since the direction of r_n is not significant. From (43b) we find

$$|a| = \hbar c [q^2 - (\Delta E/\hbar c)^2]^{\frac{1}{2}}/2(E+mc^2). \quad (118)$$

With a_0 given by (45) we find

$$\frac{a \cdot J}{a_0 F_n} < \rho = \frac{\Delta E}{E \sin \vartheta}. \quad (117a)$$

The right-hand side of (117a) is appreciable only for

$$\vartheta \lesssim \Delta E/E \sim \vartheta_m^2, \quad (118)$$

where ϑ_m is the angle introduced in (50b). In the average $\vartheta_m \sim 1/kb$ so that $\rho \sim 1$ for

$$\vartheta \sim 1/400 = 0.14°.$$

For scattering angles $\vartheta > \vartheta_m^2$, $a \cdot J \ll a_0 F_n$. Therefore over practically the entire range of integration over ϑ the current term need not be considered at all.

The Interaction Between Rotation and Oscillation in Deutero-Formaldehyde

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The unsymmetrical broadening of the Q branch toward higher frequencies in the parallel type bands near 1100 cm^{-1} in the absorption spectrum of deutero-formaldehyde is taken as a manifestation of convergence toward lower frequencies rather than, as is usual, in the case of infra-red bands, toward higher frequencies. This phenomenon is accounted for by taking into account an interaction between rotation and oscillation of the Coriolis type arising from the accidental degeneracy of the three vibration frequencies, belonging to three different symmetry classes, falling near 900 cm^{-1}, 1000 cm^{-1} and 1100 cm^{-1}.

I. Introduction

THE absorption spectrum near 10μ in the deutero-formaldehyde spectrum consists of three bands which badly overlap. Two of these are characteristic of oscillations of the electric moment normal to the axis of symmetry of the molecule, while the third is characteristic of a vibration parallel to the axis of symmetry. The first two of these consist essentially of a group of prominent lines protruding above a background which at present cannot be resolved spectroscopically, and the third contains P, Q and R branches. It has already been pointed out elsewhere[1] that the spacings between the prominent lines in the perpendicular bands in this region are noticeably greater than the spacings between the lines in a similar band near 4.6μ and it has been suggested that the explanation for this is un-

doubtedly the same as that for the similar effect observed in two overlapping perpendicular bands in the spectrum of ordinary formaldehyde near 8.0μ.[2] The effect is here quite satisfactorily explained by taking account in the energy of a Coriolis interaction between the two frequencies. In the third of the above bands referred to in the spectrum of deutero-formaldehyde the convergence is in the direction of lower frequencies

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[1] E. S. Ebers and H. H. Nielsen, J. Chem. Phys. **6**, 311 (1938).

[2] H. H. Nielsen, J. Chem. Phys. **5**, 818 (1937). The type of interaction between rotation and oscillation discussed recently by W. H. J. Childs and H. A. Jahn (Nature **141**, 916 (1938)) in connection with the methane spectrum is entirely similar to the one discussed in this work relative to H$_2$CO. The formaldehyde case is especially interesting in that both perturbing frequencies are optically active so that the convergence in opposite directions in the two bands, described by C. and J., can here actually be observed. In the case of the methane molecule the perturbing frequencies are two- and three-fold degenerate, respectively, while in this case they are nondegenerate. The importance of such terms in the interpretation of spectra was already emphasized by E. B. Wilson, Jr., in one of his early papers on this subject.

rather than in the direction of higher frequencies
as is usually the case for bands in the infra-red.
Although the P and R branches are too incom-
pletely resolved to satisfactorily study the con-
vergence it may be established that this is true
by observing that the Q branch is unsymmetri-
cally broadened toward higher frequencies. For
this to be so, what corresponds to the classical
moment of inertia of the molecule must be smaller
in the upper state than it is in the ground state.
An explanation suggests itself when one reviews
the case of ordinary formaldehyde. Here, due to
Coriolis forces, the two nearly coincident fre-
quencies which, however, belong to different
symmetry classes, suffer perturbations to their
accompanying rotational levels in such a manner
that the band of lesser frequency is strongly con-
vergent toward higher frequencies while the
other band is strongly convergent toward lower
frequencies. In this case we have, not two, but
three different oscillations of nearly coincident
frequencies, and belonging, here also, to *three*
different symmetry classes. We shall investigate
in this note what the nature of the interactions
may be here between rotation and oscillation to
see whether or not they may give rise to effects
in the spectrum such that the Q branch of the
parallel type band will be unsymmetrically
broadened toward higher frequencies and at the
same time the type of convergence retained
which is characteristic of the overlapping perpen-
dicular type bands in the spectrum of ordinary
formaldehyde.

II. SOLUTION TO THE QUANTUM MECHANICAL PROBLEM

The three oscillations which give rise to the
three bands in question are the following ones
given in the order of ascending frequencies: the
deformation frequency of the molecule in and out
of its own plane; the frequency caused by the
deformation in the plane of the molecule of the
$O-C-D$ bond angle and the frequency caused
by the deformation in the plane of the molecule
of the CD_2 bond angle. The first two of these will
give rise to changes in the electric moment per-
pendicular to the axis of symmetry, while the
third will produce an alteration of the electric
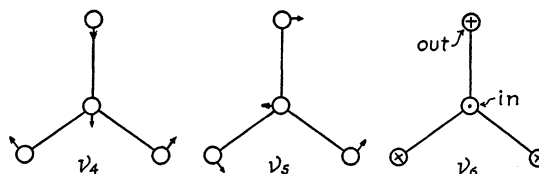moment parallel to this axis. As a simplified

FIG. 1. The three modes of oscillation which the molecular model may execute.

model of the molecule which will approximate to
the actual case when it is oscillating in these
three modes we shall adopt one where the C and
O atoms and the C and D atoms, respectively,
are rigidly joined together, an assumption which
is justified when further we adopt force fields of
the valence force type, bearing in mind that the
frequencies in which we are interested are all
deformation frequencies where no changes in the
interatomic distances take place. This simplifica-
tion is in reality tantamount to suppressing the
other three modes of oscillation of the molecule.
The xz plane has been taken as the plane of the
molecule, the z axis having been made to lie
along the axis of symmetry and the origin of the
system to coincide with the center of gravity of
the molecule. In this system the coordinates of
the C, O and D particles when they are at rest,
will be respectively, $(0, 0, z_3{}^0)$, $(0, 0, z_4{}^0)$, and
$(x_1{}^0, 0, z_1{}^0)$ and $(x_2{}^0, 0, z_2{}^0)$ where $x_1{}^0 = -x_2{}^0$ and
$z_1{}^0 = z_2{}^0$. The three modes of oscillation which this
model may execute are described in Fig. 1 and
are respectively identified with the frequencies
of the molecule, ν_4, ν_5 and ν_6 where $\nu_4 > \nu_5 > \nu_6$.

The quantum mechanical equation for this
molecular model, oscillating harmonically in
these three modes and rotating, has been de-
veloped with the neglect, however, of all terms
in the moments of inertia which arise from de-
formation of the molecule. This can be justified
on the basis that these will almost certainly con-
tribute amounts to the energy small in compari-
son with the interaction terms in which we are
interested, namely those arising from the Coriolis
forces. The derivation of the quantum mechan-
ical equation will be omitted here since the
method is a perfectly straightforward one. The
equation which is obtained may be divided into
zeroth and higher order terms of which only the
two first sets will here be set down:

$(H_0-E_0)\psi_0 = (h\nu/2)\{2E_0/h\nu+(\nu_5/\nu)(\partial^2/\partial\eta^2-\eta^2)$

$+(\nu_4/\nu)(\partial^2/\partial\zeta^2-\zeta^2)+(\nu_6/\nu)(\partial^2/\partial\xi^2-\xi^2)$

$+u^2(2\pi/h)^2[(P_x^2+P_y^2)+(2\pi/h)^2(A_0/C_0)P_z^2]$

$-2\lambda_3 u^2(A_0/C_0)[(\nu_6/\nu_5)^{\frac{1}{2}}\eta\partial/\partial\xi$

$-(\nu_5/\nu_6)^{\frac{1}{2}}\xi\partial/\partial\eta](2\pi i/h)P_z\}\psi_0=0,$ (1a)

$H_1 = -u^2h\nu\{\lambda_1[(\nu_4/\nu_6)^{\frac{1}{2}}\xi\partial/\partial\zeta$

$-(\nu_6/\nu_4)^{\frac{1}{2}}\zeta\partial/\partial\xi(2\pi i/h)]P_x+\lambda_2[(\nu_5/\nu_4)^{\frac{1}{2}}\zeta\partial/\partial\eta$

$-(\nu_4/\nu_5)^{\frac{1}{2}}\eta\partial/\partial\zeta](2\pi i/h)P_y\}.$ (1b)

In the above $u^2=(h/4\pi^2A_0\nu)$,

$\lambda_1 = [2m(M_c+M_0)\tan\alpha$
$\quad+4m(M_c\sigma-M_0\rho)\tan\alpha][(M_c+M_0)\mu^{\frac{1}{2}}_2\mu_3^{\frac{1}{2}}]^{-1}$,
$\lambda_2 = [-4m(M_c+M_0)\epsilon\tan\alpha$
$\quad+4m(M_c\epsilon-M_0\delta)\tan\alpha][(M_c+M_0)\mu_1^{\frac{1}{2}}\mu_2^{\frac{1}{2}}]^{-1}$,
$\lambda_3 = (2m+4M_c\epsilon\sigma+4M_0\delta\rho)(\mu_1^{\frac{1}{2}}\mu_3^{\frac{1}{2}})^{-1}$,

P_x, P_y and P_z are the usual angular momentum operators[3] (functions of the eulerean angles θ, φ and ψ) conjugate to the x, y and z axes, A_0, B_0 and C_0 are the principal moments of inertia. In the above m, M_c and M_0 are respectively the masses of the deuterium, carbon and oxygen atoms, σ, ρ, ϵ and δ are constants defined as follows:

$(mz_4^0-m(z_1^0-z_3^0))(M_c(z_4^0-z_3^0)+2m(z_1^0-z_3^0))^{-1}$

$(m/M_0)(M_cz_3^0-(M_c+2m)(z_1^0-z_3^0))$

$\qquad\times(M_c(z_4^0-z_3^0)+2m(z_1^0-z_3^0))^{-1}$

$m(z_4^0-(z_1^0-z_3^0+x_1^0\tan\alpha))(M_c(z_4^0-z_3^0)$

$\qquad+2m(z_1^0-z_3^0+x_1^0\tan\alpha))^{-1}$

$(m/M_0)(M_cz_3^0-(M_c+2m)(z_1^0-z_3^0+x_1^0\tan\alpha))$

$\qquad\times(M_c(z_4^0-z_3^0)+2m(z_1^0-z_3^0+x_1^0\tan\alpha))^{-1}.$

The variables η, ξ and ζ are related to the displacements of the D, C and O atoms from equilibrium in the x, y and z coordinates in the following manner:

$\eta = (4\pi^2\mu_1\nu_5/36h)^{\frac{1}{2}}(x_1+x_2-(x_3/\epsilon)+(x_4/\delta))$,

$\xi = (4\pi^2\mu_3\nu_6/36h)^{\frac{1}{2}}(y_1+y_2-(y_3/\sigma)+(y_4/\rho))$,

$\zeta = (4\pi^2\mu_2\nu_4/4h)^{\frac{1}{2}}(z_1+z_2)\cot\alpha,$

[3] E. C. Kemble, *Fundamental Principles of Quantum Mechanics* (McGraw-Hill Co., 1937), p. 232.

where:

$\mu_1 = ((2m+4M_c\epsilon^2+4M_0\delta^2)$

$\qquad+2m(1+4\epsilon+4\epsilon^2)\tan^2\alpha)$,

$\mu_2 = (2m(M_c+M_0)(1+\tan^2\alpha)$

$\qquad+4m^2\tan^2\alpha)(M_c+M_0)^{-1}$,

$\mu_3 = (2m+4M_c\sigma^2+4M_0\rho^2)$

and may be regarded as reduced masses respectively to be associated with one of the three modes.

The last term in (1a) is an interaction term between rotation and oscillation. Normally it would be retained as a part of (1b) with the other similar terms. Because of its coefficient (A_0/C_0), which for D_2CO is of the order six, this term will, however, be considerably larger than the other interaction terms so that for values of the rotational quantum numbers up to about ten it will be actually of the same order of magnitude as the rotational energy. It is therefore included as a part of H_0. The second-order terms of H, which are not given here, consist of terms which are essentially the squares of the oscillational angular momentum components along the x, y and z axes. Their contributions to the energy of the molecule will be entirely independent of the rotational quantum numbers. Since they are therefore not an interaction energy we shall not compute their value.

Following the procedure suggested in the earlier work referred to herein we take as a solution to the zeroth-order Hamiltonian for the ground and first excited states ν_4, ν_5 and ν_6, the functions:

$\psi(0) = \{(64\pi^3\mu_1\mu_2\mu_3\nu_4\nu_5\nu_6/h^3)^{\frac{1}{4}}$

$\qquad\times\exp-(\eta^2+\xi^2+\zeta^2)/2\}\Theta(\theta,J,K,M)$

$\qquad\qquad\times\exp(iK\varphi+iM\psi),$ (2a)

$\psi(\nu_5) = N(\nu_5)\{-ih[(\nu_6-\nu_5)/2$

$\qquad+((\nu_6-\nu_5)^2/4+(K\lambda_3h/4\pi^2C_0)^2)^{\frac{1}{2}}]$

$\qquad\times(2\xi\exp-(\eta^2+\xi^2+\zeta^2)/2)$

$\qquad+(K\lambda_3h^2/4\pi^2C_0)(\nu_5/\nu_6)^{\frac{1}{2}}$

$\qquad\times(2\eta\exp-(\eta^2+\xi^2+\zeta^2)/2)\}$

$\qquad\times\Theta(\theta,J,K,M)\exp(iK\varphi+iM\psi),$ (2b)

$\psi(\nu_6) = N(\nu_6) \{ (iK\lambda_3 h^2/4\pi^2 C_0)(\nu_6/\nu_5)^{\frac{1}{2}}$

$\qquad \times (2\xi \exp -(\eta^2+\xi^2+\eta^2)/2) + h[(\nu_6-\nu_5)/2$

$\qquad + ((\nu_6-\nu_5)^2/4 + (K\lambda_3 h/4\pi^2 C_0)^2)^{\frac{1}{2}}]$

$\qquad \times (2\eta \exp -(\eta^2+\xi^2+\zeta^2)/2) \}$

$\qquad \times \Theta(\theta, J, K, M) \exp (iK\varphi+iM\varphi)$,   (2c)

where

$N_k{}^2 = \{ (K\lambda_3 h^2/4\pi^2 C_0)^2(\nu_k/\nu_j) + h^2[(\nu_6-\nu_5)^2/4$

$\qquad + (K\lambda_3 h/4\pi^2 C_0)^2)^{\frac{1}{2}}]^2 \}^{-1}(16\pi^3\mu_1\mu_2\mu_3\nu_4\nu_5\nu_6/h^3)^{\frac{1}{4}}$

j and k taking the values 6 and 5 and 5 and 6, respectively.

$\psi(\nu_4) = \{ (16\pi^3\mu_1\mu_2\mu_3\nu_4\nu_5\nu_6/h^3)^{\frac{1}{4}}$

$\qquad \times (2\zeta \exp -(\eta^2+\xi^2+\zeta^2)/2) \}$

$\qquad \times \Theta(\theta, J, K, M) \exp (iK\varphi+iM\psi)$.   (2d)

$\Theta(\theta, J, K, M) \exp (iK\varphi+iM\psi)$ in the above functions is the normalized eigenfunction for the symmetric rotator problem; K and M are integers less than, or equal in the limiting case, to J. The functions (2) give the energies of H_0 as diagonal matrices except for a small contribution arising from $(\Delta\nu/\nu)$ which may be regarded as a left over from the term representing the Coriolis interaction. This term may actually be included as a part of H_1 and its contribution to the energy taken into account at a later point if this is desirable.

The zeroth-order energies for the molecules in the corresponding states are readily found to be:

$E(0) = (h/2)(\nu_5+\nu_4+\nu_6) + (J(J+1) - K^2)$

$\qquad \times (h^2/8\pi^2 A_0) + K^2 h^2/8\pi^2 C_0$

$E(\nu_4) = (h/2)(\nu_5+3\nu_4+\nu_6) + (J(J+1) - K^2)$

$\qquad \times (h^2/8\pi^2 A_0(1-\alpha-\beta)) + K^2 h^2/8\pi^2 C_0$

$E(\nu_5) = h(\nu_5+\nu_4/2+\nu_6) + h((\nu_6-\nu_5)^2/4$

$\qquad + (K\lambda_3 h/4\pi^2 C_0)^2)^{\frac{1}{2}} + (J(J+1) - K^2)$ (3)

$\qquad \times (h^2/8\pi^2 A_0(1+\beta)) + K^2 h^2/8\pi^2 C_0$

$E(\nu_6) = h(\nu_5+\nu_4/2+\nu_6) + h((\nu_6-\nu_5)^2/4$

$\qquad + (K\lambda_3 h/4\pi^2 C_0)^2)^{\frac{1}{2}} + (J(J+1) - K^2)$

$\qquad \times (h^2/8\pi^2 A_0(1+\alpha)) + K^2 h^2/8\pi^2 C_0$,

where α and β may be regarded as correction

terms to A_0 which to this approximation are, however, both equal to zero.

To evaluate the corrections to the energy contributed by H_1 we may without hesitation make use of the nondegenerate perturbation theory and proceed in the usual straightforward manner to evaluate E_1 and E_2, the first of which vanishes. We shall include in E_2 only the second-order contributions from H_1 as already suggested, and of these we may actually neglect all the terms except those where the frequency differences $(\nu_4-\nu_5)$ and $(\nu_4-\nu_6)$ occur in the denominators, since all others will be small when compared to these. The term $(\Delta\nu/\nu)\eta\xi$ of which we have already made mention will contribute an amount entirely too small to justify its evaluation and it also will be omitted. The remaining terms of E_2 when computed and added to E_0 change the expression (3) only in this respect that now α and β are no longer zero but take the values:

$\alpha = (h/8\pi^2 A_0) \{ \lambda_1{}^2(K\lambda_3 h^2\nu_5/4\pi^2 C_0\nu_6)$

$\qquad \times ((\nu_4+\nu_6)/\nu_4{}^{\frac{1}{2}}\nu_6{}^{\frac{1}{2}})^2 + \lambda_2{}^2 h^2[(\nu_6-\nu_5)/2$

$\qquad + ((\nu_6-\nu_5)^2/4 + (K\lambda_3 h/4\pi^2 C_0)^2)^{\frac{1}{2}}]^2$

$\qquad \times ((\nu_4+\nu_5)/\nu_4{}^{\frac{1}{2}}\nu_5{}^{\frac{1}{2}})^2 \} \{ (\nu_4-\nu_5)(h^2[(\nu_6-\nu_5)/2$

$\qquad + ((\nu_6-\nu_5)^2/4 + (K\lambda_3 h/4\pi^2 C_0)^2)^{\frac{1}{2}}]^2$

$\qquad\qquad + (K\lambda_3 h^2/4\pi^2 C_0)(\nu_6/\nu_5)) \}^{-1}$

and

$\beta = (h/8\pi^2 A_0) \{ \lambda_1{}^2 h^2[(\nu_6-\nu_5)/2 + ((\nu_6-\nu_5)^2/4$

$\qquad + (K\lambda_3 h/4\pi^2 C_0)^2)^{\frac{1}{2}}]((\nu_6+\nu_4)/\nu_4{}^{\frac{1}{2}}\nu_6{}^{\frac{1}{2}})^2$

$\qquad + \lambda_2{}^2(K\lambda_3 h^2/4\pi^2 C_0)(\nu_6/\nu_5)((\nu_4+\nu_5)/\nu_4{}^{\frac{1}{2}}\nu_5{}^{\frac{1}{2}})^2 \}$

$\qquad \times \{ (h^2[(\nu_6-\nu_5)/2 + ((\nu_6-\nu_5)^2/4$

$\qquad + (K\lambda_3 h/4\pi^2 C_0)^2)^{\frac{1}{2}}]^2$

$\qquad\qquad + (K\lambda_3 h^2/4\pi^2 C_0)^2(\nu_6/\nu_4))(\nu_4-\nu_6) \}^{-1}$,

both of which are quantities greater than zero.

We shall not here consider it necessary to obtain the selection rules, these having been discussed elsewhere, but shall be content with stating what these are. The transitions which may take place and which are of interest to us in this discussion are the following ones: from the ground state to the states ν_5 and ν_6, with $\Delta J = \pm 1, 0$ and $\Delta K = \pm 1$; from the ground state to the state ν_4 with $\Delta J = \pm 1, 0$ and $\Delta K = 0$.

III. The Effect of the Interaction on the Spectrum

We are now in a position to inquire into what will be the effect on the spectrum caused by these interaction terms. We may accomplish this by obtaining expressions for the frequency positions of lines in the spectrum using the above energy relations and selection rules. For the frequencies ν_5 and ν_6 only those lines arising from the transitions $\Delta J = 0$, $\Delta K = \pm 1$ are of interest, the other lines being at present spectroscopically unresolved. The frequency positions of these lines in the two bands are given by:

$$\nu = (\nu_5 + \nu_6)/2 - (h/8\pi^2)(1/C_0 - 1/A_0)$$
$$\pm [(\nu_6 - \nu_5)^2/4 + (K\lambda_3 h/4\pi^2 C_0)^2]^{\frac{1}{2}}$$
$$+ (J(J+1) - K^2)\alpha h/8\pi^2 A_0$$
$$\pm (Kh/4\pi^2)(1/C_0 - 1/A_0), \quad (5)$$

a relation which, except for the presence of a small term $\alpha h^2/8\pi^2 A_0$, confirms the one used by Ebers and Nielsen in their work on ordinary formaldehyde.

For the frequency ν_4 we obtain as frequency positions of the permitted lines, according as $\Delta J = \pm 1$, $\Delta K = 0$ and as $\Delta J = 0$, $\Delta K = 0$, respectively, the two expressions:

$$\nu = \nu_4 \pm (Jh/8\pi^2 A_0)(2 + \alpha + \beta)$$
$$+ (J^2 - K^2)(\alpha + \beta)h/8\pi^2 A_0$$
and $\quad \nu = \nu_4 + (J(J+1) - K^2)(\alpha + \beta)h/8\pi^2 A_0. \quad (6)$

Equation (5) has already been used by Ebers and Nielsen to explain the structure of the two bands ν_5 and ν_6 in the spectrum of formaldehyde, and as we have pointed out, a structure analagous to this is found in the corresponding two bands in deutero-formaldehyde. Our endeavor from the outset was, however, to account for the unsymmetrical broadening toward higher frequencies of the Q branch of the parallel band in this region. We are therefore particularly interested in the second of Eqs. (6) which sets forth the components comprising the Q branch. Since α and β are both positive quantities it becomes clear at

once that, consistent with measurement, the Q branch must spread out toward higher frequencies. The lines of Eq. (6) have been plotted with their relative intensities for comparison with the branch as actually observed. This diagram is not reproduced here, but is in reasonably good agreement with experiment both in shape and in breadth.

In determining the values of the moments of inertia of the formaldehyde molecules, it has always been assumed that the spacings of the perpendicular $C-H$ and $C-D$ vibrations near 2875 cm^{-1} and 2160 cm^{-1} are the correct ones to use, an assumption which has been justified principally on the basis that this vibration is a single perpendicular oscillation. While this is indeed true, it may be pointed out that the other CH and CD vibrations, parallel to the axis of symmetry, and therefore normal to the first ones, lie near 2780 cm^{-1} and 2056 cm^{-1}, respectively. One may then advance the argument that these frequencies might interact so as to perturb the accompaning rotation levels to such extent that also these spacings are unsuitable directly for determining the values of the moments of inertia. The extent of this perturbation can be determined by referring to Eqs. (3). Since there is only one perpendicular frequency in this region, any other perpendicular frequencies which the molecule may have must lie so far away that the difference $\nu_6 - \nu_5$ will be large compared to $(K\lambda_3 h/8\pi^2 C_0)$. The term under the radical may therefore be expanded and $E(\nu_6)$ takes the form:

$$E(\nu_6) = (h/2)(\nu_4 + \nu_5 + 3\nu_6) + (J(J+1)$$
$$- K^2)h^2/8\pi^2 A_0(1+\alpha) + K^2 h^2/8\pi^2 C_0(1+\gamma), \quad (7)$$

where γ is equal to $\lambda^2 3h/8\pi^2 C_0(\nu_5 - \nu_6)$. γ will under these conditions be small and we have already seen that α is not large. To a fair approximation then A_0 and C_0 remain unchanged as the molecule makes a transition from the ground state to this excited state so that these spacings may safely be used in making numerical determinations of the moments of inertia of the molecule.