# Addendum : Theory of Internal Over-All Rotational Interactions. III. Nonrigid Asymmetric Rotors

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The corresponding nonredundant coordinate, $S_4$, should be

$$S_4=(3+3a^2)^{-\frac{1}{2}}[\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31}-a(\Delta\beta_1+\Delta\beta_2+\Delta\beta_3)]$$

where

$$a=-\frac{\sqrt{3}\cos\beta}{\cos\frac{\alpha}{2}}.$$

Incorporation of these changes in the normal coordinate treatment leads to revised values for certain force constants as listed below. The agreement between calculated and experimental frequencies is unchanged. The author is indebted to Mr. James Scherer for first bringing this point to his attention.

| | |
|---|---|
| $F_1=$ 17.9900 md/A | $k_T=$ 17.9900 md/A |
| $F_2=$ 2.7750 | $k_R=$ 2.7750 |
| $F_4=$ 0.5230 | $k_\alpha=$ 0.2125 |
| $F_{24}=-0.2790$ | $k_\beta=$ 0.2250 |
| | $k_{\alpha\alpha}=-0.0309$ |
| | $k_{\beta\beta}=$ 0.0048 |
| | $k_{\alpha\beta}=k_{\alpha\beta}'=-0.0627$ |
| | $k_{R\alpha}=-0.0670$ |
| | $k_{R\beta}=$ 0.0836 |

## Addendum: Theory of Internal Over-All Rotational Interactions. III. Nonrigid Asymmetric Rotors

[J. Chem. Phys. 23, 2236 (1955)]

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BECAUSE of symmetry considerations, the matrix elements $(r|\mathbf{P}_z|r)$ and $(r|\mathbf{P}_z^3|r)$ appearing in the article are equal to zero. Thus all discussions pertaining to the evaluation of these elements, i.e., Appendix III, should be ignored. The following discussion should be added in order to correct the article.

The matrix elements

$$P_2(r',r)=1/2(I_{z2}/I_{z1}I_z)(r'|\mathbf{P}_z^2|r) \quad \text{(a)}$$

$$P_1(r',r)=I_{z1}^{-1}(r'|\mathbf{P}_z|r) \quad \text{(b)}$$

appear in Eq. (17) but only $(r,r)$ terms are retained, an approximation that is valid provided

$$|P_2(r',r)|\ll|W_{r'}-W_r+P_2(r',r')-P_2(r,r)| \quad \text{(c)}$$

$$|P_1(r',r)|\ll|W_{r'}-W_r+P_2(r',r')-P_2(r,r)|. \quad \text{(d)}$$

$(r'\neq r)$. In contradiction to the statements in the article, $P_1(r,r)=0$. Thus in this approximation all matrix elements of $\mathbf{P}_z$ and $\mathbf{P}_z^3$ vanish in all equations in the article, thereby simplifying the results considerably.

If the rotor is nearly symmetric, the separation between "asymmetry doublets" becomes small, and condition (d) no longer holds. In this event degenerate perturbation theory must be applied. The wave equation described in Eq. (13) should be altered by substituting $2^{-\frac{1}{2}}[\Phi_{r0}\pm\Phi_{r1}]$ in place of $\Phi_r$, where $(r0)$ and $(r1)$ represent the rigid rotor quantum numbers corresponding to the $\gamma=0$ and $\gamma=1$ members,[1] respectively, of an "asymmetry doublet." Thus if the inequality in relation (d) is reversed, the equations throughout the article must be altered in the following ways: $W_R(r)$, $(r|\mathbf{P}_z^2|r)$, and $(r|\mathbf{P}_z^4|r)$ should all be replaced by the average of the corresponding $(r0)$ and $(r1)$ values; $(r|\mathbf{P}_z|r)$ should be replaced by $\pm(r0|\mathbf{P}_z|r1)$ where the $(+)$ and $(-)$ refer to the two different states corresponding to the same limiting quantum number $K$; $(r|\mathbf{P}_z^3|r)$ should be treated analogously to $(r|\mathbf{P}_z|r)$. For a symmetric top, this procedure leads to Eq. (43), except that $\pm K$ should be substituted for $K$.

The author is greatly indebted to Mr. Dudley Herschbach for his criticisms of Appendix III which led to the present revisions.

[1] King, Hainer, and Cross, J. Chem. Phys. 11, 27 (1943).

## Errata: Theory of the Interaction of Internal Rotation with Over-All Rotations. I. Symmetric Rotors: Methyl Silane

[J. Chem. Phys. 22, 1733 (1954)]

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IN the abstract, and in Eqs. (14) and (16), $K$ should be replaced by $\pm K$. See the preceding errata for a discussion of this procedure.

## Erratum: Statistical Mechanics of Liquid-Vapor Equilibrium

[J. Chem. Phys. 26, 887 (1957)]

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THIS article should contain a reference to the earlier work of S. Katsura and H. Fujita [Progr. Theoret. Phys. Japan 5, 997 (1950)], to which it is quite closely related, and in which some of the methods of the present paper were anticipated.