The average nuclear separations are calculated for XY₂ molecules by means of the total vibrational – rotational wave function obtained by a method different from that developed by Nielsen and Amat. A small dimensionless parameter is introduced for an order-of-magnitude estimate of the vibrational – rotational interaction. Terms due to the Coriolis interaction are singled out.

The effect of vibrational and rotational interactions on the average nuclear separations in various vibrational – rotational states of molecules were calculated in [1]. An important result of this study was the conclusion that the anharmonicity of the vibrations makes the principal contribution to the change in the nuclear separations. The approximations used in [1] prevented an account of the effect of the Coriolis interaction on the nuclear separations. Below we take up this point for the case of nonlinear XY₂ molecules. The wave functions for the vibrational – rotational states are obtained by a method slightly different from that used in [1].

We write the nuclear separation as an expansion in terms of normal coordinates:

\[ r = r_e + \sum \kappa r_\kappa q_\kappa + \frac{1}{2} \sum \ell \mu r_{\ell \mu} q_\ell q_\mu + \ldots, \]  

where \( r_e \) is the equilibrium nuclear separation,

\[ r_\kappa = \left( \frac{\partial r}{\partial q_\kappa} \right)_e, \quad r_{\ell \mu} = \left( \frac{\partial^2 r}{\partial q_\ell \partial q_\mu} \right)_e, \text{ etc.} \]

Following the discussion in [2] of the evaluation of the various terms in the series expansion of the potential energy in terms of normal coordinates, we assume that series (1) decays uniformly for states far from dissociation. Direct evaluation of the coefficients of the first terms in (1) shows that the ratio of subsequent terms to preceding terms is \( \lambda \sim 10^{-1} \), as in the case of a normal-coordinate expansion of the potential energy [2], the dipole moment, etc. The assumption that all of series (1) decays uniformly is a rather crude assumption, but it allows us to obtain an order-of-magnitude classification of the various terms for an application of perturbation theory.

The average value \( \bar{r} \) in vibrational – rotational state (VR) is

\[ \bar{r} = \int \rho_{VR} r \, \rho_{VR} \, d \tau_V \, d \tau_R. \]  

In contrast with [1], the vibrational – rotational wave function here is taken as the second-order perturbation-theory solution of the Schrödinger equation [4]

\[ (H_V + H_R) + (H_R - H_V) \rho_{VR} = E_{VR}, \]  

where \( H_V \) is the Hamiltonian for anharmonic vibrations of the nuclei;

\[ H_R = \frac{1}{2} \sum \alpha \beta P_\alpha P_\beta - \frac{1}{2} \sum g_\ell P_\ell; \]

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$P_\alpha$ is the projection of the total angular momentum on the $\alpha$ axis; $g_z = \mu_z P_z + p_z \mu_{zz}$; $p_z = \sum_{\alpha} \xi_{1\alpha} q_{1\alpha} p_\alpha$ is the projection of the vibrational angular momentum on the $z$ axis; $\xi_{ik}$ is the momentum conjugate to normal coordinate $q_{ik}$; $\xi_{ik}$ are the Coriolis constants; $\mu_{\alpha\beta}$ are the matrix elements of the transformation operator; and

$$\omega = \mu (P_0 - \Pi),$$

where $\omega$ is the angular velocity;

$$H_{R}^{(V)} = \frac{1}{2} \sum_{\alpha} a_{\alpha} P_{\alpha}^2 + \frac{1}{4} \sum_{\alpha \beta} \xi_{\alpha \beta} P_{\alpha}^2 P_{\beta}^2 + \frac{1}{8} \sum_{\alpha \beta \gamma} V_{\alpha \beta \gamma} P_{\alpha}^2 P_{\beta}^2 P_{\gamma}^2$$

is the operator for the energy of a nonrigid top, $a_{\alpha\alpha}$ are the effective rotational constants with no account of the second- and third-order corrections, and $\tau$ and $\nu$ are the centrifugal distortion constants.

In the zero approximation we have

$$H_0 = H_V + H_R^{(V)}, \quad E_{VR} = E_V + E_R^{(V)}, \quad \phi_{VR} = \psi_V \psi_R^{(V)}.$$  

The second-approximation normalized wave functions are

$$\phi_{VR} = (1 + c_{VR, VR}^{(2)} \phi_{VR} + \sum_{V' R'} (c_{VR, VR}^{(1)} c_{VR' R' R}^{(2)} \phi_{V' R'}^{(2)}),$$

where

$$c_{VR', V' R'}^{(2)} = \frac{1}{A} \sum_{V' R'} b_{aa}(VV') \langle V' R' | A^2 H_{VR} | V' R' \rangle + \frac{1}{4} b_{zz}(VV') \langle R' | P^2 | R \rangle + \frac{1}{4} t_{\alpha \beta}(VV') \langle R' | P_\alpha P_\beta | P_\alpha P_\beta + P_\beta P_\alpha \rangle$$

The constants $b_{\alpha\alpha}(VV)$ are analogous to the corrections to the effective rotational constants, and $t_{\alpha \beta \gamma \delta}(VV)$ are analogous to the centrifugal–distortion constants:

$$b_{zz}(VV) = \frac{1}{2} \langle V | g_z A^2 g_z | V \rangle, \quad b_{aa}(VV) = \pm i \langle V | g_x A^2 g_y | V \rangle, \quad a = x, y,$$

$$t_{\alpha \beta}(VV) = \langle V | g_{\alpha\beta} A^2 g_{\alpha\beta} | V \rangle.$$

The constants $b_{\alpha\beta}(VV)$, $b_{\alpha\beta}(VV')$, $b_{\alpha\beta}(VV)$, and $b_{zz}$ are of the form

$$A(VV') = (-1)^n \langle V' | A^2 A^2 | V \rangle,$$

where $a$ and $b$ are the operators $g_z$ and $A$ in various combinations, and $n$ is the number of operators $g_z$ among $a$ and $b$.

For subsequent calculations it is convenient to write $\bar{r}$ as

$$\bar{r} = \sum_{n=0}^{\infty} \lambda^n \langle r_n \rangle.$$  

Straightforward arguments [3] show that the series expansion of $c_{VR, VR}^{(2)}$ in terms of $\lambda$ begins with quadratic terms, that of $c_{VR, VR}^{(2)} - c_{VR, VR}^{(1)}$ begins with fourth-degree terms, etc. Retaining terms of order no higher than $\lambda^4$ in (11), we find

$$\bar{r} = \langle V | r A \sum_{\alpha} \langle R | P_{\alpha}^2 | R \rangle \rangle V \rangle.$$

Equation (12) is essentially the same as the corresponding equation in [1], so we can evidently use the parameter $\lambda$ and refine the $\bar{r}$ value of [1]. In the calculation of $\langle V | r | V \rangle$ in [1], $\bar{r}$ was expanded in normal coordinates, and terms of up to second order inclusively were used; according to our calculations, on the other hand, terms of up to fourth order inclusively must be used. We see from Eq. (1) that centrifugal