"FORBIDDEN" TRANSITIONS IN MOLECULAR VIBRATIONAL-ROTATIONAL SPECTROSCOPY

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Dedicated to the memory of M. R. Aliev.

A review is given of the "forbidden" (more precisely: "perturbation allowed") transitions between molecular vibrational-rotational states including transitions which are induced by the electric dipole and quadrupole moments and the magnetic dipole moment. The basic theory of these transitions is outlined starting with the overall symmetry selection rules, followed by the discussion of the spin statistics isomers, approximate selection rules for the usual vibrational-rotational transitions, and forbidden transitions induced by the electric quadrupole and magnetic dipole moments. Forbidden transitions due to the vibrationally and rotationally induced electric dipole

moments are then discussed in detail for symmetric top and spherical top molecules with the emphasis on the physical nature of the various phenomena leading to these transitions. A summary is also given of the most important experimental work on the forbidden transitions in diatomic molecules and polar as well as nonpolar polyatomics.

1. INTRODUCTION

In spectroscopy, we mean by "forbidden" transitions such radiative transitions between quantum states of microscopic objects (e.g., atoms or molecules) which do not obey selection rules obtained in a certain lower order approximation.

The division of transitions into "allowed" and "forbidden" is of course artificial because it is related to our theoretical models rather than to the processes which occur in real physical systems. Actually, no transition in a real molecule (or atom) is strictly forbidden: if we consider sufficiently high order interactions, both time--dependent and time-independent, we obtain selection rules for all the transitions between the quantum states of a microscopic object.

Usually a quantum transition, which can occur due to higher order interactions, gives rise to spectrum lines with intensities that are lower than those arising through stronger interactions. Thus one could expect that the spectrum lines corresponding to allowed transitions will be stronger than lines of the forbidden transitions. However, as the experimental technique develops (increasing sensitivity and resolution), we can study more and more "forbidden" transitions, and from the experimentalist's point of view, the difference between "allowed" and "forbidden" transitions may not be sharp.

Nevertheless, it is useful to preserve the concept of "allowed" and "forbidden" transitions for several reasons. First of all, there are transitions which become allowed only through extremely weak interactions. Their intensity is therefore so small that we do not have a chance to detect them by any experimental technique now available and we will not be able to detect them in the foreseeable future. It is therefore appropriate to call them "strictly" forbidden.

Furthermore, it is well known that spectrum lines which correspond to the "allowed" transitions in axially symmetric molecules (and which in most cases are the most prominent lines in the spectrum) do not always provide a full information on the molecular parameters such as the rotational or centrifugal distortion constants.

For example, selection rules for the rotational quantum numbers J and k are $\Delta J = 0, \pm 1$ and $\Delta k = 0$ for a parallel vibrational-rotational band in symmetric top molecules (see, e.g., ref.[1] or Part 6 of this paper). These "allowed" transitions provide information on the rotational constants B_x, B_y but not on B_z or on the centrifugal distortion constants D_K, H_K etc. As a result of the centrifugal distortion of a rotating molecule, some other transitions may become weakly allowed, however, and these transitions can provide the missing information on the parameters B_z,

D_K, H_K etc. (e.g., the $\Delta k = \pm 3$ "forbidden" transitions in molecules of C_{3v} symmetry, see refs[2-5] and Fig. 1).

An extreme example of this situation are the purely rotational spectra of molecules with tetrahedral symmetry (e.g., methane CH_4). Because there is no permanent electric dipole moment in these molecules, there are no rotational transitions allowed according to the zeroth order theory and no information can be obtained on the molecular structural parameters from these transitions simply because they are missing in the spectra. However, as the molecule rotates in space, centrifugal distortion induces a small dipole moment in the molecule which allows very weak purely rotational spectra (cf., e.g., ref.[6]).

Forbidden transitions have frequently played an important role in the history of molecular spectroscopy, primarily because of the unique information on molecular properties which they provided. With the rapidly developing experimental techniques of the high resolution molecular spectroscopy, the importance of their investigation can be expected to be steadily increasing.

It might therefore be useful to summarize the present state of our investigations of "forbidden" transitions. Previous reviews of this problem have been written by Oka[7] who concentrated on the rotational spectra mainly from the experimentalist's
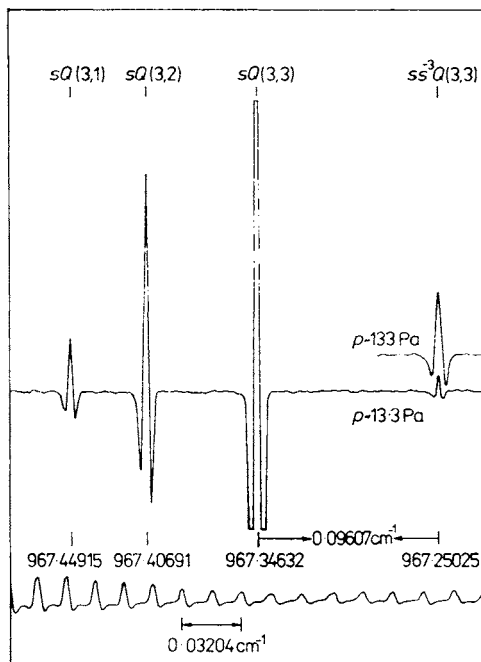

FIG. 1

Allowed ($\Delta J = 0$, $\Delta k = 0$; $sQ(J, K)$ lines) and forbidden ($\Delta J = 0$, $\Delta k = -3$; $ss^{-3}Q(3, 3)$ line) transitions in the ν_2 band of $^{14}NH_3$ (ref.[4])

point of view and by Aliev[8] who described some aspects of the theory of "forbidden" transitions. The basic theory of these transitions can also be found in monographies[1,9].

In the present review, the problem of forbidden transitions will be discussed with the emphasis on the physical nature of the various phenomena leading to the forbidden transitions in the rotational as well as vibrational-rotational spectra of molecules. In order to keep the manuscript on a manageable number of pages, we do not discuss here all the aspects of the problem. First of all, we consider molecules as isolated systems, i.e., we do not discuss transitions induced by collisions. We will also confine the discussion to the quantum processes which are due to the interaction between electromagnetic radiation and electric and magnetic moments of a molecule. We shall not therefore discuss the selection rules for Raman active transitions, partly because typical forbidden transitions have not been systematically studied in Raman spectra (cf. ref.[3]). This is probably because there are problems with measuring weak transitions in Raman spectroscopy; with the increasing sensitivity of Raman techniques one can, however, expect new results probably in the near future (see refs[10,11] as for the theory of the "forbidden" pure rotational Raman spectra of C_{3v} and T_d molecules and ref.[12] as for the theory of "forbidden" vibration-rotation Raman spectra of C_{3v} molecules).

Finally, we will not discuss here in detail selection rules for "allowed" and "forbidden" transitions for molecules in electric and magnetic fields. Instead of this, we will outline in Appendix general conditions specifying which rovibronic states can be mixed by a Stark or Zeeman effect. This almost immediately reveals how the results of the discussion of the "field-free" selection rules can be extended to molecules in electric or magnetic fields.

Because "forbidden" transitions are induced by perturbations (either time-dependent or time-independent or both), they are called perturbation allowed transitions. This is certainly a more appropriate but also a longer name, and we will simply call them forbidden transitions in further discussion.

2. ELEMENTARY FACTS ABOUT THE INTERACTION OF ELECTROMAGNETIC RADIATION WITH MOLECULES

Transitions between different quantum states of a molecule are the results of the time evolution of the molecular system due to its nondestructive interaction with electromagnetic radiation. For an isolated molecule, such processes can be described by the time-dependent Schrödinger equation (see, e.g., ref.[13])

$$\frac{ih}{2\pi} \frac{\partial \psi}{\partial t} = \mathscr{H}\psi , \qquad (2.1)$$

where ψ is the complete wavefunction depending on the spatial and spin coordinates of the particles (atomic nuclei and electrons) and on the time t.

Let us suppose that the Hamiltonian $\mathscr{H}$ can be written as a sum of two terms: $H(q, s)$ which depends on the spatial coordinates q and spin coordinates s and H' which is a time dependent term

$$\mathscr{H} = H(q, s) + H'(q, s, t) . \qquad (2.2)$$

The wavefunction which is the solution of the Schrödinger equation (2.1) can be written as an expansion in terms of φ_n, the eigenfunctions of $H(q, s)$, in the form

$$\psi(q, s, t) = \sum_n c_n(t) \, \varphi_n(q, s) , \qquad (2.3)$$

where the expansion coefficients c_n are functions of time and φ_n can be written as

$$\varphi_n(q, s) = e^{-(2\pi i E_n/h)t} \Phi(q, s) . \qquad (2.4)$$

By substituting from Eqs. $(2.2)-(2.4)$ into Eq. (2.1), we obtain (cf. ref.[13])

$$\frac{ih}{2\pi} \frac{dc_m}{dt} = \sum_n c_n(t) \, e^{-(2\pi i/h)(E_n - E_m)t} \langle \Phi_m | H' | \Phi_n \rangle , \quad m = 1, 2, \ldots \qquad (2.5)$$

Equations (2.5) represent a set of coupled differential equations for the coefficients $c_n(t)$ as unknowns. By solving these equations, we determine the complete wavefunction ψ [Eq. (2.1)]. According to quantum mechanics, the probability of a transition from the state Φ_n to any other state Φ_m is then determined by the value of $|c_m|^2 = c_m^* c_m$.

It is convenient to introduce certain approximations in solving Eqs (2.5). According to the time-perturbation theory, we consider H' as a perturbation to $H(q, s)$; if this perturbation is small and acts in a time interval from $t = 0$ upto t_1 which is not too long, we can use the first approximation, according to which Eq. (2.5) becomes

$$\frac{ih}{2\pi} \frac{dc_m}{dt} = e^{-(2\pi i/h)(E_n - E_m)t} \langle \Phi_m | H' | \Phi_n \rangle , \quad m = 1, 2, 3, \ldots \qquad (2.6)$$

In this approximation, we have for c_m:

$$c_m(t_1) = c_m(0) - \frac{2\pi i}{h} \int_{t=0}^{t_1} e^{-(2\pi i/h)(E_n - E_m)t} \langle \Phi_m | H' | \Phi_n \rangle \, dt , \quad m = 1, 2, 3, \ldots \qquad (2.7)$$

with $c_m(0) = \delta_{mn}$.

Let us now consider in more detail the time-dependent perturbation **H'**. We first recall that according to the Maxwell theory, light is a transverse electromagnetic wave with the vibrating electric vector **E** always perpendicular to the magnetic vector **B**.

The electric and magnetic fields of the radiation will interact with the electrons and atomic nuclei of the molecule to give a time-dependent perturbation **H'** [cf. Eq. (2.2)]. In the semiclassical approach, the potential energy of interaction between a system of charged particles (atomic nuclei and electrons) and the electric field that points in an arbitrary direction is (see, e.g.[14,15])

$$\mathbf{H}'_E = \sum_{F=X,Y,Z} \mathbf{H}'_{E,F} = - \sum_{F=X,Y,Z} \sum_s e_s F_s E_{F_s}, \tag{2.8}$$

where e_s and $F_s = X_s,\ Y_s,\ Z_s$ are the charge and coordinate of the s-th particle of the molecule (electrons, atomic nuclei).

For a light travelling in the Z direction, we have the following expression for the space and time variations of the components E_{F_s} of the electric vector **E**:

$$E_{F_s} = E_F^0 \cos\left(\omega t - 2\pi Z_s / \lambda\right), \quad F = X, Y, Z. \tag{2.9}$$

where $\omega = 2\pi\nu$ and $\lambda = c/\nu$ is the wavelength of the radiation.

The size of molecules is about 10^{-10} m and $\lambda \doteq 10^{-5}$ m for the infrared spectrum region. The spatial variation of the radiation's electric field (due to Z_s/λ) is therefore very small. If we expand $\cos\left(\omega t - 2\pi Z_s/\lambda\right)$ as a power series in the small quantity $2\pi Z_s/\lambda$ and substitute into Eq. (2.8), we obtain for $\mathbf{H}'_{E,F}$

$$\mathbf{H}'_{E,F}\left(\equiv \sum_{r=0}^{\infty} \mathbf{H}^{(r)}_{E,F}\right) = -E_F^0 \sum_s e_s F_s \sum_{r=0}^{\infty} \frac{1}{r!}\left(-\frac{2\pi Z_s}{\lambda}\right)^r \cos\left(\omega t + r\,\pi/2\right); \tag{2.10}$$

thus for $r = 0$ we obtain the time-dependent perturbation in the electric dipole moment approximation

$$\mathbf{H}^{(0)}_{E,F} = -E_F^0 \sum_s e_s F_s \cos\left(\omega t\right) = -E_F^0 \mu_F^{(e.d.)} \cos\left(\omega t\right), \quad F = X, Y, Z \tag{2.11}$$

where $\mu^{(e.d.)}$ is the vector of the electric dipole moment whose components with respect to the space-fixed Cartesian axes $X,\ Y,\ Z$ are

$$\mu_F^{(e.d.)} = \sum_s e_s F_s, \quad F = X, Y, Z. \tag{2.12}$$

For $r = 1$, the term

$$\mathbf{H}^{(1)}_{E,F} = \frac{2\pi}{\lambda} E_F^0 \sum_s e_s F_s Z_s \sin\left(\omega t\right); \quad F = X, Y, Z \tag{2.13}$$

has the physical meaning of the potential energy of interaction between the component $\mu_{FZ}^{(e.q.)}$ of the molecular electric quadrupole defined as

$$\mu_{FZ}^{(e.q.)} = \sum_s e_s F_s Z_s \qquad (2.14)$$

and the electric field.

Note that while the electric dipole moment is a vector, the electric quadrupole moment is a tensor of the second rank having nine components $\mu_{XX}^{(e.q.)}$, $\mu_{XY}^{(e.q.)}$, $\mu_{XZ}^{(e.q.)}$, $\mu_{YX}^{(e.q.)}$, ... (see also Fig. 2).

So far we discussed the interaction between the molecular electronic moments and the electric field of the electromagnetic wave. Orbital motions of electrons and atomic nuclei induce a molecular magnetic moment which interacts with the magnetic field of the light wave. There is also a magnetic moment associated with the spins of the electrons and atomic nuclei. Therefore the component of the magnetic moment $\mu^{(m)}$ with respect to the space-fixed axis F can be written as

$$\mu_F^{(m)} = \sum_s \frac{e_s}{2m_s c} \left(l_{F,s} + g_s s_{F,s} \right), \qquad (2.15)$$

where m_s is the mass of the s-th particle, i.e. an atomic nucleus or electron; $l_{F,s}$ is the component of the orbital angular momentum of the s-th particle, for example

$$l_{X,s} = -\frac{i\hbar}{2\pi} \left(Y_s \frac{\partial}{\partial Z_s} - Z_s \frac{\partial}{\partial Y_s} \right) \qquad (2.16)$$

and $s_{F,s}$ is the spin momentum of the s-th particle (g_s is close to 2 for electrons).
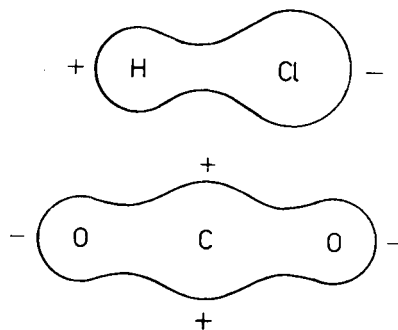

FIG. 2

Illustration of the electric dipole moment in the molecule HCl and of the electric quadrupole moment in CO_2

The potential energy of interaction between the molecular magnetic moment and the magnetic field **B** is

$$\mathbf{H}_B' = \sum_{F=X,Y,Z} \mathbf{H}_{B,F}' = -\sum_{F=X,Y,Z} \sum_s \frac{B_{F_s} e_s}{2 m_s c} \left(l_{F,s} + g_s s_{F,s} \right), \tag{2.17}$$

where for a light travelling in the Z direction, we have the following expression for the components B_{F_s} of the magnetic vector **B** with respect to the space fixed axes X, Y, Z:

$$B_{F_s} = B_F^0 \cos \left(\omega t - 2\pi Z_s / \lambda \right). \tag{2.18}$$

In analogy with Eq. (2.11), we can write

$$\mathbf{H}_{B,F}^{(0)} = -B_F^0 \mu_F^{(m)} \cos \left(\omega t \right), \tag{2.19}$$

where we have neglected the term with Z/λ in Eq. (2.18).

If we substitute from Eq. (2.10) into Eq. (2.7), we obtain that

$$^{(F)}c_m(t_1) = \delta_{mn} + \frac{i\pi E_F^0}{h} \left\langle \Phi_m \left| \left[\sum_s e_s F_s \sum_{r=0}^{\infty} \frac{1}{r!} \left(-\frac{2\pi Z_s}{\lambda} \right)^r \right] \right| \Phi_n \right\rangle \times$$

$$\times \int_0^{t_1} e^{i\omega_{mn}t} \left[e^{i(\omega t + r\pi/2)} + e^{-i(\omega t + r\pi/2)} \right] \mathrm{d}t, \tag{2.20}$$

where

$$\omega_{mn} = 2\pi(E_m - E_n)/h. \tag{2.21}$$

It can be shown (see, e.g., ref.[14]) by evaluating the second integral on the right-hand side of Eq. (2.20) that a transition between the states Φ_n and Φ_m can have a significant probability only if

$$E_m - E_n = \pm h\nu, \tag{2.22}$$

where the upper sign holds for absorption $(E_m > E_n)$ and the lower one for emission $(E_m < E_n)$. An analogous result would be obtained for the transition induced by the magnetic moment.

Eq. (2.22) represents a necessary condition for a quantum transition but not sufficient. This is obvious from the form of the terms standing before the integral on the right-hand side of Eq. (2.20). E_F^0 depends on the intensity of the incident radiation and it is always different from zero in the absorption spectroscopy (quantum field theory predicts spontaneous emission of atoms or molecules which occurs in the absence of external fields). The most interesting term, however, is the matrix element

$$\left\langle \Phi_m \left| \left[\mu_F^{(e.d.)} - \frac{2\pi}{\lambda} \mu_{FZ}^{(e.q.)} + \dots \right] \right| \Phi_n \right\rangle , \quad F = X, Y, Z \tag{2.23}$$

because it describes an important molecular property.

Eq. (2.20) holds for radiation which is plane-polarized in the F (say $F = X$) direction. If the radiation is isotropic, we also get contributions from the Y and Z directions:

$$|c_m|^2 \; (\equiv c_m^* c_m) = 2\pi t_1 \left[|\langle \Phi_m | \, \mu_X | \Phi_n \rangle|^2 + |\langle \Phi_m | \, \mu_Y | \Phi_n \rangle|^2 + \right.$$
$$\left. + |\langle \Phi_m | \, \mu_Z | \Phi_n \rangle|^2 \right] u(\nu_{mn}) . \tag{2.24}$$

Eq. (2.24) gives the probability that any one molecule will make a transition to state Φ_m from Φ_n after having been irradiated for a time t_1 with a radiation of energy per unit volume per unit frequency $u(\nu_{mn})$. Note that the number of transitions from the state Φ_n to Φ_m per second (i.e., the transition rate) is given by Eq. (2.24) multiplied by N_n and divided by t_1, where N_n is the number of molecules in state Φ_n.

If we neglect the quadrupole and higher order terms (see below), the three contributions in Eq. (2.24) are equal. Thus in the dipole moment approximation, it is sufficient to consider the properties of only one transition moment, say $\langle \Phi_m | \, \mu_Z^{(e.d.)} | \Phi_n \rangle$, because all the results also remain valid for the other two contributions.

The matrix elements of the electric dipole moment $\mu_F^{(e.d.)}$, electric quadrupole moment $\mu_{FF}^{(e.q.)}$ and of the magnetic dipole moment $\mu_F^{(m.d.)}$ [we neglect the small term Z/λ on the right-hand side of Eq. (2.18)], i.e.

$$\langle \Phi_m | \, \mu_F^{(e.d.)} | \Phi_n \rangle, \; \langle \Phi_m | \, \mu_{FF}^{(e.q.)} | \Phi_n \rangle, \; \langle \Phi_m | \, \mu_F^{(m.d.)} | \Phi_n \rangle \tag{2.25}$$

are called transition moments.

The integrated absorption coefficient for an electric dipole moment transition $\Phi_m \leftarrow \Phi_n$ is given by the relationship

$$\int \alpha_\nu \, d\nu = \frac{8\pi^3 N_0 \nu_{mn} \exp\left(-E_n/kT\right) \left[1 - \exp\left(-h\nu_{mn}/kT\right)\right]}{3hcQ} S_{mn} , \tag{2.26}$$

where a Boltzman distribution with temperature T is assumed, N_0 is the number of molecules per unit volume, ν_{mn} is the frequency of the corresponding transition (in the same units as $d\nu$), Q is the partition function and S_{mn} the linestrength given by

$$S_{mn} = \sum_{F, \mu, \nu} |\langle \Phi_{m\mu} | \, \mu_F^{(e.d.)} | \Phi_{n\nu} \rangle|^2 , \tag{2.27}$$

where μ and ν are the degenerate components of the state Φ_m and Φ_n.

Analogous expressions would be obtained for the linestrengths of transitions induced by the electric quadrupole or magnetic dipole moment. The value of Z/λ [cf. the text following Eq. (2.9)] is of the order of magnitude 10^{-5} and the electric quadrupole contribution to the intensity of the vibrational-rotational lines should be a factor of approximately 10^{-10} smaller than that of electric dipole moment [because of the different inversion parity selection rules, however, these contributions never occur simultaneously (see Parts 4 and 5)]. It can be also shown that the intensity of magnetic dipole transitions should be a factor of approximately 10^{-8} up to 10^{-10} smaller than that of the electric dipole moment transitions[14].

3. VARIOUS APPROXIMATIONS TO THE TIME-DEPENDENT AND TIME-INDEPENDENT MOLECULAR INTERACTIONS

It has been already mentioned that the division of quantum transitions into "allowed" and "forbidden" depends on the way how we decide to classify the contributions to the various terms in the Hamiltonian $\mathscr{H}$ [Eq. (2.2)] to the corresponding transition probabilities. For example, we can consider various electric and magnetic moments in the time-dependent part of $\mathscr{H}$ whose contributions to the transition probabilities are widely different. The same holds for the individual terms in the time-independent Hamiltonian $\mathbf{H}(q, s)$ [Eq. (2.2)].

We first consider various approximations to $\mathbf{H}(q, s)$ and then we will extend our discussion of the various approximations to the time-dependent part of $\mathscr{H}$.

We assume that $\mathbf{H}(q, s)$ can be separated into the electronic and nuclear parts.

$$\mathbf{H}(q, s) = \mathbf{H}_e + \mathbf{H}_{vr\,e} + \mathbf{H}_s, \qquad (3.1)$$

where $\mathbf{H}_e$ depends only on the coordinates of electrons (and the conjugate momenta) as dynamical variables and on the coordinates of the atomic nuclei as parameters; $\mathbf{H}_{vr;e}$ depends on the coordinates of the atomic nuclei (and the conjugate momenta) as the dynamical variables, and it contains the potential energy as a functional dependence of the eigenvalues of $\mathbf{H}_e$ on the internuclear coordinates for a given electronic state; $\mathbf{H}_s$ is a spin Hamiltonian which can be written separately because interactions between the spin momenta and the rovibronic (electronic, vibrational, and rotational) motions are extremely weak.

This is the well-known Born–Oppenheimer approximation (e.g., ref.[1]) which will be assumed to hold throughout the following discussion. The breakdown of this approximation in connection with the isotopic substitution has important consequencies on the transition probabilities in molecular spectra which will be mentioned later (Part 10).

In this paper, we discuss only vibrational-rotational transitions in the ground electronic state. Therefore, we omit the index e in $\mathbf{H}_{vr;e}$. It is well known[1,9] that

H_{vr} can be written for semirigid molecules in the following expanded form:

$$H_{vr} = \sum_{m,n} H_{mn} , \qquad (3.2)$$

where the first subscript in H_{mn} is the degree in vibrational operators (coordinates and momenta) and the second subscript is the degree in the components of the total angular momentum J (we will use later the symbol F for the total angular momentum to emphasize that spin momenta have been also included; see Part 5).

Pure vibrational terms in Eq. (3.5) (in cm^{-1} units) can be written as

$$H_{20} = \tfrac{1}{2}\sum_k \omega_k(p_k^2 + q_k^2) , \qquad (3.3)$$

$$H_{30} = \tfrac{1}{6} \sum_{lmn} k_{lmn}q_lq_mq_n , \qquad (3.4)$$

$$H_{40} = \tfrac{1}{24} \sum_{klmn} k_{klmn}q_kq_lq_mq_n + \sum_{\alpha=x,y,z} B_\alpha p_\alpha^2 , \qquad (3.5)$$

$$\vdots$$

where q are the dimensionless normal coordinates of vibration and p are the conjugate momenta; B_α are the rotational constants, $\omega_k/(\equiv v_k/c)$ is the wavenumber of the k-th normal vibration, k_{lmn} and k_{klmn} are the cubic and quartic force constants, respectively.

A simple physical meaning can be assigned to the individual H_{m0} in Eqs (3.3) to (3.5). For example, H_{20} is the harmonic oscillator operator, H_{30} and H_{40} describe the anharmonicity of molecular vibrations.

Similarly, we can write the terms with the rotational operators as

$$H_{02} = \sum_{\alpha=x,y,z} B_\alpha J_\alpha^2 , \qquad (3.6)$$

$$H_{12} = \sum_{\alpha,\beta} \sum_k B_k^{\alpha\beta} q_k J_\alpha J_\beta , \qquad (3.7)$$

$$H_{22} = \tfrac{3}{8} \sum_{\alpha,\beta,\gamma} \sum_{kl} B_\gamma^{-1}(B_k^{\alpha\gamma}B_l^{\gamma\beta} + B_l^{\alpha\gamma}B_k^{\gamma\beta}) q_kq_l J_\alpha J_\beta , \qquad (3.8)$$

$$H_{21} = -2\sum_{kl}(\omega_l/\omega_k)^{1/2} q_k p_l \sum_\alpha B_\alpha \zeta_{kl}^\alpha J_\alpha , \qquad (3.9)$$

$$\vdots$$

where J_α are the components of the rotational angular momentum, ζ_{kl}^α is the Coriolis coupling constant and $B_k^{\alpha\beta}$ is a molecular parameter defined as described in ref.[1].

The terms in Eqs $(3.6)-(3.9)$ have the following physical interpretation: H_{02} is the rigid rotor approximation, H_{12} and H_{22} are the centrifugal distortion operators, and H_{21} describes Coriolis interaction between rotation and vibration.

Let us now define the zeroth-order aproximation to the time-independent part of the Hamiltonian. Usually, the harmonic oscillator–rigid rotor approximation,

$$\mathbf{H}^0_{vr} = \mathbf{H}_{20} + \mathbf{H}_{02} \tag{3.10}$$

is used to derive selection rules for the allowed transitions in the dipole moment approximation (see Part 6).

The spin Hamiltonian $\mathbf{H}_s$ [Eq. (3.1)] can be considered in an extremely good approximation as a sum of the nuclear and electronic parts.

$$\mathbf{H}_s = \mathbf{H}_{s,n} + \mathbf{H}_{s,e} \,, \tag{3.11}$$

which completes the separation of the spin, electronic, vibrational, and rotational coordinates (and momenta):

$$\mathbf{H}^0_{evrs} = \mathbf{H}_e + \{\mathbf{H}_{20} + \mathbf{H}_{02}\} + \{\mathbf{H}_{s,n} + \mathbf{H}_{s,e}\} \,. \tag{3.12}$$

Thus the complete wavefunction can be written in the zeroth-approximation as a product function

$$\Phi^{(0)}_{evrs} = \Phi_e \Phi_v \Phi_r \Phi_{es} \Phi_{ns} \,, \tag{3.13}$$

where Φ_e depends on the spatial coordinates of electrons, Φ_v on the vibrational co-ordinates (the normal coordinates of vibration), Φ_r on the rotational coordinates (the Euler angles Θ, Φ, χ defining the orientation of the molecular-fixed system of axes with respect to the space-fixed system of axes); Φ_{es} depends on the electron spin coordinates and Φ_{ns} depends on the spin coordinates of the atomic nuclei.

The complete wavefunction Φ_{evrs} is called the spin-rovibronic function, $\Phi_{evr} = \Phi_e \Phi_v \Phi_r$ the rovibronic function, $\Phi_{ev} = \Phi_e \Phi_v$ the vibronic function.

We can expand the various electric and magnetic momenta in the time-dependent term $\mathbf{H}(q, s, t)$ quite analogously as we have expanded the time-independent Hamiltonian $\mathbf{H}(q, s)$ [Eq. (3.2)]. In this case, it is first convenient to express the various molecular momenta (electric or magnetic momenta, quadrupole momenta) in terms of their components with respect to the molecule-fixed axes x, y, z instead of the components with respect to the space-fixed axes X, Y, Z.

Thus the component μ_Z of the electric or magnetic dipole-moment operator μ can be expressed in terms of the components $\bar{\mu}_x$, $\bar{\mu}_y$, $\bar{\mu}_z$ of μ along the molecule-fixed axes x, y, z as

$$\mu_Z = \bar{\mu}_x \lambda_{Zx} + \bar{\mu}_y \lambda_{Zy} + \bar{\mu}_z \lambda_{Zz} \,, \tag{3.14}$$

where $\lambda_{Z\alpha}$ $(\alpha = x, y, z)$ are the direction cosines of the angles subtended by the molecule-fixed axes x, y, z and the space-fixed axis Z.

In the approximation which considers the overall wavefunctions as the product functions according to Eq. (3.13), we can write

$$\langle \Phi'_{es}\Phi'_e\Phi'_v\Phi'_r\Phi'_{ns}| \mu_Z |\Phi''_{es}\Phi''_e\Phi''_v\Phi''_r\Phi''_{ns}\rangle = \langle \Phi'_{es}| \Phi''_{es}\rangle \langle \Phi'_{ns}| \Phi''_{ns}\rangle \times$$
$$\times \langle \Phi'_e\Phi'_v\Phi'_r| \mu_Z |\Phi''_e\Phi''_v\Phi''_r\rangle \qquad (3.15)$$

because μ_Z does not depend on the spin coordinates.

By substituting from Eq. (3.14) into Eq. (3.15), we obtain

$$\langle \Phi'_e\Phi'_v\Phi'_r| \mu_Z |\Phi''_e\Phi''_v\Phi''_r\rangle = \sum_{\alpha=x,y,z} \langle \Phi'_v\Phi'_e| \bar{\mu}_\alpha |\Phi''_e\Phi''_v\rangle \langle \Phi'_r| \lambda_{Z\alpha} |\Phi''_r\rangle . \qquad (3.16)$$

The separation of the vibronic $(\Phi_e\Phi_v)$ and rotational (Φ_r) terms in Eq. (3.16) is possible because the components $\bar{\mu}_\alpha(\alpha = x, y, z)$ are functions of the vibronic coordinates only while $\lambda_{Z\alpha}$ are functions of the rotational coordinates only (i.e., of the Euler angles Θ, Φ, χ).

We can integrate over the electronic coordinates in the vibronic term in Eq. (3.16)

$$\langle \Phi'_e\Phi'_v| \bar{\mu}_\alpha |\Phi''_e\Phi''_v\rangle = \langle \Phi'_v| [\langle \Phi'_e| \bar{\mu}_\alpha |\Phi''_e\rangle] |\Phi''_v\rangle = \langle \Phi'_v| \mu_\alpha(e', e'') |\Phi''_v\rangle , \qquad (3.17)$$

where $\mu_\alpha(e', e'')$ depends still on the nuclear coordinates. In further discussion, we consider only vibrational-rotational transitions within the same singlet electronic state $(e' = e'')$ and we write simply μ_α instead of $\mu_\alpha(e', e'')$.

It is a usual practice to expand μ_α in terms of the normal coordinates of vibration q of the particular electronic state in the point of the equilibrium configuration of the atomic nuclei of that state,

$$\mu_\alpha = \mu_\alpha^{(e)} + \sum_k (\partial\mu_\alpha/\partial q_k)_e\, q_k + \tfrac{1}{2}\sum_{kl} (\partial^2\mu_\alpha/\partial q_k\partial q_l)_e\, q_k q_l + \dots , \qquad (3.18)$$

where $\mu_\alpha^{(e)}$ is the component of the permanent electric dipole or magnetic moment with respect to the axes $\alpha = x, y, z$.

The expansion of μ_α can be written as [cf. Eq. (3.2)]

$$\mu_\alpha = \sum_{m=0,1,2,\dots} \mu_{m0}^\alpha , \qquad (3.19)$$

where

$$\mu_{00}^\alpha = \mu_\alpha^{(e)} , \qquad (3.20a)$$

$$\mu_{10}^\alpha = \sum_k \left(\frac{\partial\mu_\alpha}{\partial q_k}\right)_e q_k , \qquad (3.20b)$$

$$\mu_{20}^{\alpha} = \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 \mu_{\alpha}}{\partial q_k \partial q_l} \right)_e q_k q_l \text{ etc.} \qquad (3.20c)$$

Quite analogously, we could expand the electric quadrupole moment but this will be discussed in Part 7 of this paper.

It should be mentioned that expansions $(3.3)-(3.5)$, $(3.6)-(3.9)$, and (3.19) may not work well for the so-called "floppy" molecules (molecules having large amplitudes of vibrational motions[1]). Nevertheless, they are quite useful in discussing selection rules for the allowed as well as forbidden transitions even for these nonrigid molecules; certain deviations due to the anomalously large anharmonicities of the vibrational motions in nonrigid molecules will be discussed separately (Part 10).

4. BASIC THEORY OF "ALLOWED" AND "FORBIDDEN" TRANSITIONS

Because the contributions of the electric quadrupole or magnetic moments to the transition probabilities are much smaller than those of the electric dipole moments, the quadrupole and magnetic transitions are always called forbidden transitions. This does not mean, however, that all the electric dipole moment transitions are called allowed transitions.

The concept of allowed and forbidden transitions in the electric dipole moment approximation can be discussed by using two approaches which are related to the fact that there are essentially two approaches to the treatment of intensities in the vibrational-rotational spectra of molecules.

In the first approach, the linestrengths [Eq. (2.27)] are expressed in terms of the matrix elements of the true dipole moment operator over the vibrational-rotational wavefunctions which are obtained by a variational diagonalization of the matrix representation of the vibrational-rotational Hamiltonian, usually in the basis of the harmonic oscillator and rigid rotor wavefunctions [Eq. (3.10)].

In the second approach, the true dipole moment operator is transformed to an effective dipole moment operator by a contact transformation which in a chosen approximation removes all the off-diagonal terms from the expanded vibrational--rotational Hamiltonian. The linestrengths are then expressed in terms of the matrix elements of the effective dipole moment operator over the harmonic oscillator and rigid rotor wavefunctions (see, e.g., refs[1,9]).

Let us first consider the first approach. Suppose for example that

$$\langle \Phi_m^{(0)} | \mu_F | \Phi_n^{(0)} \rangle = 0 \qquad (4.1)$$

but among the terms

$$\sum_j c_{mj} \langle \Phi_j^{(0)} | \mu_F | \Phi_n^{(0)} \rangle \equiv \langle \Phi_m | \mu_F | \Phi_n^{(0)} \rangle \qquad (4.2)$$

is at least one transition moment, say $\langle \Phi_p^{(0)} | \mu_F | \Phi_n^{(0)} \rangle$, which is different from zero [in Eqs (4.1) and (4.2), $\Phi_j^{(0)}$ are the zeroth-order wavefunctions and Φ_m is the perturbed wavefunction corresponding to the energy level E_m].

In this case, the transition $m \leftarrow n$ becomes allowed through the mixing of the zeroth-order wavefunctions by a vibrational-rotational or anharmonic interaction (perturbation allowed or forbidden transition which "borrows" its intensity from the intensity of the allowed transition $p \rightarrow n$).

If the zeroth-order transition moment in Eq. (4.1) is different from zero, then the higher-order effects change only the intensities of the allowed transitions $m \leftarrow n$ but they do not lead to forbidden transitions because the $m \leftarrow n$ transition was already allowed in the zeroth-order approximation.

Nevertheless, the experimental investigation of the intensity perturbations of the spectrum lines of the allowed transitions can provide useful results. For example, vibration-rotation interactions lead to intensity changes which provide useful information on magnitudes as well as relative signs of the transitions moments pertaining to different vibrational-rotational transitions (see, e.g., refs[16,17]).

As an illustration of this situation, let us consider the x-y Coriolis interaction between the nondegenerate (A) and degenerate (E) fundamental vibrational levels of a C_{3v} molecule[1] (Fig. 3). This interaction mixes states which are all accessible by allowed transitions from the ground state (Part 6). The interaction therefore cannot induce forbidden vibrational-rotational transitions but it certainly modifies intensities of the allowed infrared bands[16,17].

On the other hand, the same interaction leads to a new type of rotational transitions in the doubly degenerate vibrational state with the selection rules $+l \leftarrow -l$, $K + 1 \leftarrow K - 1$ which are not allowed by the usual selection rules (Part 6). It is obvious from Fig. 3 that this forbidden transition borrows its intensity from the allowed $|1, 0^0; J, K\rangle \leftarrow |0, 1^{-1}; J, K - 1\rangle$ transition.

This approach will be used in further discussion because it makes it possible to find the selection rules of forbidden transition quite simply. It is especially useful
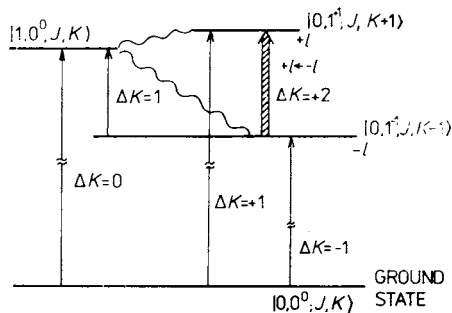

FIG. 3

Energy level scheme for the x-y Coriolis interaction between a nondegenerate and degenerate fundamental vibrational level of a C_{3v} molecule. The forbidden transition with the selection rule $+l \leftarrow -l$, $\Delta K = \pm 2$ is indicated by the bold arrow

in cases of resonances between interacting levels where the borrowing of intensities may become especially important.

The second approach makes it possible to express contributions of the individual vibrational-rotational and anharmonic terms to the linestrengths in a compact algebraic form and to classify forbidden transitions in a convenient way.

In this case, the Hamiltonian $\mathscr{H}$ in Eq. (2.2) is subject to a vibrational contact transformation[1,9], which after the separation of the electronic problem and in the dipole moment approximation can be written in the form:

$$\mathscr{\tilde{H}} = \exp{(iS)}\, H_{vr}\, \exp{(-iS)} - \exp{(iS)}\, \mu_Z\, \exp{(-iS)}\, E\cos{(\omega t)} =$$
$$= \tilde{H}_{vr} - \tilde{\mu}_Z E \cos{(\omega t)}\,. \tag{4.3}$$

By expanding $\exp{(iS)}$ in a power series, we obtain

$$\tilde{H}_{vr} = H_{vr} + i\,[S, H_{vr}] - \tfrac{1}{2}[S, [S, H_{vr}]] + \ldots \tag{4.4}$$

and

$$\tilde{\mu}_Z = \mu_Z + i\,[S, \mu_Z] - \tfrac{1}{2}[S, [S, \mu_Z]] + \ldots\,, \tag{4.5}$$

where $[A, B] = AB - BA$ and $[A, [A, B]] = A[A, B] - [A, B]\,A$ are the corresponding commutators.

The transformation function S is chosen such that $\tilde{H}_{vr}$ is diagonal in the basis of the harmonic oscillator wavefunctions. For example, if we choose in the first approximation [Eqs (3.2), (3.3)−(3.8)],

$$H_{vr} = H_{20} + H_{02} + H_{30} + H_{12} + H_{21}\,, \tag{4.6}$$

then

$$S = S_{30} + S_{12} + S_{21}\,. \tag{4.7}$$

The transformation functions S_{30}, S_{12}, and S_{21} remove the terms H_{30}, H_{12}, and H_{21}, which are off-diagonal in v, from the first-order terms in the expansion of H_{vr} (cf.[1,9]). The explicit expressions for these functions can be found in the literature[1,8,9].

A part of the effective Hamiltonian $\tilde{H}_{vr}$ is then

$$H_R = \tfrac{1}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} J_\alpha J_\beta J_\gamma J_\delta\,, \tag{4.8}$$

where

$$\tau_{\alpha\beta\gamma\delta} = -2 \sum_k \frac{B_k^{\alpha\beta} B_k^{\gamma\delta}}{\omega_k} \tag{4.9}$$

are the centrifugal distortion coefficients.

There are terms in $\mathbf{H_R}$ which are purely off-diagonal (in the rotational quantum numbers) in the rigid rotor approximation. Therefore it is possible to perform a purely rotational contact transformation which removes such terms from the effective Hamiltonian,

$$\tilde{H}_R = \exp\left(i\mathbf{S}_{03}\right)\mathbf{H_R}\exp\left(-i\mathbf{S}_{03}\right). \qquad (4.10)$$

This second transformation brings $\tilde{\mu}_Z$ to the form

$$\hat{\mu}_Z\big[\equiv \exp\left(i\mathbf{S_R}\right)\tilde{\mu}_Z\exp\left(-i\mathbf{S_R}\right)\big] = \sum_{\alpha}\mu_\alpha^{(e)}\lambda_{Z\alpha} + \sum_{\alpha}\mu_{10}^\alpha\lambda_{Z\alpha} +$$

$$+ \sum_{\alpha}\{i\left[\mathbf{S}_{21},\mu_\alpha^{(e)}\lambda_{Z\alpha}\right] + \left(\mu_{20}^\alpha + i\left[\mathbf{S}_{30},\mu_{10}^\alpha\right]\right)\lambda_{Z\alpha}\} + i\sum_{\alpha}(\left[\mathbf{S}_{12},\mu_{10}^\alpha\lambda_{Z\alpha}\right] +$$

$$+ \left[\mathbf{S}_{03},\lambda_{Z\alpha}\right]\mu_\alpha^{(e)}) + i\sum_{\alpha}(\left[\mathbf{S}_{12},\mu_\alpha^{(e)}\lambda_{Z\alpha}\right] + \left[\mathbf{S}_{21},\mu_{10}^\alpha\lambda_{Z\alpha}\right])\ldots \qquad (4.11)$$

The first sum on the right-hand side of Eq. (4.11) corresponds to the allowed purely rotational transitions due to permanent dipole moment (see Part 6 of this paper); the second sum corresponds to the allowed infrared fundamentals; the third sum is associated with the first overtones, combination and difference bands and with the forbidden rotational transitions in the degenerate vibrational states induced by vibrations (see Part 8); the fourth sum corresponds to forbidden pure rotational transitions induced by centrifugal distortion (Part 9). Finally, the last sum corresponds to forbidden infrared fundamentals induced by Coriolis or centrifugal forces and forbidden lines in allowed fundamentals (for a more complete treatment see Tables VII and VIII in ref.[9]; see also ref.[18]).

The same procedure could be used for the electric quadrupole or magnetic dipole moments but it turns out that in most cases this is not necessary. Because the corresponding transition probabilities are extremely small in comparison with those due to the electric dipole moment, it is sufficient to consider only the analogue to the first two terms on the right-hand side of Eq. (4.11) (see Part 7).

It should be noted that the electric quadrupole and magnetic moments indeed induce forbidden transitions and do not merely modify the intensities of the electric dipole moment transitions. This is because they have different overall symmetry selection rules with respect to inversion parity, which is a selection rule holding strictly (see Part 5).

5. OVERALL SYMMETRY SELECTION RULES

Before discussing the selection rules on the transitions which can be obtained from the symmetry considerations, let us briefly mention the symmetry groups which will be used throughout this paper.

We will use the Longuet-Higgins symmetry groups[19] (see also refs[1,20]) of the permutations of the positions and spins of the identical atomic nuclei, and permutation-inversion operations **PE*** = **E*P** ($\equiv$ **P***), where **E*** is the operation of inversion of the positions of electrons and atomic nuclei say in the origin of the coordinate system. Note that for semirigid molecules, the Longuet-Higgins group of the energetically completely feasible operations is isomorphic with the point group of the equilibrium configuration of the atomic nuclei of the molecule (see, e.g., refs[1,20] for more details on the concept of the permutation-inversion and point groups).

We will also use the group of rotations about the space-fixed axes which go through the center of mass of the molecule [the external rotation group $K(S)$].

In the absence of external fields, the molecular Hamiltonian is invariant with respect to both groups and we will obtain useful selection rules on the allowed and forbidden transitions by considering the transformation properties of the wavefunctions as well as of the electric and magnetic moments with respect to the operations of both groups (see Appendix as for the discussion of the situation if the external electric and magnetic fields are applied).

In general, a transition moment for the electric or magnetic dipole operator,

$$\langle \Phi_m | \, \mu_F^{(e,m)} | \Phi_n \rangle = M_{mn}^{(F)} \quad (F = X, Y, Z) \tag{5.1}$$

can be different from zero only if it is invariant with respect to all the symmetry operations of the molecular symmetry group[20]. This overall symmetry selection rule can be expressed through the direct product of the symmetry species of the three quantities which appear on the left-hand side of Eq. (5.2):

$$\Gamma(\Phi_m) \otimes \Gamma(\Phi_n) \otimes \Gamma(\mu_F^{(e,m)}) \in A_1' \,, \tag{5.2}$$

or equivalently,

$$\Gamma(\Phi_m) \otimes \Gamma(\Phi_n) \in \Gamma(\mu_F^{(e,m)}) \,. \tag{5.3}$$

We discuss in section 5.1 the overall symmetry selection rules which can be obtained from the consideration of the transformation properties of the wavefunctions Φ and the various moments $\mu_F^{(e,m)}$ which respect to the operations of the Longuet-Higgins symmetry groups[1,20]. Selection rules which can be obtained from the use of the external rotation group $K(S)$ will be discussed in section 5.2.

5.1. Selection Rules Obtained with the Use of Permutation-Inversion Groups

The overall symmetry selection rules (5.2) or (5.3) provide strong results on the allowed and forbidden transitions in the following sense. Suppose that a transition is forbidden by the overall symmetry selection rule on the basis of the symmetry

properties of the wavefunctions considered in a certain approximation. This result is independent of that approximation because the molecular Hamiltonian is invariant to all the symmetry operations of the molecular symmetry group[1,20]. Consequently, any matrix element of the type $\langle \Phi' | \mathbf{H}_{mn} | \Phi'' \rangle$ [cf. Eq. (3.2)] can be different from zero only if Φ' and Φ'' belong to the same symmetry species. In other words, the symmetry species of a wavefunction Φ does not depend on the approximation in which it is obtained.

It is important to understand that this result holds for the overall symmetry selection rules pertaining to a specified wavefunction. For example, it holds for the allowed and forbidden transitions between the rovibronic states Φ_{evr} independently on the approximation in which Φ_{evr} is considered. However, if we want to obtain selection rules for transitions between the individual electronic, vibrational or rotational states separately, then the results do depend on the approximation in which Φ_{evr} is expressed (see Parts 8 and 9).

Let us consider in more detail the transformation properties of the overall spin-rovibronic wavefunctions Φ_{evrs}. We can write the expression for the complete wavefunction [Eq. (3.13)] in the form

$$\Phi_{\text{evrs}} = \Phi_{\text{evr}}(R_j) \, \Phi_{\text{s}} \,, \tag{5.4}$$

where the rovibronic wavefunction Φ_{evr} depends on the coordinates of all particles (atomic nuclei and electrons) of the molecule with respect to the space-fixed system of axes and Φ_{s} depends only on the spin coordinates.

It can be shown[21] that the complete function Φ is either symmetric or antisymmetric with respect to inversion $\mathbf{E}^*$ whose effect on the space-fixed coordinates R_s is defined as

$$\mathbf{E}^* f(R_j) = f(-R_j) \,, \tag{5.5}$$

that is

$$\mathbf{E}^* \Phi_{\text{evrs}} = \Phi_{\text{evr}}(-R_j) \, \Phi_{\text{s}} = \left[\pm \Phi_{\text{evr}}(R_j) \right] \Phi_{\text{s}} \,. \tag{5.6}$$

Similarly, if $\mathbf{P}_2$ is the permutation of the positions and spins of the two identical atomic nuclei, it can be shown[21] that

$$\mathbf{P}_2 \Phi_{\text{evrs}} = \mp \Phi_{\text{evrs}} \,, \tag{5.7}$$

where the upper sign holds for the permutation of the nuclei with half-odd spin (e.g., ^{1}H or ^{19}F) and lower sign for nuclei with integer spin (e.g., ^{2}H or ^{16}O).

The space-fixed components of the electric dipole moment $\mu_F^{(\text{e.d.})}$, electric quadrupole moment $\mu_F^{(\text{e.q.})}$, and of the magnetic dipole moment $\mu_F^{(\text{m.d.})}$ transform as follows:

$$E^* \mu_F^{(e.d.)} = -\mu_F^{(e.d.)}, \quad P\mu_F^{(e.d.)} = +\mu_F^{(e.d.)}, \tag{5.8a}$$

$$E^* \mu_{FF'}^{(e.q.)} = +\mu_{FF'}^{(e.q.)}, \quad P\mu_{FF'}^{(e.q.)} = +\mu_{FF'}^{(e.q.)}, \tag{5.8b}$$

$$E^* \mu_F^{(m.d.)} = +\mu_F^{(m.d.)}, \quad P\mu_F^{(m.d.)} = +\mu_F^{(m.d.)} \tag{5.8c}$$

(P is now a general permutation operation).

Eqs (5.8) follow from the definition of the various electric and magnetic momenta and from the definition of the effect of E^* and P on the various space and spin coordinates [cf. Eqs (2.12), (2.14)–(2.16), and (5.5)]. Note that P permutes only the order of the terms in the expression for the various momenta, thus all of them must be invariant with respect to P. Also E^* does not affect the spin coordinates.

We obtain therefore the following overall symmetry selection rules for the allowed ($\leftrightarrow$) and forbidden ($\nleftrightarrow$) transitions between the quantum states with different inversion parities:

A. Electric dipole moment selection rules:

$$+ \leftrightarrow -, \quad + \nleftrightarrow +, \quad - \nleftrightarrow - \tag{5.9}$$

B. Electric quadrupole and magnetic dipole moment selection rules:

$$+ \leftrightarrow +, \quad - \leftrightarrow -, \quad + \nleftrightarrow -. \tag{5.10}$$

Thus the electric dipole moment allowed transitions occur between states with the opposite inversion parities while they are forbidden between states with the same parity. Weak transitions between the levels having the same parity are of course possible through the electric quadrupole or magnetic dipole moment selection rules (Fig. 4).

It should be noted that because the spin wavefunction Φ_s [Eq. (5.4)] is invariant
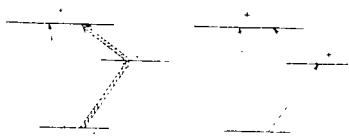

FIG. 4

Allowed (full arrows) and forbidden (dashed arrows) transitions in a three-level system with the indicated inversion parity of the wavefunctions. The electric dipole moment induces allowed transitions between the states with opposite parity while the electric quadrupole or magnetic dipole moments induce forbidden transitions between the states with the same parity

with respect to E^*, we would obtain the same overall symmetry selection rules if we considered the rovibronic wavefunction $\Phi_{evr}(R)$ instead of the complete spin-rovibronic wavefunction Φ_{evrs}.

On the other hand, the transformation properties with respect to permutation P of the rovibronic wavefunctions Φ_{evr} are different from those of the complete spin--rovibronic wavefunctions Φ_{evrs}. This can be illustrated on the following examples, which will also make it possible to explain the important concept of spin statistics isomers, i.e. of the *ortho* and *para*-modifications of molecules.

Let us first consider the molecule of water, H_2O. It belongs to the C_{2v} point group which is isomorphic with the complete permutation-inversion group[1,20] of H_2O. If α denotes the value $+1/2$ of the proton spin projection and β the value $-1/2$, and the two protons are labelled as 1 and 2, there are four proton spin states $\alpha_1\alpha_2$, $\alpha_1\beta_2$, $\beta_1\alpha_2$, $\beta_1\beta_2$. The structure of the reducible representation in the basis of the proton spin functions $\Phi_{p.s.}$ can be found to be

$$3A_1 + B_2 . \tag{5.11}$$

The spin-rovibronic wavefunctions Φ_{evrs} must change sign with respect to permutation (12),

$$(12)\,\Phi_{evrs} = -\Phi_{evrs} \tag{5.12}$$

and transform as follows with respect to E^*:

$$E^*\Phi_{evrs} = \pm\Phi_{evrs} . \tag{5.13}$$

Thus the spin-rovibronic wavefunctions Φ_{evrs} must belong either to the B_1 or B_2 species of the C_{2v} group. Species of the rovibronic wavefunctions Φ_{evr} of H_2O are A_1, A_2, B_1, B_2. We have therefore the following compatibility conditions for the spin-rovibronic wavefunctions Φ_{evrs}:

$$
\begin{array}{ccc}
\text{Proton spin} & \text{Rovibronic} & \text{Spin-rovibronic} \\
\text{states } \Phi_{p.s.} & \text{states } \Phi_{evr} & \text{states } \Phi_{evrs}
\end{array}
$$

$$(3A_1\ B_2) \otimes (A_1\ A_2\ B_1\ B_2) = (B_1 \text{ or } B_2) \tag{5.14}$$

The obvious result is that the spin states A_1 are not compatible with the rovibronic states A_1 or A_2 and the spin states B_2 are not compatible with the rovibronic states B_1 or B_2. Proton spin statistical weights of the energy levels of H_2O are therefore

$$A_1(1),\ A_2(1),\ B_1(3),\ B_2(3) \tag{5.15}$$

(see also Table I).

From Eqs (5.8) we find that the symmetry species of the individual moments are

$$\Gamma(\mu_F^{(\text{e.d.})}) = A_2 \,, \quad \Gamma(\mu_{FF'}^{(\text{e.q.})}) = A_1 \,, \quad \Gamma(\mu_F^{(\text{m.d.})}) = A_1 \,. \tag{5.16}$$

Because $\mu_F^{(\text{e.d.})}$ is independent of the spin coordinates, we can write for the transition moment of the electric dipole moment operator

$$\langle \Phi'_{\text{evrs}} | \mu_F^{(\text{e.d.})} | \Phi''_{\text{evrs}} \rangle = \langle \Phi'_{\text{p.s.}} | \, \Phi''_{\text{p.s.}} \rangle \langle \Phi'_{\text{evr}} | \, \mu_F^{(\text{e.d.})} | \Phi''_{\text{evr}} \rangle \,. \tag{5.17}$$

Because of the orthogonality of the spin wavefunctions, the condition $\Phi'_{\text{p.s.}} = \Phi''_{\text{p.s.}}$ must be satisfied for the allowed transitions (analogous condition must be satisfied for the electric quadrupole and magnetic dipole).

TABLE I

Possible combinations of the proton spin states with the rovibronic states in H_2, H_2O, and NH_3

Proton spin states[a]		Rovibronic states		Spin-rovibronic states	Modification	Spin statistical weight
			H_2 ($D_{\infty\text{h}}$ group)			
Σ_g^+	$\otimes$	Σ_g^-	$=$	Σ_g^-	*ortho*	3
Σ_g^+	$\otimes$	Σ_u^+	$=$	Σ_u^+		
Σ_u^+	$\otimes$	Σ_g^+	$=$	Σ_u^+	*para*	1
Σ_u^+	$\otimes$	Σ_u^-	$=$	Σ_g^-		
			H_2O ($C_{2\text{v}}$ group)			
A_1	$\otimes$	B_1	$=$	B_1	*ortho*	3
A_1	$\otimes$	B_2	$=$	B_2		
B_2	$\otimes$	A_1	$=$	B_2	*para*	1
B_2	$\otimes$	A_2	$=$	B_1		
			NH_3 ($D_{3\text{h}}$ group)			
A_1'	$\otimes$	A_2'	$=$	A_2'	*ortho*	4
A_1'	$\otimes$	A_2''	$=$	A_2''		
E'	$\otimes$	E'	$\in$	A_2'	*para*	2
E'	$\otimes$	E''	$\in$	A_2''		

[a] For H_2, the structure of the reducible representation of the proton spin states is $3\Sigma_g^+ + \Sigma_u^+$, for H_2O $3A_1 + B_2$, for NH_3 $4A_1' + 2E'$.

Let us now consider the overall symmetry selection rules which follow from Eq. (5.2) for the allowed and forbidden transitions between the rovibronic states of H_2O:

A. Electric dipole moment selection rules:

$$A_1 \leftrightarrow A_2, B_1 \leftrightarrow B_2 , \tag{5.18}$$

$$A_1 \nleftrightarrow A_1, A_2 \nleftrightarrow A_2, B_1 \nleftrightarrow B_1, B_2 \nleftrightarrow B_2 \tag{5.19}$$

$$A \nleftrightarrow B \tag{5.20}$$

B. Electric quadrupole and magnetic dipole moment selection rules:

$$A_1 \leftrightarrow A_1, A_2 \leftrightarrow A_2, B_1 \leftrightarrow B_1, B_2 \leftrightarrow B_2 , \tag{5.21}$$

$$A_1 \nleftrightarrow A_2, B_1 \nleftrightarrow B_2 , \tag{5.22}$$

$$A \nleftrightarrow B . \tag{5.23}$$

We can see that the transitions which are forbidden by the electric dipole moment selection rules (5.19) are relaxed by the electric quadrupole or magnetic dipole moment selection rules (5.21), although these forbidden transition will certainly be by many orders of magnitude weaker than the $A_1 \leftrightarrow A_2$ or $B_1 \leftrightarrow B_2$ transitions.

On the other hand, we see from Eqs (5.20) and (5.23) that the $A \nleftrightarrow B$ transitions are not allowed by the electric dipole nor by the quadrupole moment or the magnetic dipole moment selection rules. We can therefore distinguish between the *ortho*- and *para*-modifications (spin statistics isomers) of H_2O (cf. Table I). This is a general phenomenon (cf. Fig. 5); usually, the modification with greater statistical weight is called the *ortho*-modification, that with the smaller weight the *para*-modification (cf. Table I).

The *ortho–para* transitions, however, are not absolutely forbidden for the following reasons. For example for H_2O, the overall symmetry selection rules for the allowed transitions between the spin-rovibronic states Φ_{evrs} is obviously

$$B_1 \leftrightarrow B_2 \tag{5.24}$$

which relaxes the selection rules according to which the *ortho–para* transitions are strictly forbidden (cf. Table I), This is not in contradiction with the previous example as can be shown by the following discussion.

Let us consider two energy levels of H_2O which have the same symmetry species of spin-rovibronic wavefunctions, say B_2, but which belong to the *ortho*- and *para*-modifications of H_2O and therefore have different species of the rovibronic states (Table I). Then a mixing of both wavefunctions is possible through a spin-rovibronic

interaction. As a consequence of this mixing, the new wavefunction of the *para*--modification will be

$$\Phi_{p.s.}(B_2)\, \Phi'_{evr}(A_1) + c\Phi_{p.s.}(A_1)\, \Phi'_{evr}(B_2)\,, \qquad (5.25)$$

where $|c| \ll 1$ is the coefficient of the mixing.

The *ortho–para* transition becomes allowed through this interaction, as can be seen from the corresponding expression for the transition moment:

$$\left[\langle\Phi_{p.s.}(B_2)\,\Phi'_{evr}(A_1)| + c\langle\Phi_{p.s.}(A_1)\,\Phi'_{evr}(B_2)|\right]\mu_F^{(e.d.)}|\Phi_{p.s.}(A_1)\,\Phi''_{evr}(B_1)\rangle =$$

$$= c\langle\Phi'_{evr}(B_2)|\,\mu_F^{(e.d.)}\,|\Phi''_{evr}(B_1)\rangle\,. \qquad (5.26)$$
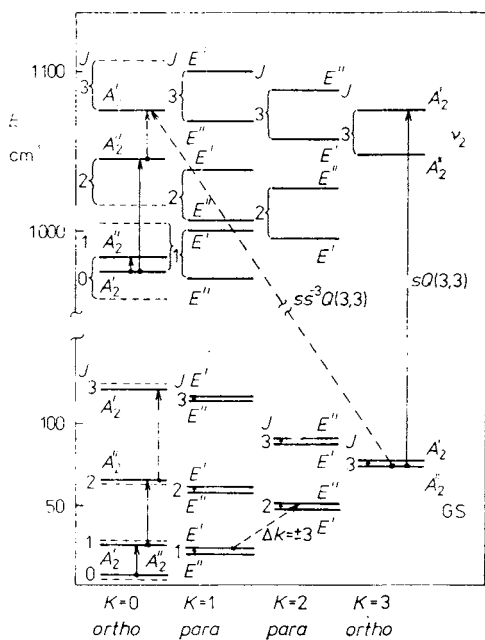
FIG. 5

Ground state and ν_2 excited state energy levels of ammonia, NH_3. Allowed transitions are indicated by full arrows, forbidden transitions (induced by rotation) are indicated by dotted arrows[4]

FIG. 6

Extremely weak spin–rotational interactions between the levels with $J = 2$, $K = 0$ and $J = 2$, $K = 1$ with the same overall symmetry A_2'' of the spin-rovibronic wavefunctions can induce transitions between the *ortho*- and *para*-modifications of ammonia, NH_3

A similar situation is illustrated by Fig. 6 for the *ortho–para* transitions in ammonia, NH_3.

For nonlinear molecules with equivalent identical nuclei an important pathway leading to equilibration of spin statistics isomers is provided by wavefunction mixing induced by the spin–rotation interaction and in some cases by the spin–spin interaction. For molecules like water, H_2O, or formaldehyde, H_2CO, the rapidity of equilibration is sensitive to the exact rotational energy level pattern. The spin–rotation interaction may be very important if there is an accidental near degeneracy of the right sort. Then most of the isomerization "tunnels" through the near-degenerate states[22–26].

For H_2, the ground state energy levels with J even belong to *para*, with J odd to *ortho*-modifications. As suggested already by Dennison[24], the even and odd rotational levels of H_2 do not equilibrate with each other. Similarly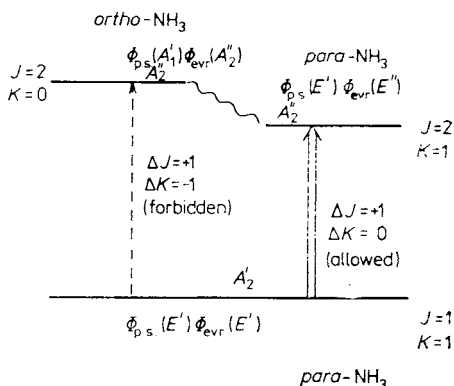, the *ortho*- and *para*-modifications of ammonia, NH_3, equilibrate extremely slowly. In methane, CH_4, there are three spin statistics isomers, which equilibrate rapidly because of the large spin–rotation interaction[26].

However, it should be noted that for example in H_2O, the $B_1 \leftrightarrow B_1$ or $B_2 \leftrightarrow B_2$ *ortho–para* transitions are strictly forbidden because they violate the inversion parity selection rule (5.9). This can also be described in terms of the quantum numbers associated with the symmetry operations. Thus parity with respect to inversion [Eq. (5.6)] is an extremely good quantum number because there are no spin interactions which could mix states with opposite inversion parity and the rules (5.9) are rigorous selection rules for the electric dipole moment transitions.

Theory of the spin-forbidden transition probabilities requires still further work[27,28] and the observation of the corresponding spectrum lines is a challenge for experimentalists.[29]

It should be mentioned that selection rules for quantum transitions between *ortho*- and *para*-modifications due to molecular collisions are essentially the same as the selection rules for radiative transitions[30] (see also Part 9.1). Thus nonequilibrium mixtures of *ortho*- and *para*-modifications of molecules with slow equilibration due to radiative processes may stay in the thermally nonequilibrium stage for months or even years without significant changes.

5.2. *Selection Rules Obtained with the Use of External Rotation Group*

The previous discussion will now be completed by using the external rotation group $K(S)$, i.e. the group of rotations around the space-fixed axes. In this way we obtain selection rules on the quantum numbers which are associated with these rotations.

If we neglect the spin moments, such a quantum number is J, the quantum number of the molecular rotational momentum[1]. If k is the quantum number of J_z, the projection of the rotational momentum along the molecule-fixed axis z, we have

$2J + 1$ rotational wavefunctions $|J, k\rangle, |J, k - 1\rangle, \ldots, |J, -k\rangle$ which form the basis of the irreducible representation $D^{(J)}$ of the group $K(S)$ (cf. refs[20,21]). According to the rules which can be obtained for the irreducible representations of $K(S)$, it holds that

$$D^{(J'')} \otimes D^{(1)} \otimes D^{(J')} \in D^{(0)}(\equiv A_1') \tag{5.27}$$

only if $J'' - J' = 0, \pm 1$ (but $J'' - J' = 0$ does not hold for $J' = J'' = 0$).

Because μ_z transforms according to the representation $D^{(1)}$ of the $K(S)$ group, we obtain the following selection rule for the isolated molecule in the absence of external fields:

$$\Delta J = 0, \pm 1 \, (J' = 0 \nleftrightarrow J'' = 0), \tag{5.28}$$

where the $\Delta J = 0$ transitions give rise to the Q branches, $\Delta J = +1$ to the R branches and $\Delta J = -1$ to the P branches.

J is a rather good quantum number, because vibrational-rotational interactions cannot mix states with different J. This follows from the fact that the Hamiltonian $\mathbf{H}_{vr}$ is invariant with respect to the operations of $K(S)$, i.e., it belongs to the representation $D^{(0)}$. Thus

$$\langle J', k' | \mathbf{H}_{vr} | J'', k'' \rangle \neq 0 \tag{5.29}$$

only if $J' = J''$.

This holds, however, only if the very small spin–rotation and spin–spin interactions are neglected. A rigorous quantum number in free space is F, the quantum number of the total angular momentum of the molecule (a vector sum of the rotational and spin momenta). Thus instead of Eq. (5.28), we have

$$\Delta F = 0, \pm 1 \, (F' = 0 \nleftrightarrow F'' = 0). \tag{5.30}$$

Sometimes in the literature J is understood to be the quantum of the total angular momentum (including the spin momenta) but we prefer to distinguish the spin contributions by using[20] F.

6. APPROXIMATE SELECTION RULES FOR THE VIBRATIONAL AND ROTATIONAL TRANSITIONS

The overall symmetry selection rules discussed in Part 5 are certainly useful because they hold rather rigorously. Nevertheless, it is convenient to have also approximate selection rules for transitions between the electronic, vibrational, and rotational states. If the harmonic oscillator–rigid rotor approximation is used [Eq. (3.10)], the effective electric dipole moment $\bar{\mu}_z$ [Eq. (4.11)] is approximated as

$$\bar{\mu}_z (\equiv \mu_z) \doteq \sum_{\alpha = x,y,z} \sum_{m = 0,1,2,\ldots} \mu_{m0}^{(\alpha)}. \tag{6.1}$$

The expression for the transition moment can be then written in the basis of the zeroth-order wavefunctions as

$$\langle \Phi_{evrs}^{(0)'} | \mu_Z | \Phi_{evrs}^{(0)''} \rangle = \langle \Phi_{es}' | \Phi_{es}'' \rangle \langle \Phi_{ns}' | \Phi_{ns}'' \rangle \times \sum_{\alpha=x,y,z} \big[\mu_\alpha^{(e)} \langle \Phi_v' | \Phi_v'' \rangle +$$

$$+ \sum_k (\partial \mu_\alpha / \partial q_k)_e \langle \Phi_v' | q_k | \Phi_v'' \rangle + \tfrac{1}{2} \sum_{kl} (\partial^2 \mu_\alpha / \partial q_k \partial q_l)_e \langle \Phi_v' | q_k q_l | \Phi_v'' \rangle + \ldots \big] \times$$

$$\times \langle \Phi_r' | \lambda_{Z\alpha} | \Phi_r'' \rangle . \tag{6.2}$$

Eq. (6.2) can be used to obtain various approximate selection rules on the allowed vibrational-rotational ($\Phi_v' \neq \Phi_v''$) and purely rotational ($\Phi_v' = \Phi_v''$) transitions.

From the orthogonality of the spin functions we obtain that the transition moment in Eq. (6.2) can be different from zero if

$$\Phi_{es}' = \Phi_{es}'' \tag{6.3a}$$

and

$$\Phi_{ns}' = \Phi_{ns}'' , \tag{6.3b}$$

i.e., we have the following selection rules for the allowed changes of the quantum numbers of the electron (S) and nuclear (I) spins:

$$\Delta S = 0 , \tag{6.4a}$$

$$\Delta I = 0 . \tag{6.4b}$$

If $\Phi_v' \neq \Phi_v''$ (vibrational-rotational transitions), the first term in the square brackets on the right-hand side of Eq. (6.2) vanishes and the permanent dipole moment $\mu_\alpha^{(e)}$ does not affect the intensity of the vibrational-rotational lines. It is the change of the electric dipole moment during the vibration $[(\partial \mu_\alpha / \partial q_k)_e, (\partial^2 \mu_\alpha / \partial q_k \partial q_l)_e$ etc. terms$]$ which controls this transition probability.

The first-order vibrational transition moment can be different from zero,

$$(\partial \mu_\alpha / \partial q_k)_e \langle \Phi_v' | q_k | \Phi_v'' \rangle \neq 0 , \tag{6.5}$$

only if the following condition is satisfied[20]:

$$\Gamma(\Phi_v') \otimes \Gamma(\Phi_v'') \in \Gamma(q_k) \big[\equiv \Gamma(\mu_\alpha) \equiv \Gamma(T_\alpha) \big] , \tag{6.6}$$

where $\Gamma(T_\alpha)$ is the symmetry species of the coordinate of translation T_α ($\alpha = x, y, z$) which is the property of the molecular symmetry group.

This is the symmetry selection rule for the allowed vibrational transitions according to which a vibrational transition can occur between the vibrational states Φ'_v and Φ''_v if the direct product of the symmetry species $\Gamma(\Phi'_v)$ and $\Gamma(\Phi''_v)$ contains the symmetry species of the coordinate of translation T_α.

Furthermore, we find that in the harmonic approximation for Φ_v,

$$\langle \Phi'_v | q_k | \Phi'_v \rangle \neq 0 \quad \text{for} \quad \Delta v = \pm 1 \tag{6.7}$$

which gives the well known approximate selection rule for the most intense vibrational transitions.

The second derivative of the dipole moment in Eq. (6.2) describes the so-called electrooptical anharmonicity; it will be discussed in more detail later (Part 8).

Vibrational transitions are accompanied by rotational transitions; selection rules for the latter are obtained from the following condition for an allowed rotational $(\Phi'_v = \Phi''_v)$ or vibrational-rotational $(\Phi'_v \neq \Phi''_v)$ transition:

$$\langle \Phi'_r | \lambda_{Z\alpha} | \Phi''_r \rangle \neq 0 , \quad \alpha = x, y, z . \tag{6.8}$$

For symmetric top molecules, we obtain from the explicit expressions for the symmetric top rotational wavefunctions and $\lambda_{Z\alpha}$ the following selection rules[1,20]:

$$\Delta k = 0 \quad \text{for} \quad \alpha = z \tag{6.9a}$$

and

$$\Delta k = \pm 1 \quad \text{for} \quad \alpha = x, y \tag{6.9b}$$

with $\Delta J = 0, \pm 1$ (the $k = 0 \leftrightarrow 0$ transition is not allowed for $J = 0$). This result holds if the z axis is identified with the rotation axes of the highest symmetry.

In a symmetric top molecule, the direction of the permanent dipole moment $\mu_z^{(e)}$ is always along the z axis (cf. Fig. 7). Thus the selection rules for the pure rotational spectra are

$$\Delta J = 0, \pm 1 ; \quad \Delta k = 0 . \tag{6.10}$$

In a symmetric top molecule, normal vibrations induce a dipole moment either along the z axis or perpendicular to it (cf. Fig. 7). In the former case we obtain selection rules for the allowed vibrational-rotational transitions in a parallel band which are the same as those in Eq. (6.10); in addition we have of course $\Delta v \neq 0$. Perpendicular vibrational-rotational bands have the following selection rules:

$$\Delta J = 0, \pm 1 ; \quad \Delta k = \pm 1 . \tag{6.11}$$

The situation for linear molecules is essentially the same as for symmetric top mole-

cules; instead of the rotational quantum number k we must consider the vibrational quantum number l of the vibrational angular momentum which is induced by the deformation vibration (Fig. 8).

Thus we have the selection rules for the allowed vibrational-rotational transitions in a parallel band of a linear molecule:

$$\Delta J = 0, \pm 1 ; \quad \Delta l = 0 \quad (\Delta J = 0 \text{ is not allowed for } l = 0) \qquad (6.12a)$$

and

$$\Delta J = 0, \pm 1 ; \quad \Delta l = \pm 1 \qquad (6.12b)$$

for a perpendicular band of a linear molecule.

The only selection rules which can be found for spherical top molecules are

$$\Delta J = 0, \pm 1 \qquad (6.13)$$

(besides selection rules which are the analogue of the $\pm l$ selection rules for symmetric top molecules; see Parts 8.2 and 9.2).

Since forbidden transitions are of lesser importance for asymmetric top molecules, we will not discuss here the selection rules for the rotational transitions in these molecules[1].

As it was discussed in the previous section, from the various quantum numbers mentioned in this section, only the quantum number J of the rotational angular momentum is a nearly good quantum number. A rigorous quantum number in free space is F with the selection rules given by Eq. (5.30).

On the other hand, k is not a good quantum number because the symmetry leading

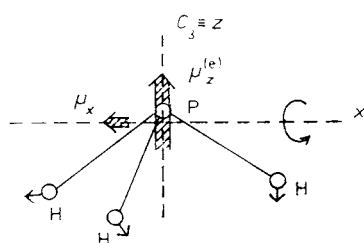Fig. 7

The equilibrium configuration of the PH_3 molecule and the directions of the permanent dipole moment $\mu_z^{(e)}$ and of the moment induced by rotation around the z axis (μ_x)
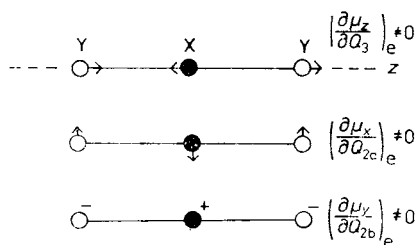
Fig. 8

The antisymmetric valence vibration in a linear molecule induces a dipole moment which is parallel with the z axis; the deformation vibration induces a dipole moment which is perpendicular to z

to it is that of the molecular geometry; the k selection rules are relaxed by the vibrational or rotational centrifugal distortion of the molecular geometry (Part 9).

7. FORBIDDEN TRANSITIONS INDUCED BY THE ELECTRIC QUADRUPOLE AND MAGNETIC DIPOLE MOMENT

As it was discussed in Part 5, the electric quadrupole and magnetic dipole moments induce transitions with different overall symmetry selection rules in comparison with those induced by the electric dipole moment. We will now discuss in more detail these typical forbidden transitions, especially from the point of view of their selection rules for the various vibrational and rotational quantum numbers (a detailed discussion of these selection rules for linear molecules can be found in ref.[31]).

7.1. *Forbidden Transitions due to the Electric Quadrupole Moment*

The electric quadrupole moment is a second rank tensor having nine components with respect to the space-fixed axes X, Y, Z:

$$\mu_{FF'}^{(e.q.)}(\equiv Q_{FF'}) = \sum_s e_s F_s F_s' \quad (F = X, Y, Z) \tag{7.1}$$

[we change the notation from $\mu_{FF'}^{(e.q.)}$ to $Q_{FF'}$ to avoid the upper index (e.q.) in further treatment; $Q_{FF'}$ is frequently used in the literature to denote components of the electric quadrupole moment].

In order to obtain the selection rules for the various vibrational and rotational quantum numbers, we proceed in analogy with the treatment of the electric dipole moment described in Parts 5 and 6. This means that we first express $Q_{FF'}$ in terms of the components $\bar{Q}_{\alpha\beta}$ of the electric quadrupole moment with respect to the molecule-fixed axes x, y, z:

$$Q_{FF'} = \sum_{\alpha,\beta} \bar{Q}_{\alpha\beta} \lambda_{F\alpha} \lambda_{F'\beta} \,. \tag{7.2}$$

If we integrate out the electronic coordinates, we obtain in analogy with Eq. (3.17)

$$Q_{\alpha\beta}(\equiv \langle \Phi_e | \bar{Q}_{\alpha\beta} | \Phi_e \rangle) = Q_{\alpha\beta}^{(e)} + \sum_k (\partial Q_{\alpha\beta}/\partial q_k)_e \, q_k + \text{higher order terms} \,, \tag{7.3}$$

where $Q_{\alpha\beta}^{(e)}$ is a component of the permanent electric quadrupole moment, $(\partial Q_{\alpha\beta}/\partial q_k)_e$ characterizes the changes of the quadrupole moment by the vibrations etc.

We obtain therefore that the pure rotational spectra induced by the electric quadrupole moment are controlled by the terms

$$Q_{\alpha\beta}^{(e)} \langle \Phi_r' | \lambda_{F\alpha} \lambda_{F'\beta} | \Phi_r'' \rangle \tag{7.4}$$

while the vibration-rotation spectra are controlled by the terms

$$[(\partial Q_{\alpha\beta}/\partial q_k)_e \langle \Phi'_v | q_k | \Phi''_v \rangle + \tfrac{1}{2}(\partial^2 Q_{\alpha\beta}/\partial q_k \partial q_l)_e \langle \Phi'_v | q_k q_l | \Phi''_v \rangle + \ldots] \times$$

$$\times \langle \Phi'_r | \lambda_{F\alpha} \lambda_{F'\beta} | \Phi''_r \rangle . \qquad (7.5)$$

Selection rules for quadrupole transitions are identical with those obtained for the Raman spectra if we consider instead of $Q_{\alpha\beta}$ the component of the molecular polarisability tensor $\alpha'_{\alpha\beta}$. For example, the component $Q_{\alpha\beta}$ of the electric quadrupole moment transforms by the symmetry operations like the product of the coordinates of translation, $T_\alpha T_\beta$, i.e., like the component $\alpha'_{\alpha\beta}$ of the molecular polarisability tensor. Thus the symmetry selection rule for the vibrational transitions induced by the electric quadrupole moment can be written as

$$\Gamma(\Phi'_v) \otimes \Gamma(\Phi''_v) \in \Gamma(T_\alpha T_\beta) \equiv \Gamma(\alpha'_{\alpha\beta}) \equiv \Gamma(Q_{\alpha\beta}) . \qquad (7.6)$$

Selection rules on the rotational quantum numbers follow from the matrix elements of the direction cosine products [Eqs (7.4) or (7.5)], thus they are the same as the selection rules for the Raman spectra[32,33].

For example, the selection rules on the rotational quantum number F are

$$\Delta F = 0, \pm 1, \pm 2 \quad (F' = 0 \leftrightarrow F'' = 0, F' = \tfrac{1}{2} \leftrightarrow F'' = \tfrac{1}{2}, F' = 0 \leftrightarrow F'' = 1) . \quad (7.7)$$

The $\Delta F = 0$ transitions give rise to the Q branches, $\Delta F = +1$ to the R branches, $\Delta F = +2$ transitions to the S branches, $\Delta F = -1$ to the P branches, and the $\Delta F = -2$ transitions to the O branches.

It should be noted that for symmetry reasons the off-diagonal elements $Q_{\alpha\beta}$ $(\alpha \neq \beta)$ can be identically equal to zero. For example, for linear and symmetric top molecules and for asymmetric top molecules of C_{2v} symmetry, we have only the diagonal elements $Q_{\alpha\alpha}$ $(\alpha = x, y, z)$; see ref.[34] for details. For a linear molecule, $Q_{xx} = Q_{yy} = -Q_{zz}/2$ (the z axis is the C_∞ rotation axis) and there is only one independent element of the molecular electric quadrupole tensor[34]:

$$Q_{\alpha\alpha} = -e \sum_i \langle 0 | 3\alpha_i^2 - r_i^2 | 0 \rangle + e \sum_j Z_j (3\alpha_k^2 - r_k^2) , \quad \alpha = x, y, z , \qquad (7.8)$$

where e is the electron charge, r_s is the position vector with respect to the molecule-fixed axis system of the s-th particle (electron or atomic nucleus), Z_j is the atomic number of the j-th nucleus. The first term on the right-hand side of Eq. (7.8) is the electronic contribution to the quadrupole moment averaged over the ground state electronic wavefunctions while the second term is the nuclear contribution.

It might seem that because of the coincidence of the ordinary Raman selection

rules with the electric quadrupole moment selection rules, the forbidden quadrupole transitions are not of large importance because it is certainly easier to measure ordinary Raman lines than the extremely weak quadrupole radiation. Nevertheless, measurement of these forbidden transitions played an important role in the history of molecular spectroscopy, namely because of the fact that the simplest molecule, H_2, does not have a permanent electric dipole moment; neither can its vibration induce one. Thus the only possibility of observing a pure rotation or a vibration--rotation spectrum of a homonuclear diatomic molecule is through the electric quadrupole interaction. The quadrupole spectrum of H_2 is therefore of considerable importance in astrophysics, because it allows the determination of H_2 abundancies in astronomical sources, in particular in planetary atmospheres[35] and also in the interstellar molecular clouds[36-38].

The astrophysical importance of the electric quadrupole rotation-vibration spectra has been recognized half a century ago[39,40]. In 1949, Herzberg[41,42] observed for the first time the electric quadrupole lines $S(0)$, $S(1)$, $S(2)$, and $Q(1)$ in the $2 \leftarrow 0$ and $3 \leftarrow 0$ vibrational-rotational bands of H_2 using the equivalent of the optical path length of about 50 km at 1 atm pressure. The observation of the electric quadrupole vibrational-rotational transitions in the $1 \leftarrow 0$ band has been reported much later[43-47] while the pure rotation quadrupole spectrum of H_2 was observed for the first time in 1978 (ref.[48], see also refs[44,45]).

These measurements provided the values of the rotational and centrifugal distortion constants in the ground and excited vibrational states as well as band origins of H_2 ($v_{1 \leftarrow 0} = 4\ 161 \cdot 1782$, $v_{2 \leftarrow 0} = 8\ 087 \cdot 000$, $v_{3 \leftarrow 0} = 11\ 782 \cdot 355\ cm^{-1}$, ref.[45]) with much better accuracy than obtained from Raman spectra of H_2 (cf. ref.[49]). Equally interesting is the information on the quadrupole moments which can be obtained from the intensity measurements of the quadrupole lines[45,48] because this makes it possible to determine the various abundances of molecular hydrogen in the planetary atmospheres and in the interstellar clouds.

It is easy to see that for H_2, Eq. (7.8) can be written as

$$Q(\equiv Q_{zz}) = -2e\langle 0| \ 3z^2 - r^2|0\rangle + eR^2 , \qquad (7.9)$$

where R is the internuclear separation and z is the coordinate of one of the electrons (both electrons give the same averaged contribution); it should be noted that some authors define the quadrupole moment as $Q^* = Q/2$.

It turns out that the various matrix elements of Q are not only strongly dependent on $\Delta v = v' - v''$ but also on the rotational quantum number J because of the vibrational-rotational interactions (Table II).

The hydrogen molecule attracts of course the attention of quantum chemists who have done many *ab initio* calculations of the quadrupole moment of the H_2 molecule and of its matrix elements between various vibrational-rotational states[52,53]. These

calculations are in a good agreement with the experimental values and are useful for predicting intensities of the quadrupole lines which have not yet been measured in the laboratory.

The observed as well as calculated values of the quadrupole moment elements indicate that the intensity of quadrupole lines is extremely small. For example, the ratio of the intensity of the $S(0)$ quadrupole line in the fundamental band of H_2 to the intensity of the $R(0)$ line of the fundamental band of HCl was found[43] to be $1 \cdot 1$ . . 10^{-8}.

Nevertheless, the extremely long optical paths in the interstellar hydrogen clouds as well as the high excitation temperatures make it possible to observe beautiful quadrupole emission spectra of interstellar H_2 (Fig. 9).

The electric quadrupole vibrational-rotational or rotational spectra for other molecules have been measured only recently. For example, the quadrupole spectra

TABLE II

Experimental and calculated values of the quadrupole moment matrix elements of H_2 (see^a)

Line	$\tilde{v}_{exp}$ cm^{-1}	$\|\langle v'; J' \| \mathbf{Q} \| v''; J'' \rangle\|_{exp}$ a.u.	$\langle v'; J' \| \mathbf{Q} \| v''; J'' \rangle_{calc}$ a.u.
$0 \leftarrow 0$			
$S(3)$	1 034·6702	0·982	0·989
$1 \leftarrow 0$			
$S(0)$	4 497·8403	0·153	0·157
$S(1)$	4 712·9050	0·147	0·144
$S(2)$	4 917·0100	0·141	0·132
$S(3)$	5 108·4051	0·123	0·119
$Q(1)$	4 155·2579	0·153	0·176
$Q(2)$	4 143·4625	0·166	0·176
$Q(3)$	4 125·8755	0·165	0·177
$2 \leftarrow 0$			
$S(1)$	8 604·2133	0·0235	$-0·0237$
$Q(1)$	8 075·3045	0·0236	$-0·0225$
$3 \leftarrow 0$			
$S(1)$	12 265·548	0·00421	0·00427
$4 \leftarrow 0$			
$S(0)$			$-0·000865$

^{a} Experimental data taken from ref.[45] (cf. also refs[51,53]) except for the $0 \leftarrow 0$ transition for which data have been taken from ref.[48]; note that only the absolute value of the quadrupole moment matrix element can be obtained from the experimental intensities. Calculated values taken from ref.[52]. The conversion factor between the atomic unit (a.u.) and Coulomb. (meter)^2 (C m^2) is 1 a.u. $= 4\cdot486499 . 10^{-40}$ C m^2.

of HD have been measured for the first time by McKellar[54] in 1974, of D_2 by McKellar and Oka[55] in 1978. The first observation of vibrational and rotational quadrupole transition in any molecule other than hydrogen have been reported in 1981 for the fundamental band of O_2 at 1 580 cm^{-1} (ref.[56]).

7.2. Forbidden Transition due to the Magnetic Moments

The component $\mu_Z^{(m)}$ of the molecular magnetic moment with respect to the space-fixed axis Z can be expressed in terms of the components $\bar{\mu}_\alpha^{(m)}$ ($\alpha = x, y, z$) along the molecule-fixed axes in the same way as the component of the electric dipole moment [Eq. (3.14)]:

$$\mu_Z^{(m)} = \sum_{\alpha=x,y,z} \bar{\mu}_\alpha^{(m)} \lambda_{Z\alpha} . \qquad (7.10)$$

While the component μ_α of the electric dipole moment transforms like the coordinate of translation, T_α [cf. Eq. (6.6)], the components $\bar{\mu}_\alpha^{(m)}$ transform like the com-
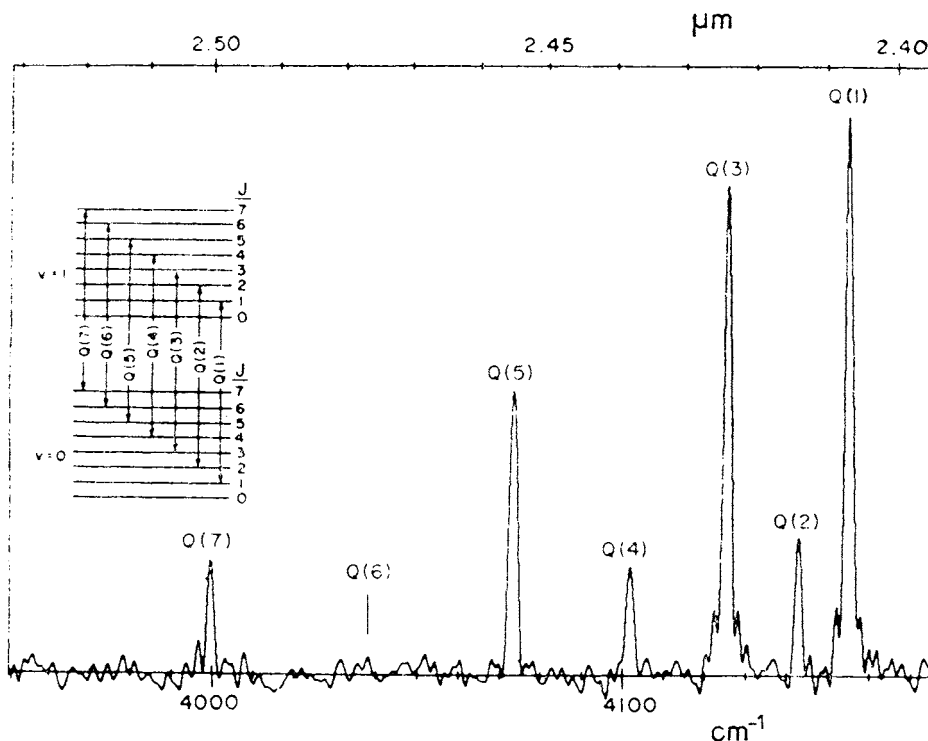

FIG. 9

Infrared emission of the Q branch of the 1-0 electric quadrupole H_2 band in the Orion nebula (according to ref.[50])

ponents of the rotational coordinate R_α [cf. Eq. (2.16)]. Thus by proceeding in the same way as for the electric dipole moment in Part 6, we find the symmetry selection rule for the vibrational transitions induced by the magnetic dipole moment

$$\Gamma(\Phi'_v) \otimes \Gamma(\Phi''_v) \in \Gamma(\mu_\alpha^{(m)}) \equiv \Gamma(R_\alpha). \qquad (7.11)$$

The species of $\Gamma(R_\alpha)$ can be found in character tables for the irreducible representations (it is the property of the symmetry group and therefore the same for all molecules belonging to that group).

Selection rules for the rotational quantum numbers are determined by the matrix elements of the direction cosines λ_{Zz} in Eq. (7.10); they are therefore the same as those induced by the electric dipole moment (Part 6).

Magnetic dipole moment transitions are particularly important for homonuclear diatomic molecules for which electric dipole infrared or microwave transitions are forbidden. From the definition of the magnetic moment [Eq. (2.15)] we see that magnetic dipole transitions within an electronic state may arise when either $\Lambda \neq 0$ (Λ is the quantum number of the electronic angular momentum) or $S \neq 0$ (S is the quantum number of the total electrone spin). This is a condition which is satisfied by some stable diatomics and many radicals in their electronic ground or quasi ground states.

A special feature is that the transition intensities do not contain unknown parameters like transition dipole moments [cf. Eq. (2.15)], thus absolute intensities of magnetic dipole moment transitions are predictable. We can see also from Eq. (2.15) that there is no component of the vibrational angular momentum for a diatomic molecule and hence the vibrational dependence of the magnetic dipole moment is extremely small. Thus we can expect that the magnetic rotational transitions will have much larger intensities in comparison with the magnetic vibrational-rotational transitions.

A well known example of a molecule with a measurable magnetic dipole rotational spectrum is oxygen, O_2. The ground electronic state of O_2 is $X^3\Sigma_g^-$, which satisfies the condition $S \neq 0$ for magnetic moment induced spectrum ($\Lambda = 0, S = 1$). In Hund's case b (ref.[57]), the angular momentum of the rotation of the nuclei and the angular momentum of the orbital motions of electrons couple to form the resultant angular momentum $\mathbf{N}$. The magnitude of $\mathbf{N}$ is defined by the quantum number N; $N = |\Lambda|, |\Lambda| + 1, \ldots$ The spin angular momentum $\mathbf{S}$ will combine with $\mathbf{N}$ to give the total angular momentum $\mathbf{F}$ whose magnitude is defined by the quantum number $F = N + S, N + S - 1, \ldots, |N - S|$ [see also Eq. (5.30)].

Thus for $S = 1$, each rotational level of O_2 is split into three components by the spin–spin and spin–orbit interactions with the selection rules for F given by Eq. (5.30) (cf. Fig. 10).

The first measurement of a rotational transition in the ground vibrational state

of O_2 with high-resolution technique has been reported by McKnight and Gordy[58] in the submillimeterwave region (Fig. 10). The fine-structure spectra of O_2 have been later extensively studied both experimentally and theoretically. For example, Amano and Hirota[59] observed the microwave spectrum of O_2 in the first excited vibrational state while Mizushima et al.[60] observed many transitions at 430 GHz using the technique of laser magnetic resonance.

Rovibrational magnetic dipole transitions are forbidden because the magnetic moment has no dependence on the internuclear distance. As discussed recently by Balasubramanian and Bellary[61] (see also ref.[59]), some intensities can result from centrifugal and spin–orbital mixing effects but they have not yet been observed in the spectra. Reid et al.[56] have not been able to observe magnetic induced transitions to the first excited vibrational level of O_2 although they observed the electric quadrupole transitions to that level.

Because the $\Delta F = 0, \pm 1$ selection rules are the same for magnetic as well as electric quadrupole transitions and both types of transitions have the same inversion parity selection rules, it is a question how they can be distinguished. In quadrupole transitions, branches obeying $\Delta F = \pm 2$ appear in addition to those with $\Delta F = 0, \pm 1$ with similar intensities. Therefore, the presence of $\Delta F = \pm 2$ branches with intensities similar to $\Delta F = 0, \pm 1$ may be the only practical criterion to rule out any magnetic dipole contribution to the intensities because usually the magnetic dipole moment contribution exceeds that of the electric quadrupole moment[62].

Magnetic dipole moment transitions (as well as electric quadrupole transitions) are important also in electronic spectroscopy and have been observed in many rovibronic bands in diatomic molecules[63,64]. Magnetic moment transitions in the rovibronic spectra of a polyatomic molecule have been observed for the first time by Callaman and Innes[65] in formaldehyde, H_2CO (a weak $0-0$ band of the 350 nm system).

Molecular magnetic moments play an important role in the theory of optical activity (and hence in the spectra of circular dichroism) because the rotational
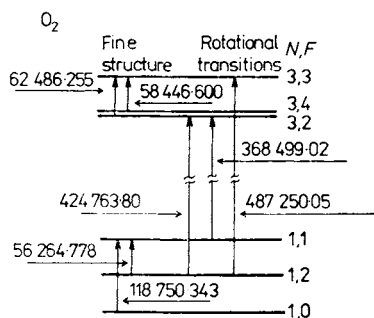

FIG. 10

The multiplet structure of the rotational energy levels in the ground $^3\Sigma_g^-$ vibronic state of O_2. Magnetic dipole moment induced transitions $\Delta F = 0, \pm 1$ are indicated by vertical arrows; transition frequencies are in GHz units (according to ref.[58])

strength of an optically active material is proportional to the product of the electric and magnetic dipole moment matrix elements[66,67]. This is, however, another story which will not be discussed here.

8. VIBRATIONALLY INDUCED ROTATION TRANSITIONS

Let us consider again the expansion of the electric dipole moment in terms of the normal coordinates of vibration q [see Eqs (3.18) and (4.11)]. We know already that

$$\mu_\alpha^{(e)} \langle \Phi_v' | \Phi_v'' \rangle \neq 0 \qquad (8.1)$$

only if $\mu_\alpha^{(e)} \neq 0$ and $\Phi_v' = \Phi_v''$, i.e., the allowed pure rotational spectra have molecules with a permanent dipole moment.

We know also that if the second term on the right-hand side of Eq. (3.18) is different from zero,

$$(\partial \mu_\alpha / \partial q_k)_e \langle \Phi_v' | q_k | \Phi_v'' \rangle \neq 0 \,, \qquad (8.2)$$

a vibrational transition with the selection rule $\Delta v = \pm 1$ is allowed (such a transition for example from the ground vibrational state gives rise to a fundamental band).

Let us consider what happens if

$$(\partial^2 \mu_\alpha / \partial q_k \partial q_l)_e \langle \Phi_v' | q_k q_l | \Phi_v'' \rangle \neq 0 \,. \qquad (8.3)$$

First of all we see that this term gives a possibility to observe transitions with $\Delta v_k = \pm 1$, $\Delta v_l = \pm 1$ if $k \neq l$ or $\Delta v_k = \pm 2$ if $k = l$ (in the first case we have a combination band for a transition from the ground state or the first overtone if $\Delta v_k = \pm 2$). In our classification of the allowed and forbidden transitions we might consider these transitions as forbidden (allowed by the electrical anharmonicity) but such a terminology is certainly not used for the combination band or first overtones [as well it is not used for the vibrational-rotational transitions which are due to the other higher-order terms on the right-hand side of the expansion (3.18)].

There is, however, another possibility that the term on the left-hand side of Eq. (8.3) gives rise to forbidden transitions. If $q_k = q_l$, then the condition

$$\langle \Phi_v' | q^2 | \Phi_v'' \rangle \neq 0 \qquad (8.4)$$

can be satisfied for $\Phi_v' = \Phi_v''$, i.e., the molecule can have a purely rotational spectrum even if it is nonpolar.

This possibility has been for the first time discussed in 1953 by Mizushima and Venkateswarlu[68] and since that time (but much later) such spectra have been observed in the microwave and infrared–microwave double resonance spectra of many

molecules. It seems appropriate to describe this type of forbidden transitions as rotational transitions which are induced by vibration.*

In this paragraph, we will first discuss the conditions which must be satisfied for a molecule to have a rotational spectrum and then we review the most important experimental work on the detection of these transitions. Following Mills, Watson, and Smith[71], we first specify general symmetry requirements on these transitions. The transitions considered here are the rotational transitions within a particular vibrational level whose intensities are due to nonvanishing integrals of the type

$$\int \Phi_v^* \mu_\alpha(q) \, \Phi_v \, d\tau_v = \langle \Phi_v | \mu_\alpha | \Phi_v \rangle \, . \tag{8.5}$$

The symmetry condition for this integral to be nonzero is [Eq. (6.6)]

$$(\Gamma_v)^2 \in \Gamma(\mu_\alpha) \left[\equiv \Gamma(T_\alpha) \right] \, . \tag{8.6}$$

Note that the direct product $\Gamma \otimes \Gamma$ of the irreducible representation Γ by itself consists of the direct sum of the symmetric square $[\Gamma^2]$ and antisymmetric square $\{\Gamma^2\}$. For example, if Φ_a, Φ_b form the basis of the doubly degenerate representation, the combination $\Phi_a \Phi_b - \Phi_b \Phi_a$ forms the basis of $\{\Gamma^2\}$. Thus only the symmetric square $[\Gamma^2]$ has to be considered in futher treatment [Eq. (8.7)].

Depending upon the fulfilment of this condition, molecules can be divided into the following two categories:

(i) If the equilibrium configuration of the molecule belongs to a point group in which the symmetry species of the three translations are non-totally symmetric (e.g. D_{3h}, D_{2d} or T_d), the molecule cannot have a purely rotational spectrum in a non-degenerate vibrational state (i.e., also in the ground state), because the square of the nondegenerate symmetry species is always totally symmetric. They can have, however, a purely rotational spectrum in the degenerate vibrational state induced by vibrations because only in this case the square of the representation $(\Gamma_v)^2$ can contain the (non-totally) symmetry species of μ_α.

This is the most important case because such molecules cannot have a permanent dipole moment $[\mu_\alpha^{(e)} \neq 0$ immediately implies $\Gamma(\mu_\alpha) \in A_1']$ but they may have a pure rotation spectrum excited by vibration in the degenerate vibrational state (for example, BCl_3, CH_4, CF_4, SiH_4 or CF_4).

It should be noted, however, that not all molecules in which all $\Gamma(\mu_\alpha)$ are non--totally symmetric can satisfy condition (8.6). For example, molecules with a center of symmetry (e.g., spherical top molecules O_h or linear molecules $D_{\infty h}$) can never

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* This prediction was for the first time verified by Uehara et al.[69], who observed two components of the $P^+(7)$ transition in the ν_3 band of CH_4 by using a Zeeman-tuned He–Ne laser as a source and showed one of them to be Stark sensitive (see also ref.[70]).

satisfy condition (8.6) because $(\Gamma_v)^2$ contains only g (gerade) species ($u \otimes u = g$) while the species of μ_α must have u (ungerade). Such centrosymmetrical molecules can never have a pure electric dipole rotational spectrum irrespective of the vibrational state (cf. however the effect of free internal rotation in ethane-like molecules discussed in Part 10).

There are some other restrictions on the molecules which can satisfy condition (8.6) but these will be discussed later.

(ii) Axially symmetric top molecules which have a permanent dipole moment, thus an ordinary pure rotation spectrum. In such molecules the axial component of the dipole moment operator μ belongs to an A species of the group. Vibration then induces a dipole moment in the direction of z and the condition (8.6) is satisfied but the spectrum is not in general, purely vibrational induced and this case is of no interest. However, if the vibration induces a dipole moment perpendicular to the z axis (μ_x, μ_y) and certain symmetry conditions are satisfied, then Eq. (8.6) can be satisfied and vibration can induce a new type of the purely rotational spectrum (in the degenerate vibrational states) with different selection rules on the quantum numbers, thus providing a new type of information on the molecular parameters.

Note that linear molecules of $C_{\infty v}$ symmetry have $\Gamma(\mu_z) = A_1$ but they cannot have an x or y-polarized pure rotational spectrum induced by vibration because we can always find a symmetry plane σ_v such that μ_x (or μ_y) is antisymmetrical with respect the reflection in it while $(\Gamma_v)^2$ in this case contains only species which are symmetrical with respect to reflection.

Let us now consider in more detail the symmetries and selection rules for the transitions induced by vibrations. We have already seen that we can exclude from this discussion all linear molecules as well as molecules with the center of symmetry. The point groups of the remaining molecules can be divided into three classes:

(i) point groups of symmetric top molecules in which the axis of highest order is (or can be chosen to be) a proper or C axis (e.g., C_{nv} or D_{nh} groups), (ii) point groups of symmetric top molecules in which the axis of highest order is an improper or S axis (e.g., D_{2d} group), (iii) spherical top molecules (T, O, I).

8.1. Rotational Transitions in Symmetric Top Molecules

C-symmetric top point groups: In C symmetric-top point groups the degenerate symmetry species E_s are labelled according to their behaviour under rotations about the highest-order rotation axis C_n by an index s which takes all integral values in the range $0 < s < n/2$.

The symmetric squares of the degenerate species are given by:

$$[E_s^2] = A + E_{2s} \quad \text{if} \quad 0 < s < n/4, \tag{8.7a}$$

$$[E_s^2] = A + B + B \quad \text{if} \quad s = n/4 , \tag{8.7b}$$

$$[E_s^2] = A + E_{n-2s} \quad \text{if} \quad n/4 < s < n/2 . \tag{8.7c}$$

In Eqs (8.7), the additional subscripts or superscripts in the species labels (e.g. E_1' or E_1'') have been ignored; in every case the A species on the right-hand side of Eq. (8.7) is the totally symmetric species (e.g. A_1 in C_{nv} groups or A_1' in $D_{(2n+1)h}$ groups).

The axial component of the electric dipole moment operator μ_z belongs always to an A species of the group and the condition (8.6) can only be satisfied if μ_z is totally symmetric. In that case, however, the molecule is allowed by symmetry to have a permanent dipole moment and the rotational spectrum with the selection rules given by Eq. (6.10) is not purely vibrationally induced.

The perpendicular components μ_x, μ_y of the dipole moment operator belong to an E_1 species, thus Eq. (8.6) can only be satisfied if Eq. (8.7c) holds and if $n = 2s + 1$. Thus the C_n axis must be of odd order, and the only vibrational levels which can show a vibrationally induced rotational spectrum are those belonging to a symmetry species E_s with $s = (n-1)/2$.

The rotational selection rules are determined by the matrix elements of the direction cosines in the expression [cf. Eq. (6.3)]

$$\langle \Phi_v' | \mu_x | \Phi_v'' \rangle \langle \Phi_r' | \lambda_{Zx} | \Phi_r'' \rangle + \langle \Phi_v' | \mu_y | \Phi_v'' \rangle \langle \Phi_r' | \lambda_{Zy} | \Phi_r'' \rangle =$$

$$= \tfrac{1}{2} [\langle \Phi_v' | \mu_x - i\mu_y | \Phi_v'' \rangle \langle \Phi_r' | \lambda_{Zx} + i\lambda_{Zy} | \Phi_r'' \rangle + \langle \Phi_v' | \mu_x + i\mu_y | \Phi_v'' \rangle \times$$

$$\times \langle \Phi_r' | \lambda_{Zx} - i\lambda_{Zy} | \Phi_r'' \rangle] , \tag{8.8}$$

where[1]

$$\langle \Phi_r' | \lambda_{Zx} \pm i\lambda_{Zy} | \Phi_r'' \rangle \neq 0 \quad \text{if} \quad \Delta k = k' - k'' = \mp 1 . \tag{8.9}$$

Since we are dealing with degenerate vibrational levels, the question of the "$\pm l$" selection rules also arises. In a degenerate vibrational level each rotational level with $K \neq 0$ ($K \equiv |k|$), the Coriolis interaction for rotation around the symmetry axis z splits the degeneracy by a factor

$$\mp 2B_z \zeta^{\text{eff}} K , \tag{8.10}$$

where ζ^{eff} is the effective Coriolis constant; the upper sign refers to the $+l$ pair of levels, the lower sign to the $-l$ pair.

By using standard methods[1,71], we find the following selection rule on J, K and the l components for rotational transitions induced by vibrations:

$$K + 1, -l \leftrightarrow K, +l \tag{8.11a}$$

$$\Delta J = 0, \pm 1 . \tag{8.11b}$$

As an example, let us consider molecules belonging to C_{3v} point groups (e.g., PH_3, CH_3F) and D_{3h} point groups (e.g. BCl_3).

The species of μ_Z, the space-fixed component of the electric dipole moment in a C_{3v} molecule is A_2. The species of the molecule-fixed components of $\boldsymbol{\mu}$ are those of T_x, T_y, T_z, i.e. μ_z is A_1, (μ_x, μ_y) are E_1 $(\equiv E)$. The permanent dipole moment has the direction of the molecule-fixed axis z (Fig. 7) and the molecule has an ordinary pure rotation spectrum in a nondegenerate vibrational state with the selection rules $\Delta J = 0, \pm 1$ and $\Delta k = 0$ [Eq. (6.10)]. The permanent dipole moment induces of course an ordinary pure rotation spectrum in a degenerate vibrational state with the same selection rules on J, k and the selection rules $+l \leftrightarrow +l$ and $-l \leftrightarrow -l$ $(+l \leftrightarrow -l)$.

Vibrations inducing a dipole moment parallel with the z axis do not induce forbidden rotational spectra because $(\partial^2 \mu_z / \partial q^2)_e$ has of course the same selection rules as $\mu_z^{(e)}$. On the other hand, a new type of rotational transitions with the selection rules (8.11) arises through the perpendicular vibrations because Eq. (8.7c) holds for C_{3v} group.

For D_{3h} molecules, μ_Z is of the species A_1'' and the species of the molecule-fixed components are A_2'' for μ_z and E' for (μ_x, μ_y). There is no permanent dipole moment and these molecules do not have an ordinary pure rotation spectrum. However, Eq. (8.7c) holds for D_{3h} groups and the vibrationally induced rotational spectra with the selection rules given by Eqs (8.11) can exist.

S-symmetric-top point groups: In S-symmetric-top point groups the label s on the degenerate symmetry species E_s refers to the behaviour with respect to the rotation-reflection operation S_m; s takes all integral values in the range $0 < s < n/2$ and Eqs (8.7) also hold.

The perpendicular components (μ_x, μ_y) of the dipole moment operator belong to an E_1 species and consequently, a perpendicular vibrationally induced rotational spectrum is allowed if $n = 2s + 1$. However, since

$$S_{(2s+1)}^{2s+2} = C_{(2s+1)}, \tag{8.12}$$

an odd S axis is necessarily coincident with a C axis of the same order. Thus these groups should be regarded as C point groups rather than S point groups; the induced rotational spectra of molecules having this symmetry are as described above (see the example of D_{3h} molecules).

An important difference between the C and S point groups consists however in that the axial component μ_z of the electric dipole moment belongs to a B species. Thus, the condition (8.6) with $\alpha = z$ can be satisfied if Eq. (8.7b) holds, i.e. if $n = 4s$ (the order n of the axis S_n must be a multiple of four). The component μ_z has the

selection rules $\Delta J = 0, \pm 1$; $\Delta k = 0$ and $\pm l \leftrightarrow \pm l$ and a parallel-type rotational spectrum can be induced in the doubly degenerate vibrational states $E_{(n/4)}$.

The D_{2d} point group is likely to be the most important in practice (e.g., allene CH_2CCH_2). There is an S_4 symmetry axis (and no C_4 axis) in D_{2d} molecules. The species of μ_z is B_2, that of (μ_x, μ_y) is E. There is no permanent dipole moment in molecules of this kind but a parallel rotational spectrum in the excited vibrational state of the species E can be induced.

8.2. *Rotational Transitions in Spherical Top Molecules*

The point groups that qualify are T, T_d, O, and I (no center of symmetry). The three components of the electric dipole moment vector with respect to the molecule-fixed axes (μ_x, μ_y, μ_z) form the basis of a triply degenerate irreducible representation F_2 for the T and T_d groups, F_1 for O and I groups; thus there is no permanent dipole moment in these molecules.

From the direct product of the species of these point groups[72], we obtain that the only vibrational species whose symmetric squares satisfy condition (8.6) are the F levels of molecules belonging to the point group T and the F_1 and F_2 levels of molecules belonging to the point group T_d. The latter point group is the most important in practice as is illustrated by molecules of the methane type (GeH_4, SiF_4, CF_4 or CCl_4).

We have the usual selection rule $\Delta J = 0, \pm 1$ on J for the vibrationally induced rotational spectrum of tetrahedral molecules in the triply degenerate vibrational states. The analogue of the $\pm l$ selection rule is the selection rule on the approximate momentum $\mathbf{R} = \mathbf{J} - \mathbf{L}$, where $\mathbf{J}$ is the total angular momentum and $\mathbf{L}$ is given by

$$\mathbf{L} = \sum_t \mathbf{l}_t = \sum_t \mathbf{Q}_t \times \mathbf{P}_t . \tag{8.13}$$

In Eq. (8.13), $\mathbf{Q}_t$ is the vector (Q_{tx}, Q_{ty}, Q_{tz}) of the component normal coordinates of species F while $\mathbf{P}_t$ is the corresponding vector of the conjugate momenta; $\zeta_t \mathbf{l}_t$ is therefore the vibrational angular momentum associated with the t-th normal mode (ζ_t is the Coriolis coupling constant).

The rotational levels are then labelled by the quantum number J and the approximate number R which is the eigenvalue of $\mathbf{R}^2$. For the fundamental levels of F vibrations, R assumes the values $J + 1$, J, and $J - 1$ respectively for the sublevels $F^{(+)}(J)$, $F^{(0)}(J)$, and $F^{(-)}(J)$, whose rotational energies are given approximately by[1]:

$$F^{(+)}(J) = B_v J(J + 1) + 2B_v \zeta_v (J + 1) \quad (R = J + 1), \tag{8.14a}$$

$$F^{(0)}(J) = B_v J(J + 1) \quad (R = J), \tag{8.14b}$$

$$F^{(-)}(J) = B_v J(J + 1) - 2B_v \zeta_v J \quad (R = J - 1). \tag{8.14c}$$

8.3. *Observations of the Vibrationally Induced Rotational Transitions*

Intensities of the vibrationally induced transitions depend essentially on the following two factors: (i) the effective dipole transition moment which for the fundamental vibrational level can be approximately written as[71] [see also Eq. (4.11)]

$$\langle 1^{-1}| \, (\mu_x + i\mu_y)_{\text{eff}} \, |1^{+1}\rangle = \langle 1^{+1}| \, (\mu_x - i\mu_y)_{\text{eff}} \, |1^{-1}\rangle =$$
$$= (\partial^2 \mu_x/\partial q_{tx}^2)_e - 2\pi \sum_{t'} k_{t_x t_x t'_x} (\partial \mu_x/\partial q_{t'_x})_e / h\lambda_t^{1/2} , \qquad (8.15)$$

where $k_{t_x t_x t'_x} = (\partial^3 V/\partial q_{t_x}^2 \partial q'_{t_x})_e$ is a cubic force constant and we use the notation $|v_t^{l_t}\rangle$ for the vibrational wavefunctions; (ii) on the Boltzman factor $\exp(-E_t/kT)$ which reduces the intensity of the spectrum lines due to the decreased population of the excited vibrational level.

If the anharmonic contributions were negligible, the transition moment (8.15) would depend only on $(\partial^2 \mu_x/\partial q_t^2)_e$, i.e. would be simply related to that of the first overtone vibrational transition. If we assume that the transition moment for the ordinary pure rotational spectra is of the order of magnitude 1 D (= 0·33356 . . 10^{-29} C m), then the order of magnitude estimate of the effective transition moment of the induced transition is 10^{-2} D (Table III) and because the line intensity is proportional to the square of the transition moment, we have the factor 10^{-4} by which the intensity of the induced rotational transition is decreased in comparison with that of the ordinary rotational spectrum. The Boltzman factor decreases the intensity typically by two orders of magnitude, thus the intensity of the forbidden transition is about 10^{-6} of the intensity of the rotational spectrum of an ordinary polar molecule.

The unfavourable population factor can be eliminated by using the technique of the infrared–microwave double resonance[73] in which an infrared laser source is used to pump the molecules to the excited vibrational state and then a microwave frequency is swept across the rotational transition. In this way, Curl and Oka[74] measured for the first time the vibrationally induced rotational transition: the $F_1^{(2)} \leftrightarrow F_2^{(2)}$ transition in the $J_R = 6_7$, $v_3 = 1$ level of methane, CH_4. They used a 3·39 μm He–Ne laser whose frequency nearly coincides with the frequency of the $P^+(7)$ vibrational--rotational line (the $F_1^{(2)} \leftrightarrow F_2^{(2)}$ transition) to pump the molecules to the $v_3 = 1$ level and to measure the frequency (6 895·3 MHz) of the $\Delta J = 0$ induced rotational transition in the triply degenerate vibrational level (Fig. 11).

A more favourable region for a direct observation of the induced rotational spectra is the far infrared, where the frequency and induced emission factors are less prohibitive. Ozier and Rosenberg[75] have measured such transitions for the first time in the spectra between 80 and 180 cm^{-1} of the $v_4 = 1$ state of methane.

Nevertheless, the most important data on the vibrationally induced rotational transitions in the excited vibrational states have been later obtained by the infrared–

microwave double resonance technique[73] and relatively recently by the extremely sensitive technique of the microwave Fourier transform spectroscopy[76].

Pure rotational transitions by vibrationally induced dipole moments have been observed in the triply degenerate vibrational levels by use of infrared–microwave

TABLE III

Vibrationally induced dipole moments in the excited vibrational states

Molecule	Dipole moment		Vibrational state	Ref.
	in D . 10^2	in Cm . 10^{32}		
$^{12}CH_4$	$\begin{cases} 2 \cdot 00(1) \\ 3 \cdot 47 \end{cases}$	$6 \cdot 67(3)$ $11 \cdot 6$	$\nu_3 = 1$ $\nu_4 = 1$	70 (see also 87a) 87b
$^{12}CD_4$	$\sim 2 \cdot 6$	$\sim 8 \cdot 67$	$\nu_4 = 1$	86
$^{13}CD_4{}^f$	$0 \cdot 940$ (see^d)	$3 \cdot 137$	$\nu_4 = 1$	85
CF_4	$3 \cdot 6$	12	$\nu_3 = 1$	79–82
$SiH_4{}^{a,f}$	$1 \cdot 46(5)$	$4 \cdot 87(17)$	$\nu_3 = 1$	see footnote b in Table VII
BF_3	~ 4	~ 13	$\nu_3 = 1$	91, 92
CDF_3	$\begin{cases} 1 \cdot 222(49) \\ 0 \cdot 760(66) \text{ (see}^c) \end{cases}$	$\left.\begin{matrix} 4 \cdot 076(163) \\ 2 \cdot 535(220) \end{matrix}\right\}$	$\nu_5 = 1$	90a 90c
CD_3Cl	$0 \cdot 601(57)$	$2 \cdot 00(19)$	$\nu_5 = 1$	90b
CH_2CCH_2 (allene)	$\begin{cases} 4 \cdot 41(5) \text{ (see}^b) \\ 4 \cdot 52(6) \text{ (see}^c) \\ \leqq 0 \cdot 5 \end{cases}$	$\left.\begin{matrix} 14 \cdot 7(17) \\ 15 \cdot 1(20) \end{matrix}\right\}$ $\leqq 1 \cdot 7$	$\left.\begin{matrix} \nu_{10} = 1 \\ \nu_{11} = 1 \end{matrix}\right\}$	89 (see also 216)

^{a} See footnote ^{b} in Table VII. ^{b} Dipole moment calculated from Stark shifts but neglecting polarization effects[89]. ^{c} The contribution of polarization was taken into account approximately[89]. ^{d} Average value (see[85]). ^{e} Corrected for the contribution of the "2, 1" l-type interaction[90c]. ^{f} See note added in proof.
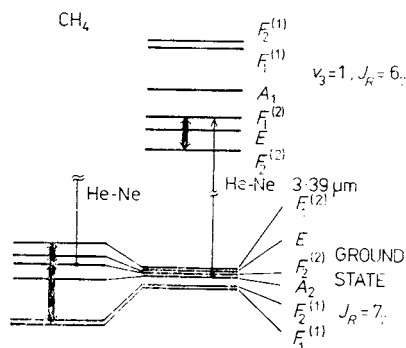

FIG. 11

Energy level diagram for the infrared–microwave double resonance experiment in CH_4 (ref.[74]). The vibrationally induced rotational transition in the $\nu_3 = 1$ state of species F_2 is indicated by the bold arrow. The magnified ground state splitting on the left pertains to an experiment described in Part 9.2.

or infrared–radiofrequency double resonance for several tetrahedral molecules: SiH_4 (ref.[77]), GeH_4 (ref.[78]), CF_4 (refs[79–82]), SiF_4 (ref.[83a]), SnH_4 (ref.[83b]) and OsO_4 (ref.[84]). Recently, Magerl et al.[85] used the infrared laser sideband spectroscopy to determine the vibrationally induced dipole moment in the $v_4 = 1$ fundamental of $^{13}CD_4$ as a function of the quantum number R.

The microwave Fourier transform spectroscopy has been used for the first time to observe pure rotational transitions in the $v_4 = 1$ vibrational state of $^{12}CD_4$ by Oldani et al.[86] and later it has been used also for $^{12}CH_4$ (ref.[87a]) and SiH_4 (ref.[88]). Hilico et al.[87b] increased the vibrational population in the $v_4 = 1$ state of $^{12}CH_4$ by using an electric discharge and observed the vibrationally induced rotational transitions in the $v_4 = 1$ state between 120 and 268 GHz (Table III).

The vibrationally induced rotational spectra of a symmetric top molecule have been detected for the first time in the $v_5 = 1$ state of CDF_3 by laser-Stark spectroscopy[90]. The first measurement of these transitions for a nonpolar symmetric top molecule have been reported by Yamamoto et al.[91] for $^{11}BF_3$ using the infrared––microwave double resonance technique (see ref.[92] as for $^{10}BF_3$).

Schematic energy diagram for this double resonance experiment is illustrated by Fig. 12. The $^RQ(J, K = 3)$ transition is pumped by a tunable diode laser (TDL) and simultaneous resonance of the microwave (MW) transition is detected as an increase in the infrared absorption.

It has been already mentioned that forbidden transitions can provide information on certain spectroscopical parameters which cannot be obtained from the frequencies of the allowed transitions. We will use the example of the BF_3 molecule to illustrate this situation.
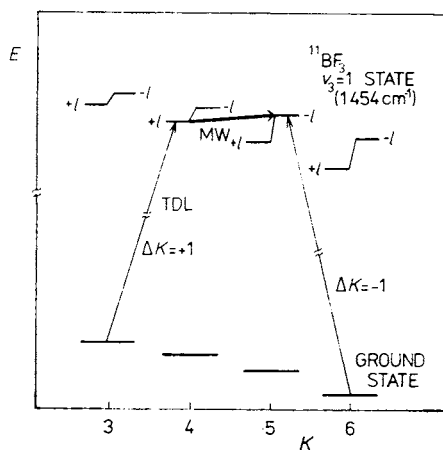

FIG. 12

Energy level diagram for the infrared–microwave double resonance experiment in $^{11}BF_3$ (ref.[91]). The vibrationally induced rotational transition $K = 5 \leftarrow K = 4$ ($-l \leftarrow +l$, $\Delta J = 0$) in $v_3 = 1$ state of species E' is indicated by the bold arrow

It is well known that the expression for the ground state rotational energy levels of a C_{3v} molecule can be written as[1]

$$E_r(J, K) = B_x J(J + 1) + (B_z - B_x) K^2 - D_J J^2(J + 1)^2 - D_{JK} J(J + 1) K^2 -$$
$$- D_K K^4 + H_J J^3(J + 1)^3 + H_{JK} J^2(J + 1)^2 K^2 + H_{KJ} J(J + 1) K^4 +$$
$$+ H_K K^6 + \ldots + E_{split} , \qquad (8.16)$$

TABLE IV

Ground state values of B_z and D_K for symmetric top molecules (in cm^{-1})

Molecule	Symmetric top: prolate (p) oblate (o)	B_z (see[a])	$D_K \cdot 10^4$	Ref.
$^{14}NH_3$	o	6·2275053(24) (see[b])	9·1383(11) (see[b])	146 (see[f])
		6·2295057(26) (see[c])	8·8207(15) (see[c])	
$^{15}NH_3$	o	6·2279438(78) (see[b])	9·14394(85) (see[b])	147
		6·2298495(78) (see[c])	8·84755(85) (see[c])	
PH_3	o	3·91903115(95)	1·412966(289)	122 (see also 106—108, 119—121)
PD_3	o	1·967101(100)		107
AsH_3	o	3·498555092(392)	1·11661086(4063)	116
SH_3^+	o	4·228258(26)	2·216(20)	138
$^{11}BF_3$	o	0·17217368(26)	0·0035488(40)	93
CH_3D	p	5·2508231(43)	−0·7869(230)	128
CD_3H	o	2·62896(4)	0·138(2)	129
CH_3F	p	5·182009(12)	0·7033(25)	137
$CD_3{}^{35}Cl$	p	2·613332(25)	0·1797(42)	90b
$CD_3{}^{37}Cl$	p	2·613372(54)	0·1923(108)	90b
CH_3I	p	5·17285(8)	0·70(28)	136a (see also 136b)
CHF_3	o	0·189246(3)	$(3·3)^d$	135a
CDF_3	o	0·189238(3)	$(3·1)^d$	135a
		0·1892380(28)	0·0015(5)	90c
SiH_3D	p	2·86354(46) (see[e])		130
POF_3	p	0·16050200(6)	−0·0003716(40)	132 (see[g])
		0·1605029(1)		135b
CH_2CCH_2	p	4·811842(12)	0·974(69)	216

[a] $B_z = A_0$ for prolate (p) symmetric tops, $B_z = C_0$ for oblate (o) symmetric tops. [b] Lower component of the inversion doublet. [c] Upper component of the inversion doublet. [d] Calculated from the force field [e] $A_0 - 5D_K$. [f] Ground state $\Theta_x^{xx} = 1·241(70) \cdot 10^{-4} D$ (ref.[152]). [g] Ground state $\Theta_x^{xx} = 4·0(1·4) \cdot 10^{-6} D$.

where E_{split} is a term which describes the small A_1–A_2 splitting of energy levels with $K = 3n$ $(n = 1, 2, 3, ...)$ and is absent otherwise.

The ordinary rotation spectra do not provide information on the parameters B_z, D_K, H_K, ... because of the $\Delta k = 0$ selection rule. No information can be obtained from the combination differences for the allowed parallel or perpendicular vibrational-rotational bands because they provide only the differences between the ground state levels $(J + 1, K)$, (J, K), and $(J - 1, K)$. However, it can be seen from Fig. 12 that a simple combination of the allowed vibrational-rotational and forbidden rotational transitions determines the differences between the levels differing by ± 3 in the rotational quantum number k (see Table IV).

9. FORBIDDEN TRANSITIONS INDUCED BY VIBRATIONAL-ROTATIONAL INTERACTIONS

In Part 8 of this paper, forbidden rotational transitions have been discussed in symmetric top and spherical top molecules which are induced by vibrations due to the electrical and mechanical anharmonicities [Eq. (8.15)]. In Part 9, forbidden rotational and vibrational-rotational transitions are discussed which are induced by vibrational-rotational interactions. They are also important because they give rise to purely rotational spectra in the ground vibrational states of nonpolar molecules as well to various forbidden vibrational-rotational transitions providing unique information on the molecular constants.

9.1. Symmetric Top Molecules

The vibronic wavefunction Φ_{ev} for a molecule with an axis of rotation C_n (point group I) can be characterized by a vibronic number G_{ev} such that[1,94]

$$\mathbf{C}_n \Phi_{\text{ev}} = \exp\left(-2\pi i G_{\text{ev}}/n\right) \Phi_{\text{ev}}, \tag{9.1}$$

where G_{ev} can be expressed in terms of vibrational and electronic quantum numbers

$$G_{\text{ev}} = G_{\text{e}} + G_{\text{v}} = G_{\text{e}} + \frac{n}{2}\sum_B v_B + \sum_t s_t l_t ; \tag{9.2}$$

G_{e} and G_{v} characterize the transformation properties of the electronic wavefunction Φ_{e} and of the vibrational wavefunction, respectively ($G_{\text{e}} = 0$ if the molecule is in a totally symmetric electronic state). In nonlinear molecules, G_{v} is composed of two parts. If n is even, the molecule may have vibrational modes of species B and the first term in G_{v} adds up the total number of quanta of such vibrations excited for the state in question. If n is odd, there can be no B vibrations, and this term vanishes. The second term in G_{v} involves a sum over the (signed) vibrational quantum numbers

associated with degenerate vibrations; s_t specifies the representation E_{s_t} in which the s-th degenerate vibration belongs.

It should be mentioned that the classification of the vibronic wavefunctions based on their transformation properties with respect to $\mathbf{C}_n$ does not give full information on their symmetry in the case of D_{nd} (n even) and S_m ($m/2$ even) point groups[94] (point group II). In this case C_n should be replaced by S_m and G_v is

$$G_v = n \sum_B v_B + \sum_t s_t l_t \,. \qquad (9.3)$$

Although $\mathbf{C}_n$ has been introduced as the point group operation, it should be understood also as the completely feasible symmetry operation $\mathbf{P}_n$ which permutes n symmetrically equivalent atomic nuclei[1,20] (similarly $\mathbf{S}_m$ is the corresponding permutation followed by inversion $\mathbf{E}^*$).

The effect of $\mathbf{C}_n$ on the symmetric top rotational wavefunctions $|J, k\rangle$ is therefore

$$\mathbf{C}_n |J, k\rangle = \exp\left(2\pi\mathrm{i}k/n\right) |J, k\rangle \qquad (9.4)$$

and the vibrational-rotational Hamiltonian $\mathbf{H}_{vr}$ commutes with $\mathbf{C}_n$,

$$\mathbf{C}_n \mathbf{H}_{vr} \mathbf{C}_n^{-1} = \mathbf{H}_{vr} \,. \qquad (9.5)$$

According to Eqs (9.1) and (9.4), it holds that

$$\mathbf{C}_n |\Phi'_{ev}\rangle |J, k'\rangle = \exp\left[2\pi\mathrm{i}(k' - G'_{ev})/n\right] |\Phi'_{ev}\rangle |J, k'\rangle \qquad (9.6)$$

and

$$\langle\Phi''_{ev}| \langle J, k''| \mathbf{C}_n^{-1} = \exp\left[-2\pi\mathrm{i}(k'' - G''_{ev})/n\right] \langle\Phi''_{ev}| \langle J, k''| \,. \qquad (9.7)$$

By using Eqs $(9.4)-(9.7)$ we find

$$\langle\Phi''_{vr}| \mathbf{H}_{vr}|\Phi'_{vr}\rangle = \langle\Phi''_{vr}| \mathbf{C}_n^{-1}\mathbf{C}_n\mathbf{H}_{vr}\mathbf{C}_n^{-1}\mathbf{C}_n|\Phi'_{vr}\rangle =$$

$$= \exp\left\{2\pi\mathrm{i}[(G''_v - k'') - (G'_v - k')]/n\right\} \langle\Phi''_{vr}| \mathbf{H}_{vr}|\Phi'_{vr}\rangle \,, \qquad (9.8)$$

where

$$\Phi_{vr} = |\textstyle\prod_i v_i\rangle |\textstyle\prod_t v_t^{l_t}\rangle |J, k\rangle \,. \qquad (9.9)$$

Following Hougen[94], we introduce the quantum number G defined as

$$G = G_v - k \,. \qquad (9.10)$$

Thus we see that the following condition must be satisfied in order that $\langle \Phi''_{vr}| \, \mathbf{H}_{vr} |\Phi'_{vr}\rangle$ be nonvanishing for groups I

$$G'' - G' = pn , \tag{9.11}$$

where p is an arbitrary integer (positive as well as negative) including zero. For groups II this condition is

$$G'' - G' = (1 + 2p)\, n . \tag{9.12}$$

Because the component of the electric dipole moment operator μ_Z along the space--fixed Z axis is invariant with respect to the operation $\mathbf{C}_n$ (ref.[1]), the electric dipole transition between two states is allowed if and only if the condition (9.11) is satisfied (groups I) or (9.12) is satisfied (groups II).

Since G classifies the wavefunctions only with respect to C_n (groups I) or S_{2n} (groups II) elements of symmetry, the quantum number G gives the complete information on the symmetry of states only for the groups C_n or S_{2n} (n even). For other groups additional restrictions must be imposed, following from the presence of symmetry elements such as i, σ_h or σ_v which can further distinguish the species of the vibronic wavefunctions. These restrictions can, however, be imposed as the last step.

The rotation and vibration-rotation transitions can be divided with the help of G into the following groups[95]: (i) Strictly forbidden are transitions for which $\Delta G \neq pn$ for groups I or $\Delta G \neq (1 + 2p)\, n$ for groups II. Such transitions are possible only through extremely small spin–rotation and spin–spin interactions (cf. Part 5). (ii) Strongly allowed are transitions which satisfy conditions (9.11) or (9.12) and $\Delta k = 0$ or ± 1 (Part 6). (iii) Approximately forbidden are transitions which satisfy conditions (9.11) or (9.12) but $\Delta k \neq 0, \pm 1$. These transitions are forbidden in the zeroth-order approximation (Part 6) but can be allowed in higher approximation.

Before discussing in more detail the radiative selection rules which follow from Eqs (9.11) or (9.12), let us mention that the intermolecular interaction has the same permutation symmetry as $\mathbf{H}_{vr}$ (ref.[30]). Therefore, in both radiative and collisional processes we have the same selection rules for Δk.

As an example of the application of the general selection rule (9.11), let us consider the rotation and vibration-rotation transitions of C_3-symmetric top molecules (the most important in practice among these molecules are the C_{3v} and D_{3h} molecules).

Pure rotational transitions: By applying Eq. (9.11), we find the following selection rules for the pure rotational transitions in the nondegenerate vibrational states (including of course the ground vibrational state):

$$\Delta k (\equiv k' - k'') = 3p \quad (p = 0, \pm 1, \pm 2, \ldots), \tag{9.13}$$

that is

$$\Delta k = 0, \pm 3, \pm 6, \ldots \quad (\equiv \Delta k = 0 \bmod 3) . \qquad (9.13b)$$

For the fundamental vibrational level of the doubly degenerate vibration ($v_t = 1$, $l_t = 1$), we find that

$$\Delta k = p \quad (p = 0, \pm 1, \pm 2, \ldots) \qquad (9.14a)$$

that is

$$\Delta k = 0, \pm 1, \pm 2, \ldots (\equiv \Delta k = 0 \bmod 1) . \qquad (9.14b)$$

In terms of the rotational quantum number $K(\equiv |k|)$, Eq. (9.13) can be written as

$$\Delta K (\equiv K' - K'') = 0 ; \quad K \leftrightarrow K , \qquad (9.15)$$

$$\Delta K = \pm 3 ; \quad K + 3p \leftrightarrow K , \qquad (9.16)$$

$$\Delta K = \pm 1 ; \quad 3K + 2 \leftrightarrow 3K + 1 \qquad (9.17)$$
$$\vdots \qquad\qquad\qquad\qquad \vdots$$

The rule (9.14) has to be supplemented by the selection rules on the $\pm l$ components of the rotational levels with $k \neq 0$ which are split by the Coriolis interaction for the rotation around the z axis [Eq. (8.10)]. In the $+l$ level, the signs of k and l_t are the same, in the $-l$ levels opposite. Using Eq. (9.11), we find for $|\Delta K| = |\Delta k|$ the following selection rules on K and l:

$$\Delta K = 0 ; \quad (K, \pm l) \leftrightarrow (K, \pm l) , \qquad (9.18)$$

$$\Delta K = \pm 1 ; \quad (K + 1, -l) \leftrightarrow (K, +l) , \qquad (9.19)$$

$$\Delta K = \pm 2 ; \quad (K + 2, +l) \leftrightarrow (K, -l) , \qquad (9.20)$$

$$\Delta K = \pm 3 ; \quad (K + 3, \pm l) \leftrightarrow (K, \pm l) \qquad (9.21)$$
$$\vdots \qquad\qquad\qquad\qquad\qquad \vdots$$

(with the signs of l correlated).

Besides these rules, there are rules for $|\Delta K| \neq |\Delta k|$, which hold for special values of K. For example

$$K = 1 ; \quad \Delta K = 0 \quad \text{but} \quad \Delta k = \pm 2, +l \leftrightarrow +l , \qquad (9.22)$$

$$K = 2 ; \quad \Delta K = 0 \quad \text{but} \quad \Delta k = \pm 4, -l \leftrightarrow -l , \qquad (9.23)$$

$$K = 3 ; \quad \Delta K = 0 \quad \text{but} \quad \Delta k = \pm 6, -l \leftrightarrow +l \qquad (9.24)$$
$$\vdots \qquad\qquad\qquad\qquad\qquad\qquad \vdots$$

Vibrational-rotational transitions: The selection rules for the vibrational-rotational transitions between the nondegenerate vibrational states as for the quantum number k are the same as those given in Eq. *(9.13)*. As for the transitions between a nondegenerate (species A) and doubly degenerate (species E) vibrational level, they can be found to be

$$\Delta k = 3p \pm 1 \quad (p = 0, \pm 1, \pm 2, \ldots) \qquad (9.25a)$$

that is

$$\Delta k = \pm 1, \pm 2, \pm 4, \pm 5, \ldots \quad (\equiv \Delta k = \pm 1 \bmod 3). \qquad (9.25b)$$

The $\pm l$ selection rules for $|\Delta K| = |\Delta k|$ are the following (all the signs are correlated):

$$\Delta K = \pm 1 ; \quad (K \pm 1, \pm l) \leftrightarrow K, \qquad (9.26)$$

$$\Delta K = \pm 2 ; \quad (K \pm 2, \mp l) \leftrightarrow K, \qquad (9.27)$$

$$\Delta K = \pm 4 ; \quad (K \pm 4, \pm l) \leftrightarrow K \qquad (9.28)$$

$$\vdots \qquad\qquad\qquad\qquad\qquad \vdots$$

For $|\Delta K| \neq |\Delta k|$, we have for special values of K for example the following rules:

$$K = 1 ; \quad \Delta K = 0 \quad \text{but} \quad \Delta k = \pm 2, \quad (K' = 1, -l) \leftrightarrow K'' = 1 \qquad (9.29)$$

$$K = 2 ; \quad \Delta K = 0 \quad \text{but} \quad \Delta k = \pm 4, \quad (K' = 2, +l) \leftrightarrow K'' = 2 \qquad (9.30)$$

$$\vdots$$

or

$$K = 1 ; \quad \Delta K = +2 \quad \text{but} \quad \Delta k = \pm 4 ; \quad (K' = 3, +l) \leftrightarrow K' = 1 . \qquad (9.31)$$

Because C_3 is not the only symmetry operation for the C_{3v} or D_{3h} groups, these rules are necessary but not sufficient conditions for a transition to be at least approximately allowed. For example, reflection σ_v distinguishes between the A_1 and A_2 species in the C_{3v} and D_{3h} groups while σ_h between the ' and " species in the D_{3h} group. The overall symmetry selection rule is $A_1 \leftrightarrow A_2$, $E \leftrightarrow E$ for C_{3v} group and $A_1 \leftrightarrow A_1$, $A_2 \leftrightarrow A_2$, $E \leftrightarrow E$, and ' $\leftrightarrow$ " for the D_{3h} group. This makes it possible for example to decide which components of the A_1–A_2 splitting of energy levels are involved in a particular transition (Fig. 13). Similarly, the $\Delta k = 0$ or ± 6 transitions are not allowed in the D_{3h} group because they violate the ' $\leftrightarrow$ " selection rule (Tables V and VI).

The possibility of forbidden transitions in the rotational and vibrational-rotational spectra of C_{3v} molecules has been considered for the first time by Hanson[96], who derived expressions for the linestrengths of the $\Delta k = \pm 3$ pure rotational transi-

tions and for some forbidden vibrational-rotational transitions (unfortunately some of the results cannot be correct because the proposed forbidden transitions violate the overall symmetry selection rule).

Actually the first complete theory of the forbidden pure rotational spectra in symmetric top molecules has been worked out by Watson[97] (see also ref.[98]) and independently by Aliev and Mikhaylov[99-101] (see also ref.[102] for the purely rotational spectra in the excited vibrational states of nonpolar molecules). The third-order theory of the line intensities in the allowed and forbidden vibrational-rotational bands of C_{3v} molecules has been worked out by Aliev, Papoušek, and Urban[18], for the D_{3h} molecules (with emphasis on H_3^+) by Aliev and Mikhaylov[103] (see also refs[104,105]). Sarka[95] discussed general conditions under which observation of the forbidden vibration-rotation transitions can be expected in the infrared spectra of symmetric top molecules with the special emphasis on the determination of the rotational constant B_z (C in oblate symmetric tops, A in prolate tops[1]).
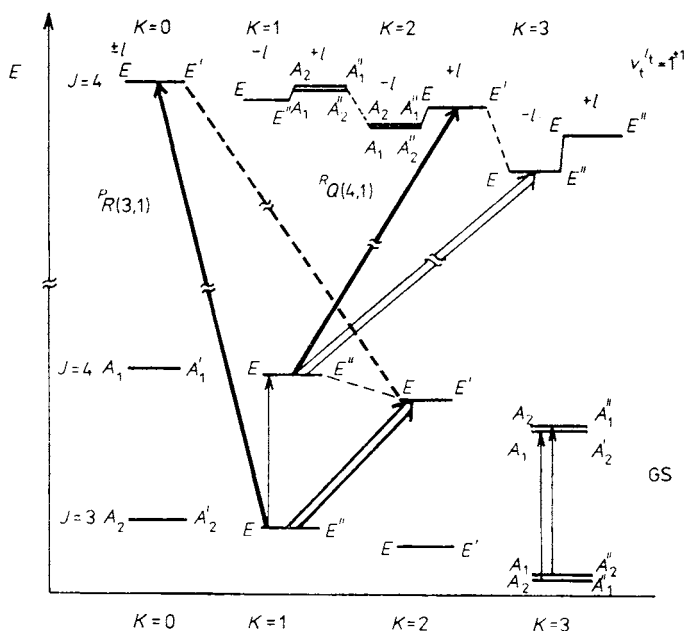

FIG. 13

Energy level diagram of the rotational levels in the ground vibrational state (GS) and in the first excited vibrational state $v_t^{lt} = 1^{\pm 1}$ of the doubly degenerate normal vibration for C_{3v} and D_{3h} molecules. The overall symmetry species for C_{3v} group are indicated on the left side, those for D_{3h} on the right side of each level. Dashed lines indicate vibrational-rotational interactions, lines with arrows indicate allowed or approximately allowed transitions. Bold lines (full or dashed) mean that a given transition or interaction occurs in both C_{3v} or D_{3h} groups

TABLE V

Symmetry classification of the rovibrational states in a nondegenerate vibrational state of C_{3v} and D_{3h} molecules[a]

$\lvert v_n\rangle\lvert J,k\rangle$	C_{3v} species		D_{3h} species		D_{3h} (see[b]) $\lvert\Phi_i(\varrho)\rangle\lvert v_n\rangle\lvert J,k\rangle$ species			
					sym.		antisym.	
	J even	J odd	J even	J odd	J even	J odd	J even	J odd
$\lvert v_n\rangle\,\lvert J,0\rangle$	A_1	A_2	A'_1	A'_2	A'_1	A'_2	A''_2	A''_1
$\lvert v_n\rangle\,\lvert J,+1\rangle,\,\lvert v_n\rangle\,\lvert J,-1\rangle$	E		E''		E''		E'	
$\lvert v_n\rangle\,\lvert J,+2\rangle,\,\lvert v_n\rangle\,\lvert J,-2\rangle$	E		E'		E'		E''	
$\lvert v_n\rangle\,(\lvert J,+3\rangle + \lvert J,-3\rangle)$	A_2	A_1	A''_1	A''_2	A''_1	A''_2	A'_2	A'_1
$\lvert v_n\rangle\,(\lvert J,+3\rangle - \lvert J,-3\rangle)$	A_1	A_2	A''_2	A''_1	A''_2	A''_1	A'_1	A'_2

[a] The symmetry species for C_{3v} group hold for k with modulo 3 (those for the D_{3h} group for k with modulo 6). In the D_{3h} group, the species of the states with $K + 3$, $K + 4$, $K + 5$ are obtained from those with K, $K + 1$, $K + 2$ by changing ′ into ″ and vice versa. [b] Symmetry classification of the states in XY_3 molecules with a large amplitude inversion motion.

TABLE VI

Symmetry classification of the rovibrational states in the fundamental vibrational level of the doubly degenerate vibration in C_{3v} and D_{3h} molecules[a]

$|v^l; J, k\rangle$	C_{3v} species		D_{3h} species		D_{3h} (see[b]) $\quad |\Phi_i(\varrho)\rangle \, |v^l; J, k\rangle$ species			
					sym.		antisym.	
	J even	J odd	J even	J odd	J even	J odd	J even	J odd
$\pm l \begin{cases} |1^{+1}; J, 0\rangle \\ |1^{-1}; J, 0\rangle \end{cases}$	E	E	E'	E'	E'	E'	E''	E''
$+l \begin{cases} |1^{+1}; J, +1\rangle + \\ |1^{-1}; J, -1\rangle \end{cases}$	A_2	A_1	A_1''	A_2''	A_1''	A_2''	A_2'	A_1'
$\begin{cases} |1^{+1}; J, +1\rangle - \\ |1^{-1}; J, -1\rangle \end{cases}$	A_1	A_2	A_2''	A_1''	A_2''	A_1''	A_1'	A_2'
$-l \begin{cases} |1^{+1}; J, -1\rangle \\ |1^{-1}; J, +1\rangle \end{cases}$	E	E	E''	E''	E''	E''	E'	E'
$+l \begin{cases} |1^{+1}; J, +2\rangle \\ |1^{-1}; J, -2\rangle \end{cases}$	E	E	E'	E'	E'	E'	E''	E''
$-l \begin{cases} |1^{+1}; J, -2\rangle + \\ |1^{-1}; J, +2\rangle \end{cases}$	A_1	A_2	A_1'	A_2'	A_1'	A_2'	A_2''	A_1''
$\begin{cases} |1^{+1}; J, -2\rangle - \\ |1^{-1}; J, +2\rangle \end{cases}$	A_2	A_1	A_2'	A_1'	A_2'	A_1'	A_1''	A_2''
$+l \begin{cases} |1^{+1}; J, +3\rangle \\ |1^{-1}; J, -3\rangle \end{cases}$	E	E	E''	E''	E''	E''	E'	E'
$-l \begin{cases} |1^{+1}; J, -3\rangle \\ |1^{-1}; J, +3\rangle \end{cases}$	E	E	E''	E''	E''	E''	E'	E'

[a] See footnote "a" in Table V. [b] See footnote "b" in Table V.

The experimental observations of the forbidden transitions in polar and nonpolar symmetric top molecules are now an interesting part of the history of microwave, submillimeterwave, and high-resolution infrared spectrscopy. The $\Delta k = \pm 3$ transitions in the pure rotational spectra of PH_3, PD_3, and AsH_3 were first detected in the microwave spectra by Chu and Oka[106,107] who were helped in their measurements by the line frequency predictions based on the previous observations of $\Delta(k - l) = \pm 3$ vibrational-rotational transitions of PH_3 by Maki, Sams, and Olson[108] and by Olson et al.[109] for AsH_3. Measurements of the $\Delta k = \pm 3$ forbidden transitions in the ground vibrational state have been later extended to the submillimeterwave region for PH_3 (refs[110-112]) and AsH_3 (refs[113-115], see also refs[116,117]). Kazakov et al.[118] have observed the $\Delta K = 2$ and 3 pure rotational spectra in the $v_2 = 1$ (A_1) and $v_4 = 1$ (E) vibrational states of AsH_3 using the extremely sensitive technique of submillimeterwave spectroscopy with acoustic detection (RAD).

Many forbidden transitions have also been observed in the high-resolution vibrational-rotational spectra of PH_3 (refs[108,119-123]) and AsH_3 (refs[109,124]). Especially the work of DiLonardo et al.[124] is an excellent example of the importance of the studies of forbidden transitions: they recorded the infrared absorption of AsH_3 between $750-1\,200$ cm^{-1} at a resolution of 0.006 cm^{-1} and among $2\,419$ transitions, nearly 700 forbidden transitions with $\Delta(k - l) = \pm 3$, ± 6, ± 9 have been assigned to the $v_2 = 1$ (A_1) and $v_4 = 1$ (E) bands.

When one of the protons in methane, CH_4, is replaced with a deuteron, the T_d symmetry is reduced to C_{3v}, and the associated changes in the zero-point vibration and molecular charge distribution induce a small permanent dipole moment[101] $\mu_z^{(e)} \approx 5 \cdot 10^{-3}$ D. The allowed rotational spectrum $(\Delta k = 0)$ has been observed in CH_3D by Ozier et al.[125] between $40-120$ cm^{-1} with a low signal-to-noise ratio, but later many forbidden vibrational-rotational transitions have been observed[126-128] from which the ground state rotational constant A_0 and the centrifugal distortion constant D_K^0 could be determined accurately $[A_0 = 5\cdot2508231(43)$ cm^{-1}, $D_K^0 = -7\cdot869(230) \cdot 10^{-5}$ cm^{-1}, ref.[128]]. In $^{12}CD_3H$, 50 forbidden $\Delta(k - l_6) = \pm 3$ transitions have been observed allowing to determine the pure "K-dependent" constants $C_0 = 2\cdot62896(4)$ cm^{-1}, $D_K^0 = 1\cdot38(2) \cdot 10^{-5}$ cm^{-1} besides B_0 and other quartic and sextic centrifugal distortion constants[129]. The SiH_3D forbidden spectra have been measured by Lovejoy and Olson[130]. Kagann et al.[131,132] have observed a large number of $\Delta k = \pm 3$ Q-branch microwave transitions in POF_3 and from an analysis of the frequencies have determined $A_0 - B_0 = 7\cdot2557 \cdot 10^{-3}$ cm^{-1} and the ground state quartic and sextic centrifugal distortion constants. Due to the small value of $A_0 - B_0$, POF_3 is a near-spherical top so that the energy separation of J, k and J, $k \pm 3$ levels with $k = \mp 1$ is only ~ 3 $(A_0 - B_0)$. Thus an application of a relatively low Stark field in the laser-Stark spectroscopy can create an attempted crossing of the levels. However, as a result of centrifugal distortion [Eq. (9.36)], a small nonzero matrix element connects the corresponding states and consequently

the levels cannot cross (avoided crossing). From the resonant field of the anticrossing and knowledge of the Stark effect it is possible to calculate the zero-field splitting of these levels and therefore the value of $A_0 - B_0$ (see, e.g. refs[133-135]). This is an alternative to the determination of the "spectroscopically forbidden" rotational constants from measuring forbidden transitions, but as indicated above, it is limited by certain requirements on the molecular structural parameters.

The first observation of the forbidden vibrational-rotational transition with the selection rule $\Delta K = \pm 2$ [Eq. (9.27)] has been described by Matsumura et al.[136] (see also[137]) for CH_3I (these transitions are induced by the $x-y$ Coriolis interaction between the $+l$ level, $K = 3$ of the $v_5 = 1$ level and the closely lying $-l$ level, $K = 4$ of the $v_3 = 1$, $v_6 = 1$ combination level).

Nakanaga and Amano[138] have recently observed the $(K' = 1, -l) \leftarrow K'' = 2$ [Eq. (9.26)] and the $(K' = 3, +l) \leftarrow K'' = 1$ forbidden transitions [Eq. (9.31)] to the $v_1 = 1$ and $v_3 = 1$ vibrational levels in the difference frequency laser spectra of the molecular ion SH_3^+ which are enhanced by state mixing by a higher-order Coriolis interaction.

Observation of the pure rotational transition for a D_{3h} molecule is more difficult than those for C_{3v} or T_d molecules. Since no first-order Stark effect exists in a D_{3h} molecule (Appendix), neither Stark modulation microwave spectroscopy nor laser Stark is applicable in this case, unlike a T_d or C_{3v} molecule. Yamamoto et al.[92,139] have used the technique of the infrared–microwave double resonance to measure the frequencies of the pure rotational transitions[92] $K = 0 \leftarrow K = 3$ in the ground vibrational state of[10]BF_3 [the infrared diode laser was used to decrease the population of the ground state $K = 0$ level via the strongly allowed $K = 1, +l$ $(v_3 = 1) \leftarrow$ $\leftarrow K = 0$ vibrational-rotational transition and then a microwave frequency was swept across the ground state rotational transition].

The first direct observation of pure rotational transitions of a nonpolar symmetric top, [11]BF_3, have been reported by Oldani and Bauder[93]. They used the extremely sensitive technique of the pulsed microwave Fourier transform spectroscopy and observed 60 $\Delta k = \pm 3$ rotational transitions in the ground state of [11]BF_3, which made it possible to arrive at very precise spectroscopical parameters (Table IV) of this molecule.

In ammonia, NH_3, because of the larger separation of the energy levels with different k $(C - B \approx -3.7 \text{ cm}^{-1})$, the probability of observing forbidden transitions is small. However, ammonia is a classic example of a nonrigid molecule with a large amplitude inversion motion[1], in which the tunneling between the two symmetrically equivalent equilibrium molecular configuration leads to a measurable splitting of the energy levels. In [14]NH_3, the inversion splitting in the $v_2 = 1$ state compensates for the separation between J, k and $J, k \pm 3$ levels, leading to an accidental degeneracy of the $J = 3, K = 0$ and $J = 3, K = 3$ levels which are separated only by 0.0962 cm^{-1} and interact by the centrifugal distortion effect (Fig. 5). This coincidence

was exploited by Laughton et al.[140], who identified the first forbidden transitions in $^{14}NH_3$ $(K = 0, v_2 = 1 \leftarrow K = 3$, ground state) by using the sensitive technique of infrared–microwave and laser Stark spectroscopy (the same transition in Fig. 1 was obtained by using the diode laser spectroscopy technique[4]). Belov et al.[141] used this coincidence to measure forbidden rotational transitions $J', K = 0 \leftarrow J'', K = 3$ $(J'' = 2, 3, 9)$ in the $v_2 = 1$ state of $^{14}NH_3$ in the submillimeterwave region. In $^{15}NH_3$, the $J = 3, K = 3$ separation is $0·9595$ cm^{-1} and the mixing of both states is therefore so weak that these forbidden transitions could not be observed in $^{15}NH_3$.

A substantial progress in studying forbidden transition in both $^{14}NH_3$ and $^{15}NH_3$ was achieved by Weber and Cohen[142–144] who found forbidden transitions to the $v_4 = 1$ level (species E) in the Fourier transform and laser Stark spectra of $^{14}NH_3$ with the $\Delta K = \pm 2$ selection rule given by Eq. (9.27). In a subsequent series of papers in which the high-resolution Fourier transform spectroscopy has been used, Urban et al.[145–149] have assigned an entire band of the $\Delta K = \pm 2$ forbidden transitions to the $v_4 = 1$ state of $^{14}NH_3$ and $^{15}NH_3$. This has been the most extensive work on forbidden transitions in polyatomic molecules published so far because more than 900 of the forbidden transitions have been assigned by Urban in his pioneering work[146] for $^{14}NH_3$ and more than 800 $\Delta k = \pm 2$ and 60 $\Delta k = \pm 3$ forbidden transitions to the $v_4 = 1$ and $v_2 = 2$ levels of $^{15}NH_3$, respectively[147] (see also ref.[148]). Recently, about 300 $\Delta k = \pm 2$ transitions to the $v_3 = 1$ (species E) level of $^{14}NH_3$ have been assigned[149].

Although the $\Delta k = \pm 3$ transitions in the ground vibrational state of ammonia have been considered long time ago by Oka et al. (ref.[98]) in connection with the possible rotational equilibration of interstellar ammonia by these radiative transitions[7], they have been observed for the first time much later by Urban et al.[150] as the extremely weak lines of the $\Delta J = 0$, $\Delta k = 0 \leftarrow \pm 3$ transitions in the submillimeter-wave spectrum of $^{14}NH_3$. A decisive solution to this problem represents the recent work of Tanaka et al.[151], who have measured 14 microwave transition $\Delta J = 0$, $\Delta k = \pm 1 \leftarrow \mp 2$ in $^{14}NH_3$ with much better accuracy (see also ref.[152]).

More about the theory of forbidden transitions in symmetric tops:

The $\Delta k = \pm 3$ pure rotational transitions in C_{3v} and D_{3h} molecules. According to Eq. (4.11), the part of the effective dipole moment operator which describes the intensity of the pure rotational transitions is

$$\widetilde{M}_{03} = i \sum_{\alpha} ([\mathbf{S}_{12}, \mu_{10}^{\alpha} \lambda_{Z\alpha}] + [\mathbf{S}_{03}, \lambda_{Z\alpha}] \mu_{\alpha}^{(e)}) . \qquad (9.32)$$

We use the notation $\widetilde{M}_{mn}$ for the individual terms in the effective dipole moment which is analogous to the notation $\mathbf{H}_{mn}$ of the expanded vibrational-rotational Hamiltonian [Eq. (3.2)], i.e., the first subscripet in $\widetilde{M}_{mn}$ denotes the degree of the

vibrational operators (coordinates q and momenta $\mathbf{p}$) and the second subscript the degree of the rotational operators ($\mathbf{J}_\alpha$ and λ_{Z_z}).

The transformation function $\mathbf{S}_{12}$ in Eq. (9.32) can be written as[1]

$$\mathbf{S}_{12} = -\sum_k \sum_{\alpha\beta} \mathbf{J}_\alpha \mathbf{J}_\beta B_k^{\alpha\beta} \mathbf{p}_k / \omega_k \qquad (9.33)$$

while

$$\mathbf{S}_{03} = \sum_{\alpha\beta\gamma} s_{\alpha\beta\gamma} \mathbf{J}_\alpha \mathbf{J}_\beta \mathbf{J}_\gamma , \qquad (9.34)$$

where the explicit expressions for the coefficient $s_{\alpha\beta\gamma}$ can be found in ref.[153].

The expression for $\widetilde{\boldsymbol{M}}_{03}$ can be then written in the form

$$\widetilde{\boldsymbol{M}}_{03} = \tfrac{1}{2} \sum_{\alpha\beta\gamma} \Theta_\gamma^{\alpha\beta} (\mathbf{J}_\alpha \mathbf{J}_\beta \lambda_{Z\gamma} + \lambda_{Z\gamma} \mathbf{J}_\beta \mathbf{J}_\alpha) , \qquad (9.35)$$

where the coefficients $\Theta_\gamma^{\alpha\beta}$ are components of a third-rank tensor given by

$$\Theta_\gamma^{\alpha\beta} = \sum_k (B_k^{\alpha\beta} / \omega_k)(\partial \mu_\gamma / \partial q_k)_e + 3 \sum_{\delta\varepsilon} s_{\alpha\beta\delta} e_{\delta\varepsilon\gamma} \mu_\varepsilon^{(e)} , \qquad (9.36)$$

where $e_{\alpha\beta\gamma}$ is the unit antisymmetric tensor ($e_{xyz} = e_{yzx} = e_{zxy} = 1$, $e_{xzy} = e_{yxz} = e_{zyx} = -1$, $e_{\alpha\beta\gamma} = 0$ if any pair from α, β, γ is identical).

In view of the symmetry property $\Theta_\gamma^{\alpha\beta} = \Theta_\gamma^{\beta\alpha}$, ther are in the most general case 18 independent $\Theta_\gamma^{\alpha\beta}$. It can be shown by symmetry considerations[97] that there is at least one nonzero parameter for all molecules except (i) molecules with centers of symmetry and (ii) molecules belonging to the point groups C_{nh} $(n > 3)$, S_n $(n > 4)$, D_{nh} $(n > 3)$, D_{nd} $(n > 2)$, O, and I.

The first term on the right-hand side of Eq. (9.36) describes intensity borrowing from the allowed infrared fundamentals through the vibrational-rotational interactions, while the second term describes intensity borrowing from the allowed pure rotational transitions through these interactions (both type of interactions are centrifugal distortion effects). This second term vanishes for nonpolar molecules.

As an illustration, let us consider the example of C_{3v} and D_{3h} molecules (Fig. 13). There are three nonzero parameters Θ_x^{xx}, Θ_x^{yy}, and Θ_y^{xy} which for C_{3v} and D_{3h} groups obey the same relations

$$\Theta_x^{xx} = \Theta_x^{yy} = -\Theta_y^{xy} \qquad (9.37)$$

(in C_{3v} molecules, the z axis lies along the C_3 axis and one of the σ_v planes is taken in the xz plane; in D_{3h} molecules, the x axis lies along one of the C_2 axis).

In C_{3v} molecules, the mixing of states is due to the $\Delta k = \pm 3$ matrix elements of the following centrifugal distortion operator which is obtained after the vibrational

contact transformation [Eq. (4.8)]:

$$\widetilde{H}_{04} = (\tau_{xxxz}/4)\left[(J_+^3 + J_-^3)J_z + J_z(J_+^3 + J_-^3)\right]. \qquad (9.38)$$

This purely off-diagonal term can be removed by a unitary transformation [Eq. (4.10)], where the transformation function S_{03} is

$$S_{03} = \frac{i\tau_{xxxz}}{4(B_z - B_x)}(J_+^3 + J_-^3). \qquad (9.39)$$

Thus $(\Theta_x^{xx})_{\mathrm{eff}}$ for an XY_3 pyramidal molecule can be found to be

$$(\Theta_x^{xx})_{\mathrm{eff}} = \sum_{t=3,4}(B_{tx}^{xx}/\omega_t)(\partial\mu_x/\partial q_{tx})_e + \tau_{xxxz}\mu_z^{(e)}/[2(B_x - B_z)], \qquad (9.40)$$

where $t = 3, 4$ denotes the doubly degenerate normal coordinates of vibration.

A quantum mechanical picture of this interaction is in Fig. 13. In C_{3v} molecules, the centrifugal distortion operator $\widetilde{H}_{04}$ mixes the states $J, k = \mp 1$ with $J, k = \pm 2$, thus the $J = 4, k = \pm 2 \leftarrow J = 3, k = \mp 1$ forbidden transition borrows its intensity from the allowed rotational transition $J = 4, K = 1 \leftarrow J = 3, K = 1$. This interaction is described by the second term on the right-hand side of Eq. (9.40). The second contribution to the intensity of the $\Delta k = \pm 3$ forbidden transitions comes through the interaction between the ground state $J = 4, K = 2$ level with the $J = 4, K = 0$ level of the doubly degenerate fundamental level due to a vibrational-rotational term

$$H_{12} = -\frac{(2\pi)^2 c^{1/2}}{h\nu_t}\left(\frac{\partial I_{xx}}{\partial q_{tx}}\right)_e (q_{t+}J_-^2 + q_{t-}J_+^2), \qquad (9.41)$$

where

$$q_{t\pm} = q_{tx} \pm iq_{ty} \qquad (9.42)$$

pertain to the doubly degenerate normal coordinates of vibration.

Thus the $k = \pm 2 \leftarrow k = \mp 1$ transition borrows its intensity also from the intensity of the allowed $^P R(3, 1)$ line (Fig. 13). This contribution to the effective dipole moment is described by the first term on the right-hand side of Eq. (9.40).

The second type of centrifugal distortion interaction occurs in the C_{3v} as well as D_{3h} molecules; the nonpolar D_{3h} molecules can have the $\Delta k = \pm 3$ purely rotational spectra[92,93,139]. Because the spin statistical weights of the rotational energy levels of the D_{3h} molecules XY_3 with a half-odd spin of the atomic nuclei Y are $A_1'(0)$, $A_2'(4)$, $E'(2)$, $E''(2)$, $A_1''(0)$, $A_2''(4)$, the ground state rotational energy levels of BF_3 with J even, $K = 0$ are missing (Table V) and the $\Delta J = 0, K = 0 \leftarrow K = 3$ transitions occur only for J odd[139].

In ammonia, each rotational level is split into inversion doublets (Fig. 5). The symmetry classification of the energy levels is therefore different from that for a planar D_{3h} molecule although we have to use the permutation-inversion group for ammonia which is isomorphic with the D_{3h} point group[1,20] (Tables V and VI). We can consider the ammonia energy levels as those of a D_{3h} point group (planar) molecule with a potential hump over the potential energy of the out-of-plane vibration of the A_2'' symmetry species. The effect of the hump is illustrated by the correlation of the energy levels in Fig. 14. Thus instead of the functions $|J, k\rangle$ or $|v_t^{l_t}; J, k\rangle$ we have to classify the wavefunctions

$$|\Phi_i(\varrho)\rangle |J, k\rangle \quad \text{or} \quad |\Phi_i(\varrho)\rangle |v_t^{l_t}; J, k\rangle, \qquad (9.43)$$

where the (inversion) wavefunction $\Phi_i(\varrho)$ is either A_1' (s, symmetric) or A_2'' (a, antisymmetric); ϱ is the coordinate measuring the large amplitude inversion motion in ammonia[154]. Because the species of the molecule-fixed component μ_z of the electric dipole moment is A_2'', the selection rule for the allowed pure rotational transitions ($\Delta k = 0$) is $s \leftrightarrow a$. Because the matrix elements of the operator $\tilde{H}_{04}$ [Eq. (9.38)] connect states with the opposite parities[146] of $\Phi_i(\varrho)$, the selection rule for the $\Delta k = \pm 3$ forbidden trnsitions in ammonia-like molecules must be augmented by the selection rule $s \leftrightarrow s$ and $a \leftrightarrow a$. Thus the scheme for the allowed and
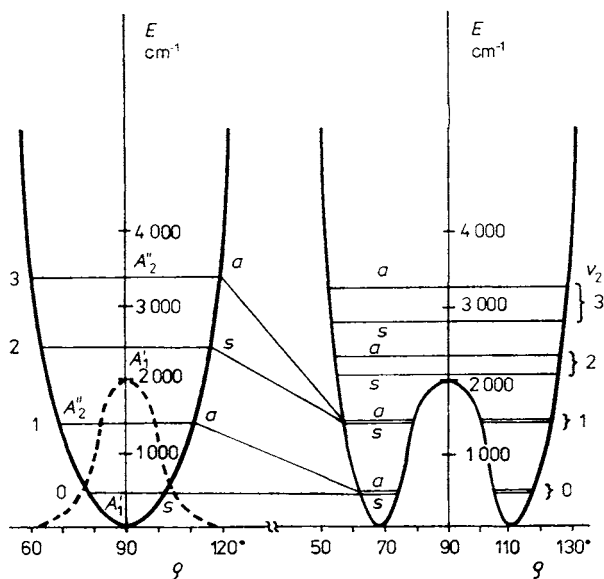

Fig. 14

Correlation of energy levels between a planar D_{3h} point group molecule BCl_3 and ammonia, NH_3

forbidden transitions of the ammonia-like molecules is that of a C_{3v} point group molecule although we classify the states in the D_{3h} group.

The contributions of both terms on the right-hand side of Eq. (9.40) are of comparable magnitudes. For example, Tanaka et al.[151] evaluated for NH_3 the first term as $0.473 \cdot 10^{-4}$ D (using the derivatives from the infrared band intensities) and the second term as $0.704 \cdot 10^{-4}$ D (see also ref.[98]).

The $\Delta k = \pm 2$ and $\Delta k = \pm 3$ vibrational-rotational transitions in C_{3v} and D_{3h} molecules: Fig. 13 can be used to illustrate interactions leading to forbidden vibrational-rotational transitions to the doubly degenerate fundamental vibrational levels. In C_{3v} molecules, the "2, -1" l-type interaction[155,156]

$$\mathbf{H}_{2,-1} = r_t[\bar{q}_{t+}\mathbf{J}_+(\mathbf{J}_z - \tfrac{1}{2}) + \bar{q}_{t-}^2(\mathbf{J}_z - \tfrac{1}{2})\mathbf{J}_-], \qquad (9.44)$$

where

$$\bar{q}_{t\pm}^2 = q_{t\pm}^2 + \mathbf{p}_{t\pm}^2 ; \qquad (9.45)$$

$q_{t\pm}$ is defined by Eq. (9.42) and $\mathbf{p}_{t\pm}$ is similarly

$$\mathbf{p}_{t\pm} = \mathbf{p}_{tx} \pm i\mathbf{p}_{ty} . \qquad (9.46)$$

Thus $\mathbf{H}_{2,-1}$ connects the $+l, K - 1$ levels with the $-l, K$ levels in the $v_t^{l_t} = 1^{\pm 1}$ vibrational level (Fig. 13). Consequently, the $\Delta K = \pm 2$ forbidden transitions with the Δl selection rule defined by Eq. (9.27) borrow their intensities from the allowed $\Delta K = \pm 1$ vibrational-rotational transitions.

This does not hold for semirigid molecules with the D_{3h} point group symmetry where the $\mathbf{H}_{2,-1}$ operator vanishes for symmetry reasons but it does hold for ammonia-like molecules where the selection rule for the $\Delta K = \pm 2$ forbidden transitions must be supplemented by the selection rule[143-149] $s \leftrightarrow a$ [the species of (μ_x, μ_y) is E' for ammonia, thus the selection rules for the $\Delta K = \pm 1$ allowed transitions to the doubly degenerate vibrational level are $s \leftrightarrow s$ and $a \leftrightarrow a$].

The $\Delta k = \pm 3$ forbidden transitions to a nondegenerate vibrational level can be observed for C_{3v} as well as D_{3h} point group molecules. For ammonia, they have the $s \leftrightarrow s$ and $a \leftrightarrow a$ additional selection rule (Fig. 5).

Theory of the intensities of the allowed and forbidden vibrational-rotational transitions in C_{3v} and D_{3h} molecules has been recently worked out by Aliev et al.[18,103].

9.2. Spherical Top Molecules

Forbidden rotational spectra: T_d molecules can be considered as a special case of D_{2d} molecules in which there is only one independent parameter[97]

$$\Theta_x^{yz} = \Theta_y^{xz} = \Theta_z^{xy}, \tag{9.47}$$

where the x, y, z axes lie along the S_4 axes of the molecule.

These molecules are nonpolar, thus according to Eq. (9.36) the parameter Θ_z^{xy} is given by [157-159]

$$\Theta_z^{xy} = \frac{h}{\pi} \sum_t \frac{B^2}{\omega_t^2} \left(\frac{\partial I_{xy}}{\partial q_{tx}}\right)_e \left(\frac{\partial \mu_z}{\partial q_{tx}}\right)_e . \tag{9.48}$$

Methane, CH_4, has the following structure of the vibrational representation in the basis of the normal coordinates of vibration:

$$\Gamma_v = A_1 + E + 2F_2 ; \tag{9.49}$$

the coordinates q_t in (9.48) are restricted to the triply degenerate coordinates F_2.

The expression for the ground state rotational levels of a T_d molecule can be written as

$$F(J, \kappa) = BJ(J + 1) - D_s J^2(J + 1)^2 + H_s J^3(J + 1)^3 +$$
$$+ \left[D_t + H_{4t} J(J + 1)\right] f(J, \kappa) + H_{6t} g(J, \kappa) , \tag{9.50}$$

where B is the rotational constant, D_s and H_s are the coefficients of the quartic (D_s) and sextic (H_s) scalar centrifugal distortion which does not lead to a fine splitting of the rotational levels; D_t, H_{4t}, and H_{6t} are the coefficients of the quartic (D_t) and sextic (H_{4t}, H_{6t}) tensor centrifugal distortion introducing the so-called tetrahedral splitting: $f(J, \kappa)$ and $g(J, \kappa)$ are eigenvalues of the quartic (f) and sextic (g) centrifugal distortion operators which are tabulated up to $J = 20$ in refs[157,160].

The selection rules are $\Delta J = 0, \pm 1$. The Q branch transitions $(\Delta J = 0)$ will occur as an irregular radiofrequency or microwave spectrum of transitions between the components of the centrifugal fine structure. If this fine structure is ignored, the frequencies of the R-branch transitions $J + 1 \leftarrow J$ are given by the usual equation

$$\tilde{v} = 2B(J + 1) ; \tag{9.51}$$

they tend to occur in the far infrared spectrum.

Watson[97] predicted $\Theta_z^{xy} = 2 \cdot 6 \cdot 10^{-5}$ D from the observed intensities of the $v_3 = 1$ and $v_4 = 1$ fundamental bands and the force field of CH_4. The existence of the rotation-induced dipole moment in CH_4 was first demonstrated by Ozier[161] using molecular beam magnetic resonance technique. In an avoided crossing experiment Ozier obtained $\Theta_z^{xy} = 2 \cdot 41 \cdot 10^{-5}$ D in a good agreement with Watson's prediction.

The $\Delta J = +1$ forbidden rotational spectrum of CH_4 was later reported by Rosenberg et al.[162] (see also[163]) between $80-200 \text{ cm}^{-1}$ using a path length of 139 m and pressure in the range $0\cdot076-0\cdot16$ MPa. Rosenberg and Ozier observed similar spectra for SiH_4 (refs[164,165]) and GeH_4 (refs[166,167]). The rotational constant B_0, the scalar centrifugal distortion constant D_s, and Watson's coefficients Θ_z have been determined for these molecules from the frequencies and intensities of the lines.

The Q branch transitions between the components of the fine structure of the ground state level are much more difficult to observe. Because of the small energy differences between the components, the intensities of these transitions are very weak $(\approx 10^{-11} \text{ cm}^{-1})$. On the other hand, they provide important information on the parameters of the tetrahedral splitting.

In a unique double-resonance experiment, Curl et al.[168,169] reported the first observation of the $\Delta J = 0$ transitions in the ground vibrational state of CH_4. The basic idea behind the double-resonance experiment is to change the energy level population with respect to thermal population and thus to increase the absorption coefficient. Curl et al.[168,169] used the coincidence of the He–Ne $3\cdot39\ \mu\text{m}$ laser frequency with the $P^+(7)$ vibrational-rotational transition frequency in CH_4 (see Part 8, Fig. 11). The He–Ne laser radiation depletes the population of the ground state level $F_2^{(2)}$ and the radiofrequency radiation is swept across the frequency of transition pertaining to that level (Fig. 11).

From the observed frequencies of the $\Delta J = 0$ forbidden rotational transitions in CH_4, Curl[169] determined the quartic (D_t) and sextic (H_{4t}, H_{6t}) centrifugal distortion constants. This enabled him to predict with sufficient accuracy the frequencies of other rotational transitions of CH_4 in the microwave region. Based on these predictions, Holt et al.[170] observed further $\Delta J = 0$ rotational transitions in CH_4 by using a Stark modulation microwave spectrometer.

The infrared–microwave double-resonance spectroscopy turned out to be a powerful technique for measuring the weak $\Delta J = 0$ rotational spectra in tetrahedral molecules, especially because other infrared laser sources $(CO_2$ or N_2O lasers) make it possible to study forbidden rotational spectra in molecules heavier than CH_4.

Because of the rotation-induced dipole moment and the vibration-induced dipole moment in the excited state, molecular transitions are shifted due to Stark effect when an electric field is applied (see, e.g., ref.[171]). Thus the infrared–microwave double resonance Stark spectroscopy can also be used to determine the rotation-induced dipole moments in tetrahedral molecules.

Relatively recently, the extremely sensitive technique of the microwave Fourier transform spectroscopy[76] has been succesfully used to measure directly the ground state $\Delta J = 0$ forbidden rotational transitions in T_d molecules.

The most important results on the determination of the effective dipole-moment parameters and coefficients of the tetrahedral splittings are summarized in Tables VII and VIII.

Forbidden vibrational-rotational spectra: The component μ_Z of the electric dipole moment along the space-fixed axis Z in the T_d group is of species A_2 and the overall selection rule for the rovibronic transitions is

$$\Gamma(\Phi'_{\text{evr}}) \otimes \Gamma(\Phi''_{\text{evr}}) \in A_2 . \qquad (9.52)$$

All the components of the electric dipole moment vector of tetrahedral molecules with respect to the molecule-fixed axes x, y, z are of the species F_2 and rovibronic transitions are possible only between vibronic levels which are connected by the species F_2. This means that the infrared active transitions from the ground vibronic state are possible only to the fundamental level of species F_2.

The vibrational-rotational wavefunctions of the methane molecule can be written as[1] $|J, l^*, R, k_R\rangle$, where R is the eigenvalue of the operator $\mathbf{R}^2$ (see Part 8) and k_R is the eigenvalue of the operator $\mathbf{R}_z$.

TABLE VII

Centrifugal distortion dipole moments Θ_z^{xy} in the ground vibrational states of tetrahedral molecules

Molecule	Θ_z^{xy}		Method[a]	Ref.
	in D . 10^5	in Cm . 10^{35}		
$^{12}CH_4$	2·406(45)	8·04(15)	molecular beam magnetic resonance	161
$^{12}CD_4$	1·15(9)	3·84(30)	RF–IR, Stark	177
$^{13}CD_4$	1·20(10)	4·01(33)	RF–IR, Stark	178
SiH_4[b]	3·73(4)	12·44(13)	MW, Stark	179 (see also 180)
SiF_4	0·19(9)	0·63(30)	MW, Stark	181
GeH_4	3·33(5)	11·11(17)	MW–IR, IR–IR, Stark	182
SnH_4	4·26(12)	14·21(40)	IR–IR, Stark	183

[a] RF–IR: radiofrequency–infrared double resonance; MW–IR: microwave–infrared double resonance; IR–IR: infrared–infrared double resonance. [b] Oka, Kreiner et al.[213,214] reported independent determination of the vibration-induced dipole moment in the $v_4 = 1$ state of SiH_4 (1·46(5) . 10^{-2} D) and $\Theta_z^{xy} = 2·97(19) . 10^{-5}$ D by measuring the first-order Stark effect on the infrared vibration-rotation lines in the triply degenerate fundamental bands (see also ref.[215] as for the second-order Stark effect in SiH_4 and ref.[77] as for the rotational transitions in the $v_3 = 1$ state).

TABLE VIII

Parameters of the tetrahedral splitting in the ground vibrational state of T_d molecules (in Hz units)

Molecule	D_t	H_{4t}	H_{6t}	Method[a]	Ref.
$^{12}CH_4$	132 930	−16·6	10·2	MW	170, 184 (see also 169, 185
	132 943·57(97)	−16·9790(90)	10·9956(38)[b]	MWFTS	for RF–IR), 6
$^{13}CH_4$	132 980·81(122)	−16·9791(112)	11·1786(45)[b]	MWFTS	186
$^{12}CD_4$	32 657·9(18)	−2·087(13)	1·1496(10)[b]	MMFTS	6
	32 649·7(17)	−1·9797(44)	1·1027(16)	RF–IR	187
$^{13}CD_4$	32 660·0(12)	−2·0302(61)	1·1692(29)[b]	RF–IR, MMFTS	188
$^{28}SiH_4$	74 861(15)	−7·14(30)	6·57(110)	RF–IR	189
	74 749·87(22)	−6·03530(120)	2·59885(51)	MWFTS	190 (see also 191)
$^{28}SiF_4$	147·55(10)			RF–IR	192
$^{70}GeH_4$	67 774·66(14)	−5·38483(9)	2·96868(27)[b]		
$^{72}GeH_4$	67 775·865(99)	−5·38735(68)	2·97188(20)[b]	MMFTS	193 (see also 194 for MW–IR)
$^{74}GeH_4$	67 776·47(10)	−5·38545(69)	2·97435(24)[b]		
SnH_4[c]	53 398·6(70)	−4·297(46)	2·340(16)		183
$^{189}OsO_4$	72(18)			RF–IR	195
$^{192}OsO_4$	80(26)				

[a] MW microwave; MWFTS microwave Fourier transform; RF–IR radiofrequency–infrared double resonance. [b] Octic parameters have also been determined. [c] The resonances from different isotopic species (^pSn, p = 116, 117, 118, 119, 120, 122, 124) were found to yield almost identical transition frequencies.

Selection rules for the allowed transitions from the ground vibrational level to the fundamental vibrational level can be summarized as follows[1]:

$$\Delta v_t = 1 , \quad t = 3 \quad \text{or} \quad 4 ,$$

$$\Delta R = \Delta k_R = 0 . \tag{9.53}$$

However, R is not a good quantum number because higher-order vibrational-rotational interactions can mix states with different R. Furthermore, the $\Delta R = 0$ selection rule has been obtained in the approximation which neglects second and higher-order derivatives in the expansion of the dipole moment [Eq. (3.18)]. Thus forbidden transitions with

$$\Delta R \neq 0 \tag{9.54}$$

can also occur if they do not violate the overall symmetry selection rule (9.52).

There is another "selection rule" for allowed and forbidden transitions. This rule is related to the counter number N which is added as right numerical superscript if a given symmetry species occurs more than once in a group of levels F^+, F^0, F^- [Eq. (8.14)]. In F^+, F^- groups, we start counting from the highest level, in F^0 from the lowest level (Figs 11 and 15). In an allowed transition,

$$\Delta N = 0 \tag{9.55}$$
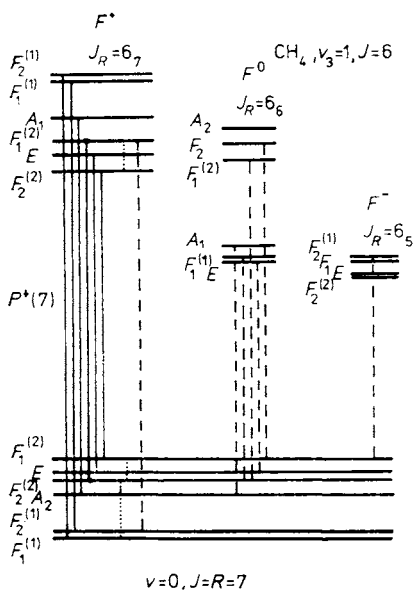
FIG. 15

Allowed (full lines) and forbidden (dashed lines) transitions between the ground vibrational level and the $v_3 = 1$ level in CH_4. The scale in the upper vibrational state is compressed tenfold with respect to that of the ground state and the distances between the F^+, F^0, and F^- centers of gravity are much larger than shown (according to ref.[196])

but

$$\Delta R = 0 \, , \quad \Delta N \neq 0 \hspace{5cm} (9.56)$$

are approximately allowed transitions[1] (Fig. 15).

Although the $\Delta J = +1$ pure rotational transitions in T_d molecules provide information on the rotational constants B and scalar centrifugal distortion coefficients[162, 163,172], the most precise values of the scalar parameters so far have been obtained by measuring the frequencies of forbidden vibrational-rotational transitions (see, e.g., refs[173-176]). For example, for $^{12}CH_4$ they are[175] (in MHz units):

$$B_0 = 157\ 122\cdot28(64) \, , \quad D_S = 3\cdot3240(43) \, , \quad H_S = 173\cdot0(96)\,.\,10^{-6} \, .$$

10. FINAL REMARKS

Although it is difficult to predict further development in a research field, there is little doubt that measurement of forbidden transitions will soon become almost routine whenever the sensitive high-resolution techniques will be used to study vibrational-rotational spectra of highly symmetric polyatomic molecules.

The theory of these transitions is now well understood for symmetric top as well as spherical top molecules but molecules with large amplitude motions require further work. For example, as it was discussed in Parts 8 and 9, centrosymmetrical molecules cannot have vibrationally or rotationally induced forbidden transitions. Ethane, C_2H_6, is generally thought of as containing a center of symmetry and belonging to the point group D_{3d}, corresponding to the equilibrium configuration of the rigid molecule. The hindered internal rotation, allowing tunneling between symmetrically equivalent equilibrium configurations, is not included as a symmetry operation in the group D_{3d} [the (123) permutation of the hydrogen atomic nuclei in CH_3 group is not in the D_{3d} group]. Hougen[197] has shown that the proper symmetry group which takes into account all the feasible permutations and permutation-inversion symmetry operations in ethane-like molecules, is G_{36}^+. According to this group, ethane-like molecules contain no center of symmetry and pure rotational transitions are therefore not strictly forbidden.

Rosenberg and Susskind[198] have developed the theory of pure rotational transitions in doubly degenerate torsional states of ethane but so far they have not yet been observed. A suitable candidate for this investigation is certainly 2-butine, $CH_3{-}\!\equiv\!CCH_3$, with an almost free internal rotation of both CH_3 groups (see ref.[199] as for the forbidden torsional spectra in CH_3SiH_3).

It is obvious that any asymmetric substitution of isotopes in a nonpolar molecule reduces the original high symmetry, thus making the molecule slightly polar. For example, CH_3D or CD_3H have the C_{3v} point group symmetry and observable pure

rotational spectra obeying the usual selection rules for C_{3v} groups. The isotopically induced dipole moments are of course very small ($\approx 10^{-3} - 10^{-4}$ D). Because the rotational transitions have the usual selection rules of a polar molecule, they will not be discussed here. An excellent review of this subject has been recently published by Hirota[200] (see also ref.[201]).

Much further work should also be done on the theory as well as experiment concerning selection rules for transitions in extremely strong light fields, which are different from those discussed here. This subject may be important for example for laser induced chemistry or laser isotope separation processes, but its discussion is outside the scope of the present review.

Finally, let us mention an interesting problem of the ultrahigh resolution spectroscopy concerning forbidden transitions in tetrahedral and octahedral molecules. A tetrahedral or octahedral molecule such as $^{189}OsO_4$ or $^{235}UF_6$, having a central atom with nuclear spin $I \geqq 1$ and outer atoms with $I \leqq 1/2$, does not, to a first approximation, show nuclear quadrupole splittings in the rovibrational states of a totally symmetric electronic state. For even though the central nucleus may possess an electric quadrupole moment, the electric field gradient at the central position vanishes because of the high symmetry. In many excited vibrational and/or rotational states of a totally symmetric electronic state, however, the high symmetry is broken and a small electric quadrupole coupling is produced.

The vibrationally induced nuclear quadrupole coupling in tetrahedral and octahedral molecules is therefore an analogue of the vibrationally induced dipole moment problem first treated by Mizushima and Venkateswarlu[68] (Part 8). There is also a rotationally induced nuclear quadrupole coupling which is closely related to the rotationally induced dipole moment problem discussed in Part 9 of this review.

The quadrupole hyperfine structure in the infrared rovibrational spectrum of $^{189}OsO_4$ arising from such quadrupole couplings was first reported by Letokhov et al.[202-204] by using saturation spectroscopy. Later Bordé et al.[205] by using a high pressure CO_2 waveguide laser, succeeded in observing three hyperfine patterns in $^{189}OsO_4$.

Hougen and Oka[206] developed a theory of the vibrationally induced nuclear quadrupole coupling in tetrahedral and octahedral molecules and applied it to the analysis of the hyperfine patterns observed by Bordé et al.[205]. Subsequently Palma and Bordé[207] developed a theoretical treatment for the rotationally induced quadrupole coupling and applied it to $^{189}OsO_4$. Bordé et al.[208] succeeded in measuring the scalar and tensor coupling constants due to the rotationally induced effects in the ground state of this molecule. Scappini et al.[209] have recently observed the hyperfine structure in the v_3 fundamental band of $^{189}OsO_4$ due to the vibrationally induced nuclear quadrupole coupling by using the technique of microwave modulation CO_2 laser sideband spectroscopy with the inverse Lamb dip.

Although all this seems to be a highly academic research, it is not. Extremely important practical applications can be anticipated in quadrupole coupling investigations, since observable quadrupole splittings can provide a very simple tool for discriminating between lines of $^{238}UF_6$ $(I = 0)$ and $^{235}UF_6$ $(I = 7/2)$ in laser isotope separation techniques.

APPENDIX

Mixing of the Rovibronic States by the External Electric and Magnetic Fields (see refs[210-212])

As a result of applying an external electric field E_Z in the direction of the space-fixed axis Z, the molecular vibration-rotation Hamiltonian $\mathbf{H}_{vr}$ is augmented by the term

$$\mathbf{H}_{Stark} = -\mu_Z^{(e)} E_Z ,\qquad (A.1)$$

where $\mu_Z^{(e)}$ is the electric dipole moment operator along the field direction [see also Eq. (2.11)].

As discussed in Section 5, $\mu_Z^{(e)}$ belongs always to the antisymmetric representation Γ^* of the molecular symmetry group (Γ^* has $+1$ for all permutation operations and -1 for all permutation-inversions). Because $\mathbf{H}_{Stark}$ has the symmetry of $\mu_Z^{(e)}$, we obtain that

$$\langle \psi'_{evr} | \mathbf{H}_{Stark} | \psi''_{evr} \rangle \neq 0 \qquad (A.2)$$

if

$$\Gamma(\psi'_{evr}) \otimes \Gamma(\psi''_{evr}) \in \Gamma^* . \qquad (A.3)$$

In other words, we can write the selection rule for the states which are mixed by the Stark effect as $\Delta\Gamma_{evr} = \Gamma^*$.

Furthermore, $\mu_Z^{(e)}$ transforms according to the representation $D^{(1)}$ of the external rotation group $K(S)$, thus $\mathbf{H}_{Stark}$ mixes states with the $\Delta J = 0, \pm 1$ (if we neglect the nuclear hyperfine structure) or $\Delta F = 0, \pm 1$ (if we take it into account). Note that in the presence of an external electric field, J (or F) is no more a good quantum number.

As an example, let us consider a molecule of C_{3v} symmetry. Here $\Gamma(\mu_Z) = A_2$ and therefore only A_1 states can be mixed with the A_2 rovibronic states and the E states with the E states. Thus the $A \leftrightarrow E$ transitions between the *ortho*- and *para*-states are not allowed by the Stark effect but the $A_1 \leftrightarrow A_1$ or $A_2 \leftrightarrow A_2$ transitions (which are forbidden by the overall symmetry selection rules in the absence of an external electric field) are allowed in the Stark spectroscopy.

The $\Delta J = 0$ rule gives us the condition for a first-order Stark effect which results from the matrix elements of the Stark Hamiltonian between the degenerate components:

$$\langle J, m, \Gamma, n| \mathbf{H}_{\text{Stark}}|J, m', \Gamma', n'\rangle = - \langle J, m, \Gamma, n| \mu_Z^{(e)}|J, m', \Gamma', n'\rangle E_Z , \quad (A.4)$$

where m is the quantum number of J_Z for the space-fixed Z axis; Γ is the rovibronic symmetry species; n labels the components of Γ (other quantum numbers are not important in the present consideration, and are ignored).

Thus Eq. $(A.3)$ gives us the simple symmetry condition for a first-order Stark effect

$$\Gamma(\mu_Z) \in \Gamma^2 . \quad (A.5)$$

However, Watson[211] has shown that Eq. $(A.5)$ is only necessary but not sufficient condition for a first-order Stark effect to occur. A more restrictive condition obtained by Watson is

$$\Gamma(\mu_Z) \in \left[\Gamma^2\right]_{\text{antisym}} \quad (A.6)$$

requiring $\Gamma(\mu_Z)$ belong to the antisymmetric component of Γ^2. In order for this condition to be satisfied, Γ must be degenerate.

For example, for the E rovibronic levels of a C_{3v} molecule we have $E \otimes E = = A_1 + A_2 + E$ and $\Gamma(\mu_Z)$ belongs to the antisymmetric component A_2. Thus a first-order Stark effect is allowed. For the E rovibronic levels of a D_{2d} molecule we have $\left[E^2\right]_{\text{antisym}} = A_2$ and $\Gamma(\mu_Z) = B_1$. In this case a first-order Stark effect is forbidden. In general, a nonpolar symmetric top molecule cannot have a first-order Stark effect (except in cases of accidental degeneracy).

Quite analogously, if B_Z is the external magnetic field in the direction Z, the Zeeman Hamiltonian is

$$\mathbf{H}_{\text{Zeeman}} = - \mu_Z^{(\text{m})} B_Z , \quad (A.7)$$

where $\mu_Z^{(\text{m})}$ is the magnetic dipole moment operator along the Z axis [cf. Eq. (2.15)]. Because $\mu_Z^{(\text{m})}$ is invariant with respect to all the operations of the molecular symmetry group and belongs to $D^{(1)}$, states which are mixed by the Zeeman effect are

those which satisfy the following rule:

$$\Delta J = 0, \pm 1 ; \quad \Delta \Gamma_{\text{evr}} = 0 . \qquad (A.8)$$

In other words, H_{Zeeman} has the symmetry of H_{vr}.

Approximate selection rules for the vibrational quantum numbers and rotational quantum numbers (K for a symmetric top, and K_a and K_b for an asymmetric top) can be deduced by expressing $\mu_Z^{(e)}$ and $\mu_Z^{(m)}$ in terms of the components along the molecule-fixed axes [cf. Eq. (3.14)].

Note added in proof: H. Prinz et al. found recently [J. Mol. Spectrosc. *135*, 144 (1989)] that the vibration-induced dipole moment in the $v_4 = 1$ state of $^{13}CD_4$ and SiH_4 is modified considerably by the vibration interaction with $v_2 = 1$ [$\mu_{44} = -2 \cdot 627(11) \cdot 10^{-2}D$ in $^{13}CD_4$ and $\mu_4 = -1 \cdot 203(11) \cdot 10^{-2}D$ in SiH_4].

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