or microwave regions of the spectrum by means of the maser principle.

DISCUSSION

General (Refs. 1,2,3,4)

Transitions between rotational states of gas molecules usually give rise to line spectra in the microwave region. The frequencies of these spectral lines can be measured with great accuracy. If the energy of the stationary states can be determined from these measurements, and if expressions for the energy in terms of the physical parameters (bond lengths, bond angles, and atomic masses) can be derived, then a precise determination of these parameters can be made. Values of bond lengths and mass ratios have been obtained by this method to an accuracy of 1 part in 10^4 or better.

Molecules may be classified dynamically as spherical tops, symmetric tops, or asymmetric tops, depending on the configuration of their nuclei. The moment of inertia I about any axis is defined by

$$I = \sum_i m_i r_i^2 \qquad (1)$$

where m_i is the mass and r_i the distance from the axis of the i^{th} nucleus. The locus of $I^{-\frac{1}{2}}$ plotted along axes passing through the center of gravity is an ellipsoid, called the inertial ellipsoid, whose equation (Ref. 4) is

$$I_x x^2 + I_y y^2 + I_z z^2 = 1 \quad , \qquad (2)$$

where I_x, I_y and I_z, are the principal moments of inertia. The inertial ellipsoid is fixed in the body and rotates with it, providing a convenient device for describing rotational motion in rigid bodies.

The most important parameters in a description of rotational motion of molecules are the three principal moments of inertia. If two of these moments are equal, the molecule is classed as a symmetric top. This class includes all diatomic molecules and polyatomic linear molecules, as well as molecules having an axis of n-fold symmetry with $n > 2$. In the latter case, a rotation through $2\pi/n$ radians about the symmetry axis leaves the inertial ellipsoid unchanged. Molecules having three unequal principal moments of inertia are called asymmetric tops. This type, which includes the majority of naturally occurring molecules, has the most complicated system of energy levels and microwave spectra.

The rotational properties of asymmetric tops can best be understood in relation to those of symmetric tops; that is, the energy levels for the asymmetric case fall between those of the two limiting symmetric cases, the prolate and the oblate tops.

Symmetric Top Molecules (Refs. 1,2,3,5,6)

The prolate symmetric top molecule is elongated so that its moment of inertia about the symmetry axis is smaller than the two equal moments. The oblate symmetric top is flattened so that the two equal moments are smaller than the moment about the symmetry axis.

According to classical mechanics, (Ref. 2) the total angular momentum $\vec{P}$ of a body, in the absence of external forces, has a direction and magnitude fixed in space. $\vec{P}$ is not fixed in the body however. Instead, the top rotates about its symmetry axis with angular momentum $\vec{P}_z$, while the symmetry axis precesses with constant angular velocity around the direction of $\vec{P}$.

According to quantum mechanics (Refs. 1,2,3), $\vec{P}$ is quantized, taking on values given by

$$|P| = [J(J+1)]^{\frac{1}{2}} \frac{h}{2\pi} \qquad (3)$$

where h is Planck's constant and J is the angular momentum quantum number, taking on only integral positive values, starting

with zero. Likewise, $\vec{P}_z$ is quantized, taking on values given by

$$|P_z| = \frac{Kh}{2\pi} \qquad (4)$$

where $K = J, J-1, J-2, \ldots, -J$.

The energy of rotation W is given classically (Ref. 1) by

$$W = \tfrac{1}{2} I_x \omega_x^2 + \tfrac{1}{2} I_y \omega_y^2 + \tfrac{1}{2} I_z \omega_z^2$$

$$= \frac{P_x^2}{2I_x} + \frac{P_y^2}{2I_y} + \frac{P_z^2}{2I_z} \quad . \qquad (5)$$

According to convention, the principal moments of inertia of symmetric and asymmetric rotors are labelled I_A, I_B and I_C, such that $I_A \leq I_B \leq I_C$. If z is the direction of the symmetry axis, and x and y the directions of the other two axes of the inertial ellipsoid, then for an oblate symmetric top

$$I_y < I_z$$

$$I_x = I_y = I_A = I_B \qquad (6)$$

$$I_z = I_C \quad .$$

Also

$$P^2 - P_z^2 = P_x^2 + P_y^2 \qquad (7)$$

so that

$$W = \frac{P^2}{2I_B} + P_z^2 \left\{\frac{1}{2I_C} - \frac{1}{2I_B}\right\} . \qquad (8)$$

Three rotational constants are defined (Ref. 1) as:

$$A = \frac{h}{8\pi^2 I_A} , \quad B = \frac{h}{8\pi^2 I_B} , \quad C = \frac{h}{8\pi^2 I_C} \qquad (9)$$

and Eq. (8) becomes

$$\frac{W}{h} = BJ(J+1) + (C-B)K^2 \qquad \text{(oblate top)} . \qquad (10)$$

For a prolate top, the energy equation takes the form of Eq. (10), but has A in place of C. It can be seen from Eq. (10) that the energy is independent of the sign of K. Thus there are J+1 different values of energy for each value of J.

The rules for allowed transitions between rotational energy levels (selection rules) can be derived in a semiclassical fashion (Refs. 1,2,3). A molecule can absorb or radiate microwave energy only if it has an electric dipole moment which can interact with the radiation field. In symmetric top molecules the dipole moment must be aligned with the symmetry axis. Thus the torque due to the interaction can not have a component along the symmetry axis, and $\vec{P}_z$ (or K) can not be changed by a transition. Only the precessional energy of the molecule can be altered by interaction with the radiation field. The minimum allowable change in total angular momentum $\vec{P}$ corresponds to a change of one unit in the quantum number J, so that the selection rules for a transition between rotational energy states become

$$\Delta J = \pm 1$$

$$\Delta K = 0 . \qquad (11)$$

The frequency observed for a transition from quantum number J to J + 1 (Ref. 1) is

$$\nu = \frac{W_{J+1} - W_J}{h} = 2B(J+1) \ . \qquad (12)$$

For an oblate top B is greater than C in Eq. (10), so that the energy of levels with the same J decreases for increasing |K|. For a prolate top A is greater than B, and W increases for increasing |K|. This is represented schematically in Fig. 1 (redrawn from Ref. 1), for levels corresponding to J = 3 and K = 0, 1, 2, and 3. The meaning of J_τ, κ, and $J_{K_{-1}; K_1}$ will be explained later.

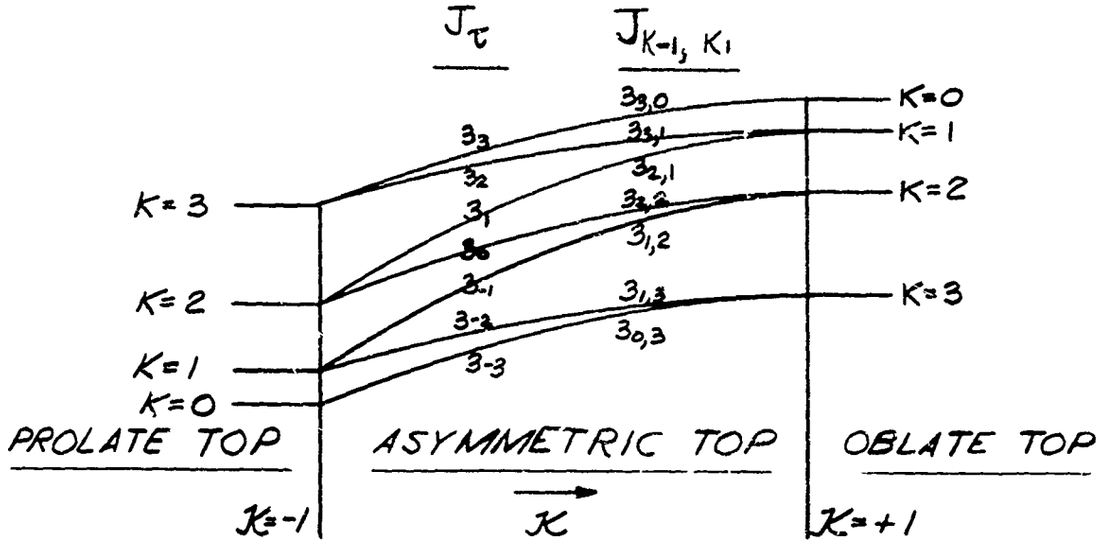

Fig. 1. Energy Levels of Symmetric and Asymmetric Top Molecules for J = 3.

The derivation of the quantum conditions for a symmetric top (Refs. 1, 5, 6) will now be outlined. The wave equation is written

$$H \Psi_i = E_i \Psi_i \tag{13}$$

where H is the Hamiltonian operator and E_i and Ψ_i are the total energy and the wave function of the i^{th} state, respectively. The total energy E_i consists of 5 terms (Refs. 1, 5, 6).

$$E_i = T + V + U + 0 + R \tag{14}$$

representing, respectively, the translational kinetic energy T, the internuclear potential energy V, the electronic energy U, the vibrational energy 0 and the rotational energy R. In general the variables cannot be separated and the wave equation cannot be solved exactly. It can, however, be shown that to a first approximation the rotational transitions are not affected by the other energy states, at least for the lower rotational and vibrational states, so that no interaction terms involving rotation need be written in the Hamiltonian. The translational energy is due to motion of the center of mass and may be treated separately (Ref. 6). In the ground vibrational state, the average internuclear distances do not change during rotation of the molecule, at least to a first approximation, so that V and 0 remain constant. Furthermore, the electronic motion is so fast that the electronic wave function does not change significantly as the nuclei rotate. This last approximation is due to Born and Oppenheimer (Ref. 1, 5), and holds only for the lower rotational and vibrational states. Therefore, the Hamiltonian operator can be written as a sum of separate terms and the wave function as a product of separate terms, allowing the rotational variables to be separated and the rotational wave equation to be written independently. This is most conveniently accomplished in terms of Euler's angles ϕ, θ, and χ (Ref. 1) which give the orientation of the body axes relative to those in the fixed coordinate system. The time-independent rotational wave equation in terms of Euler's angles (Ref. 1) is

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}+\left(\frac{\cos^2\theta}{\sin^2\theta}+\frac{C}{B}\right)\frac{\partial^2\Psi}{\partial\chi^2}$$

$$-\frac{2\cos\theta}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\chi\,\partial\phi}+\frac{W}{hB}\Psi=0 \qquad (15)$$

where W is the energy and Ψ the wave function. Physically significant solutions are possible only for certain discrete values W_J, with corresponding wave functions Ψ_J.

The variables here may be separated, and Ψ written in the form

$$\Psi = \Theta(\theta)\, e^{iM\phi}\, e^{iK\chi} \qquad (16)$$

where M and K must be integers $0, \pm1, \pm2$, for Ψ to be single-valued. $\Theta(\theta)$ is a power series which must terminate and become just a polynomial in order for the wave function to be normalized (Ref. 1), i.e., the integral of $|\Psi|^2$ over all space made equal to unity. From this condition, an expression

$$\frac{W}{h} = BJ(J+1) + (C-B)K^2 \qquad \text{(oblate top; } B > C\text{)} \qquad (17)$$

for the energy can be derived. This is just Eq. (10), previously derived by a semiclassical argument. The analytical expression for J requires that it be a positive integer, equal to or larger than $|K|$ or $|M|$.

$$\therefore J = 0, 1, 2, \ldots$$

$$K = 0, \pm1, \pm2, \ldots, \pm J$$

$$M = 0, \pm1, \pm2, \ldots, \pm J \ . \qquad (18)$$

The expressions for the angular momenta, Eqs. (3) and (4), are derived from the solutions Eq. (16) to the wave equation.

In addition to quantum numbers K and J, a third quantum number M appears. This represents the component of $\vec{P}$ along an arbitrary axis, such as that introduced by a magnetic field. In the absence of such a field, the energy levels for different M are degenerate.

Asymmetric Top Molecules (Refs. 1,2,3,7,8,9,10)

Since asymmetric top molecules do not have an axis of symmetry, there is no preferred direction which carries out a simple rotation around the total angular momentum $\vec{P}$. Although $\vec{P}$ is still quantized, and the quantum number J is defined, the quantum number K and the selection rule $\Delta K = 0$ cease to have meaning. The approximate energy levels are derived using the symmetric top wave functions as a basis, but derivation of the exact levels is very difficult in the general case, since they cannot be represented by an explicit formula analogous to that for the symmetric top (Refs. 1, 2, 3, 7). Furthermore, the interactions which were neglected in deriving the levels for the symmetric top are more significant for the asymmetric top (Refs. 1, 2, 7). Despite these difficulties, however, the effort involved is well worth while; it has already made possible the determination, by microwave techniques, of many asymmetric molecule structures.

Although the quantum number K has no meaning for the asymmetric top there are still 2J+1 energy levels for each value of J, just as for the symmetric top (Ref. 1, 2, 7). The degenerate levels of the symmetric case are separated; each level of the asymmetric top has a different energy. For slight deviations from the symmetric top the splitting of the levels is slight, the quantum number K is approximately defined and the energy levels may be obtained by perturbation methods. In the more general case, however, there is no quantum number with any physical meaning to distinguish between the 2J+1 levels of equal J (Ref. 7). The sublevels are labelled simply as

$$J_\tau \quad (\tau = -J, -J+1, -J+2, \ldots +J)$$

in order of increasing energy, the lowest level being J_{-J}, the next J_{-J+1}, and so on up to J_J. An expression for the energy levels has been derived by King, Hainer, and Cross (Ref. 8).

$$W = \tfrac{1}{2}(A+C)J(J+1) + \tfrac{1}{2}(A-C)E_\tau \qquad (19)$$

where A, B, and C are the rotational constants defined in Eq. (9). E_τ is a numeric, called the reduced energy, which is a function of J and of an asymmetry parameter κ, defined by Ray (Ref. 9) as

$$\kappa = \frac{2B - A - C}{A - C} . \qquad (20)$$

For a prolate top, $\kappa = -1$, and for an oblate top, $\kappa = +1$.

The behavior of the asymmetric top energy levels is shown in Fig. 1. These levels lie between those of the two symmetric tops, their position depending on the relationship of the intermediate moment of inertia I_B to I_A and I_C. Specifically, a given asymmetric top level connects a K level (designated K_{-1}) of the limiting prolate top ($I_B = I_C$) with a K level (designated K_1) of the limiting oblate top ($I_B = I_A$). This leads to an alternate designation for each J_τ level as J_{K_{-1},K_1}, and for each reduced energy E_τ as E_{K_{-1},K_1}. Both designations are currently used in the literature. For example, the third lowest level in Fig. 1 connects the level $K_{-1} = 1$ with $K_1 = 2$. Thus in the K_{-1}, K_1 designation it is the $J_{1,2} = 3_{1,2}$ level. The reduced energy is designated $E_{1,2}$. The levels for the same J and for different E_{K_{-1},K_1} do not cross each other.

The 2J+1 values of E_τ for a given J are the roots of a secular determinant (Ref. 7) of degree 2J+1, obtained by the application of group theory to the symmetry properties of the molecule. The determinant can be factored into a number of determinants of smaller degree, leading to a number of algebraic equations in each case. Some of these equations are listed in various texts (Refs. 1, 2, 7). Their degree increases with increasing J, however, so that calculation of the E_τ values is extremely difficult.

Tables of Reduced Energy Values (See Part II of this report)

Numerical values of E_τ have been tabulated (Ref. 1,8,10) for values of κ in steps of 0.01 and for values of J up to 12. In these previous tables the intervals of κ are not small enough for microwave work; interpolation does not give the required accuracy (Refs. 1, 2). To correct this situation, the present table, giving E_τ values for intervals of 0.001 in κ, sufficiently close for accurate interpolation (Ref.10), has been prepared. This table, which is the first part of a larger effort, gives the reduced energy values E_τ, computed by the IBM 704, for J = 1 to J = 5. It is presently planned, with the aid of the IBM 7090, to extend this table to include values of J from 6 to 12. This addition will be published at a later date.

Strictly speaking, these E_τ values are a first approximation, valid only at lower J values (no centrifugal distortion), and lower vibrational and electronic states. In their derivation two assumptions were made; that the molecule is a rigid body, and that the interaction of the rotational states with electronic and vibrational states is negligible. The validity of the approximation, therefore, depends strongly on the molecule considered; for many molecules it leads to accurate prediction of line frequencies (Ref. 1, 2, 7). In other cases, comparison with experimental results is useful in giving the magnitude of the effects neglected in the approximation, so that the theory can be extended (Ref. 2).

The number of significant figures in κ probably needs to be no more than three, since the rigid rotor is only an approximation (Ref.10).

In microwave spectra, the positions of spectral lines can be measured to six significant figures. Thus if the rigid rotor is used as a first approximation, the energy levels should be calculable to one more place, i.e. seven significant figures. The numbers in this table, as in the previously published tables (Refs. 1, 10), have been calculated to this accuracy, which, in general, means five decimal places. Additional figures printed by the machine are meaningless, having been included only because of the physical difficulty of blocking them out.

To calculate the energy of a rotational level for a given asymmetric top molecule, one must first select from the table the E_τ value corresponding to the desired J and κ values. Interpolation may be used if necessary. For negative κ values, E_τ can be found from the relation (Ref. 9)

$$E_\tau (\kappa) = E_{-\tau} (-\kappa) \quad . \tag{21}$$

Substitution in Eq. (19) gives the energy of the level.

CONCLUSION

This table should prove valuable in predicting the frequencies of spectral lines for asymmetric top molecules, in determining molecular structures and other parameters, and in selecting molecules suitable for maser operation in any given region of the spectrum.

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