A Note on the Centrifugal Stretching in Axially Symmetric Molecules

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It is demonstrated that the degenerate Coriolis splitting of a rotational level, $K\neq 0$, of a molecule which is in an excited perpendicular vibration state is influenced by centrifugal distortion. The effect is of the form $a\,K^3+bJ(J+1)K$. The effect of this distortion on the infra-red spectrum is of the same order of magnitude as the ordinary centrifugal distortion. It is further shown that by redefining the Coriolis coupling coefficient ζ_t the rotational energy of a symmetric molecule may be written in the form $(E/hc)=[J(J+1)-K^2]B_v+L^2C_v-[J(J+1)-K^2]^2D_J-[J(J+1)-K^2]L^2D_{JL}-L^4D_L$ where $L=K-\Sigma_t l_t\zeta_t{}^{(z)}$.

THE problem of centrifugal stretching of axially symmetric molecules in their normal vibration states has been dealt with by Slawsky and Dennison.[1] They have also made estimates of the magnitudes of the centrifugal distortion coefficients D_J, D_{JK}, and D_K for molecules of the variety CH_3X. It is known that the coefficients D must vary with the vibration quantum numbers. This variation is, however, small in general and it has been the practice to set the D_v equal to the equilibrium value D_e. The centrifugal distortion of a molecule for a given set of rotational quantum numbers would then be the same in the excited vibration states as in the normal vibration state when this simplification is made. It is the purpose of this note to point out that this is not actually so in an axially symmetric molecule when its perpendicular vibrations are excited.

The terms in the energy which represent the centrifugal distortion originate with a second-order perturbation calculation of the first-order corrections to the moments of inertia and the products of inertia of a molecule and may be written:

$$H^{(1)}=\cdots-\tfrac{1}{2}\sum_{s\sigma}(\hbar^2/\lambda_s)^{\frac{1}{2}}\times\{\sum_{\alpha\beta}a_{s\sigma}{}^{(\alpha\beta)}(P_\alpha P_\beta/I_{\alpha\alpha}{}^{(e)}I_{\beta\beta}{}^{(e)})\}q_{s\sigma},\quad(\alpha,\beta=x,y,z),\quad(1)$$

where the $a_{s\sigma}{}^{(\alpha\alpha)}$ are the quantities $a_{s\sigma}$, $b_{s\sigma}$, etc., and the $a_{s\sigma}{}^{(\alpha\beta)}$ the $-d_{s\sigma}$, $-e_{s\sigma}$, etc., defined in an earlier work[2] and where $\lambda_s=4\pi^2c^2\omega_s{}^2$. These give rise to second-order terms proportional to $P_\alpha P_\beta P_\gamma P_\delta$ which yield energy contributions which, in general, depend upon the fourth power of the rotational quantum numbers.

There occur terms in the second-order Hamiltonian for a molecule of the form

$$H^{(2)}=\cdots\sum_{s\sigma}(\hbar^2/\lambda_s)^{\frac{1}{2}}\{\sum_{\alpha\beta}a_{s\sigma}{}^{(\alpha\beta)}(p_\alpha P_\beta/I_{\alpha\alpha}{}^{(e)}I_{\beta\beta}{}^{(e)})\}q_{s\sigma},\quad(2)$$

where p_α will be

$$\sum_{s'\sigma'}\sum_{s''\sigma''}\zeta_{s'\sigma's''\sigma''}{}^{(\alpha)}[(\lambda_{s''}/\lambda_{s'})^{\frac{1}{2}}q_{s'\sigma'}p_{s''\sigma''}-(\lambda_{s'}/\lambda_{s''})^{\frac{1}{2}}q_{s''\sigma''}p_{s'\sigma'}]$$

in which the $\zeta_{s'\sigma's''\sigma''}{}^{(\alpha)}$ are the Coriolis coupling coefficients. These are the first-order corrections to the Coriolis contribution or the second-order Coriolis terms which, in general, do not contribute to the energy in second order of approximation. An exception to this rule occurs, however, in the case of a perpendicular vibration which in an axially symmetric molecule is twofold degenerate. In this event $s'=s''$ and $\lambda_{s'}=\lambda_{s''}$. It is then convenient to replace $q_{s'1}$ and $q_{s'2}$ by $r_{s'}\cos\chi_{s'}$ and $r_{s'}\sin\chi_{s'}$, respectively.

The solution to the two dimensionally isotropic oscillator in quantum mechanics has been studied by Dennison[3] and by Shaffer[4] and the solution is known to be of the form $\psi=e^{\pm il\chi}R_v(r)$, where $R_v(r)$ is a function of r only which may be expressed in terms of the associated Laguerre polynomial. The quantum number v is the total vibration quantum number and l is a quantum number signifying the angular momentum associated with the vibration state which takes the values v, $v-2$, $v-4$, $\cdots 1$ or 0. The operator p_z, when $q_{s'\sigma'}$ and $p_{s'\sigma'}$ have been replaced by their equivalents in $r_{s'}$ and $\chi_{s'}$, will contain a term

$$-i\hbar\sum_{s'}\zeta_{s'}{}^{(z)}\partial/\partial\chi_{s'}$$

and then (2) becomes of the same order of magnitude as (1) in the states where $l_{s'}$ is different from zero. It is, therefore, an advantage to include the portions of (2), each of which depends upon a single twofold degenerate frequency with $H^{(1)}$ before carrying out the perturbation calculation which yields the centrifugal distortion. When this is done, we have:

$$H^{(1)}=\cdots-\tfrac{1}{2}\sum_{s\sigma}(\hbar^2/\lambda_s)^{\frac{1}{2}}\{\sum_{\alpha\beta}a_{s\sigma}{}^{(\alpha\beta)}(P_\alpha-2p_\alpha{}^*)P_\beta/I_{\alpha\alpha}{}^{(e)}I_{\beta\beta}{}^{(e)}\}q_{s\sigma}.\quad(3)$$

The perturbation calculation is straightforward and leads to the following terms which are diagonal in K and $l_{s'}$ in addition to the usual ones which depend upon the fourth power of the rotational quantum numbers.

$$hc\sum_{s'}l_{s'}\zeta_{s'}{}^{(z)}\{(4D_K+2D_{JK})K^3+2(2D_J+D_{JK})J(J+1)K\}.\quad(4)$$

[1] Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. **7**, 509 (1939).
[2] H. H. Nielsen, Phys. Rev. **60**, 794 (1941).
[3] D. M. Dennison, Phys. Rev. **41**, 304 (1932).
[4] W. H. Shaffer, Rev. Mod. Phys. **16**, 245 (1944).

The relation (4) shows that the centrifugal stretching now depends also upon the third power of the rotational quantum numbers. This is tantamount to stating that not only the positions of the centers of gravity of the two components into which a rotation level of a molecule in an excited perpendicular vibration state where $K\neq 0$ is split by the degenerate Coriolis forces, but the actual splitting itself is influenced by the centrifugal forces. This is, what might be expected, of course, if the centrifugal distortion is regarded as the effect of the change of the moment of inertia by the rotational motion itself. It may be seen further that the effect upon the infra-red spectrum will be of the same order of magnitude as will the usual centrifugal distortion effects. The terms here described are proportional to l_s'. In the normal vibration state $l_s'=0$. The terms will therefore be zero in the normal state, but will occur in a state where $l_s'\neq 0$. The position of a line in a perpendicular band in the spectrum is the difference of a spectral term in the excited state where $l_s'\neq 0$ and a term level in the normal state where $l_s'=0$. The effect upon the spectrum is, therefore, proportional to the third power of the rotational quantum numbers just as is the effect due to the usual centrifugal distortion. It has already been pointed out by Nielsen[5] that this effect is measurable and necessary to explain the positions of lines in the microwave spectrum of symmetric molecules.

It may be regarded as convenient to combine the contribution (4) with the usual energy of a symmetric molecule. This may be done in the following manner. The energy is normally written

$$(E/hc)=(E_{\text{vib}}/hc)+[J(J+1)B_v+K^2(C_v-B_v)] \pm 2K\sum l_{s'}\zeta_{s'}^{(z)}\bar{C}_v-D_JJ^2(J+1)^2 -D_{JK}J(J+1)K^2-D_KK^4, \quad (5)$$

where[6]

$$B_v=B_e-\textstyle\sum_s \alpha_s(v_s+g_s/2), \quad C_v=C_e-\sum_s \gamma_s(v_s+g_s/2),$$

$$\bar{C}_v=C_e-\textstyle\sum_s \bar{\gamma}_s(v_s+g_s/2), \quad B_e=(h/8\pi^2 I_{xx}^{(e)}c)$$

and $C_e=h/8\pi^2 I_{zz}^{(e)}c$. The constant $\bar{\gamma}_s$ is equal to

$$\gamma_s+\sum_{s''}(C_e^2/\omega_s)[(3\lambda_s+\lambda_{s''})/(\lambda_s-\lambda_{s''})](\zeta_{ss''\sigma''}^{(z)})^2.$$

[5] H. H. Nielsen, Phys. Rev. **77**, 130 (1950).
[6] H. H. Nielsen, Phys. Rev. **70**, 184 (1946).

The coefficient $\bar{C}_v$ may be replaced by C_v in (5) if we set

$$\sum_{s'} l_{s'}(\zeta_{s'}^{(z)})_v C_v=\sum_{s'} l_{s'}\zeta_{s'}^{(z)}\bar{C}_v.$$

One obtains then for $(\zeta_{s'}^{(z)})_v$

$$(\zeta_{s'}^{(z)})_v=\zeta_{s'}^{(z)}\{1-2\sum_{s\sigma}\sum_{s''\sigma''}(C_e/\omega_s g_s) \times[(3\lambda_s+\lambda_{s''})/(\lambda_s-\lambda_{s''})] \times(\zeta_{ss''\sigma''})^2](v_s+g_s/2)\}. \quad (6)$$

The vibration energy contains the constants $xl_{s'}l_{s'}$ and $xl_{s'}l_{s'''}$. These in turn are proportional to $(l_{s'}\zeta_{s'}^{(z)})^2C_e$ and $(l_{s'}l_{s'''}\zeta_{s'}^{(z)}\zeta_{s'''}^{(z)})C_e$. We may to this approximation replace these by $[l_{s'}(\zeta_{s'}^{(z)})_v]^2C_v$ and $[l_{s'}l_{s'''}(\zeta_{s'}^{(z)})_v \times(\zeta_{s'''}^{(z)})_v]C_v$. The rotational energy may now be written in the form

$$(E_{\text{rot}}/hc)=[J(J+1)-K^2]B_v+L^2C_v -[J(J+1)-K^2]^2D_J -[J(J+1)-K^2]L^2D_{JL}-L^4D_L \quad (7)$$

if the portion of $xl_{s'}l_{s'}$ and $xl_{s'}l_{s'''}$ which depends upon $(\zeta_{s'}^{(z)})^2$ and $\zeta_{s'}^{(z)}\zeta_{s'''}^{(z)}$ is included with the rotational energy. The number L will in general not be quantized and will be equal to

$$L=K-\sum_{s'} l_{s'}(\zeta_{s'}^{(z)})_v.$$

The new centrifugal distortion coefficients D_{JL} and D_L may be shown to be expressible in terms of the usual D_{JK} and D_K as

$$D_{JL}=2D_J+D_{JK}, \quad D_L=D_J+D_K+D_{JK}. \quad (8)$$

It is of interest to note that for a linear molecule where the Sayvetz[7] condition demands that

$$K=\sum_{s'} l_{s'}\zeta_{s'}^{(z)},$$

i.e., $L=0$, the relation (8) becomes exactly that for a linear molecule.

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[7] A. Sayvetz, J. Chem. Phys. **7**, 282 (1939).