Errata: The Vibration-Rotation Energies of Polyatomic Molecules

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IN the recent paper by the above title a few errors which are essentially of a typographical nature have occurred. While none of these affects the final results in any manner, it has seemed desirable to call attention to them for the benefit of anyone wishing to work through the problem from the beginning. The changes are as follows:

1. From the foregoing definitions it is obvious that what in Eq. (15) has been termed I_{zz} should have been I_{yz} and similarly that I_{yz} should be I_{zx}. This error is purely typographical.

2. In the second-order Hamiltonian H_2 there is an error in the coefficient of $q_{s\sigma}p_{s'\sigma'}$. It should read:

$$(-i\hbar/2)\sum_{s\sigma}\sum_{s'\sigma'}(\lambda_{s'}/\lambda_s)^{\frac{1}{2}}[(A_{s\sigma s'\sigma'}/I_{xx}^{(e)})+(B_{s\sigma s'\sigma'}/I_{yy}^{(e)})$$
$$+(C_{s\sigma s'\sigma'}/I_{zz}^{(e)})-(a_{s\sigma}a_{s'\sigma'}/2(I_{xx}^{(e)})^2)-(b_{s\sigma}b_{s'\sigma'}/2(I_{yy}^{(e)})^2)$$
$$-(c_{s\sigma}c_{s'\sigma'}/2(I_{zz}^{(e)})^2)-(d_{s\sigma}d_{s'\sigma'}/(I_{xx}^{(e)})(I_{yy}^{(e)}))$$
$$-(e_{s\sigma}e_{s'\sigma'}/(I_{yy}^{(e)})(I_{zz}^{(e)}))-(f_{s\sigma s'\sigma'}/(I_{zz}^{(e)})(I_{xx}^{(e)}))].$$

This term contributes to the energy only in E_0/hc which, as we have pointed out, is of no physical interest and its value was not calculated in this paper.

3. In the coefficient of $(P_xP_y+P_yP_x)$ and $(P_xP_z+P_zP_x)$ in the second-order Hamiltonian H_2 the algebraic sign preceding the terms $(e_{s\sigma}f_{s''\sigma''}/I_{zz}^{(e)})$ and $(d_{s\sigma}e_{s''\sigma''}/I_{yy}^{(e)})$ should be $+$. Moreover, the third term in the coefficient of $(P_xP_z+P_zP_x)$ and the second term in the coefficient of $(P_yP_z+P_zP_y)$ should be, respectively, $-(c_{s\sigma}f_{s''\sigma''}/I_{zz}^{(e)})$ and $-(e_{s\sigma}b_{s''\sigma''}/I_{yy}^{(e)})$. These errors also are purely typographical and what is more, terms of the above type cannot contribute to the energy in second order of approximation.

4. In the second-order transformed Hamiltonian H_2' an error in copying from the author's original manuscript has occurred. In the coefficients of the terms $(P_\alpha^2P_\beta^2+P_\beta^2P_\alpha^2)$ the quantities $d_{s\sigma}^2$, $e_{s\sigma}^2$ and $f_{s\sigma}^2$ should be deleted so as to read:

$$[a_{s\sigma}b_{s\sigma}/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2](P_x^2P_y^2+P_y^2P_x^2)$$
$$+[a_{s\sigma}c_{s\sigma}/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2](P_x^2P_z^2+P_z^2P_x^2)$$
$$+[b_{s\sigma}c_{s\sigma}/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2](P_y^2P_z^2+P_z^2P_y^2).$$

The quantities $[d_{s\sigma}^2/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2]$, $[e_{s\sigma}^2/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2]$ and $[f_{s\sigma}^2/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2]$ are the coefficients of the terms $(P_\alpha P_\beta+P_\beta P_\alpha)^2$, respectively. The transformed Hamiltonian H_2' should therefore include also the following terms:

$$+[d_{s\sigma}^2/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2](P_xP_y+P_yP_x)^2$$
$$+[e_{s\sigma}^2/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2](P_yP_z+P_zP_y)^2$$
$$+[f_{s\sigma}^2/(I_{zz}^{(e)})^2(I_{xx}^{(e)})^2](P_zP_x+P_xP_z)^2.$$

The actual energy relations stated in Eqs. (26) to (30) and in Section IV are believed to be correct as they stand except that the algebraic sign within the parentheses of the numerators of the last two terms in (27) should be $+$ and that the definitions of x_0 and y_0[1] in (28) should be interchanged.

I am indebted to Dr. Samuel Silver of the University of Oklahoma who has verified the calculations reported in the earlier paper and who has called my attention to some of the errors corrected herein.

[1] The terms x_0, y_0, and z_0 are of the order of magnitude of the coefficients of centrifugal distortion; D_J, D_{JK}, and D_K. These latter terms become important only for larger values of J, say $J>6$, and then only because they are multiplied by quantities quartic in J and K. The terms x_0, y_0, and z_0, on the other hand are multiplied by terms only quadratic in J and K and will contribute amounts to the energy small even as compared to the centrifugal distortion. The terms x_0, y_0, and z_0 may, therefore, actually be omitted from the effective reciprocals of inertia.