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NOTES

Centrifugal Distortion in Water and Hydrogen Sulfide[1]

It is the intent of this note to present specific results pertaining to the changes in molecular geometry of water and hydrogen sulfide which are induced by centrifugal effects in rotational states of the molecules. Hydrogen, deuterium, and tritium substitutions are considered. A general expression for centrifugally induced geometry changes has been presented by Toyama *et al.* (*1*) but specific results included only the symmetric forms of water, H_2O and D_2O. A sign error is present in that work but appears to be only typographical, as the numerical results given are correct. The term $\mu \sin \alpha$ in Eq. (53) should be negative. Considerable simplification occurs in the symmetric cases and a calculation of centrifugal distortion in HDO, DTS, etc., must proceed from the most general approach.

TABLE I. Coefficients of Eq. (3) for Water and Hydrogen Sulfide[a]

	ρ	Δr/r	Δα		Δr/r	Δα
H_2O	a	1.016	-10.742	H_2S	0.300	-2.878
	b	0.293	3.041		0.212	2.238
	c	0.247	0.000		0.126	0.012
D_2O	a	0.565	-5.976	D_2S	0.159	-1.525
	b	0.147	1.521		0.106	1.120
	c	0.126	0.070		0.064	0.025
T_2O	a	0.415	-4.390	T_2S	0.112	-1.075
	b	0.098	1.016		0.071	0.748
	c	0.086	0.090		0.044	0.029

	ρ	$\Delta r_1/r_1$	$\Delta r_2/r_2$	Δα		$\Delta r_1/r_1$	$\Delta r_2/r_2$	Δα
HDO	a	0.969	0.673	-9.192	HDS	0.372	0.083	-2.639
	b	0.065	0.293	1.488		0.008	0.179	0.705
	c	0.111	0.204	0.030		0.046	0.088	0.013
HTO	a	0.955	0.606	-9.160	HTS	0.374	0.075	-2.855
	b	0.028	0.232	0.857		0.002	0.125	0.370
	c	0.066	0.170	0.034		0.026	0.074	0.012
DTO	a	0.541	0.449	-5.334	DTS	0.189	0.071	-1.359
	b	0.072	0.157	1.117		0.021	0.116	0.632
	c	0.084	0.117	0.076		0.037	0.054	0.022

[a] All coefficients have been multiplied by 10^4; angles are in radians; r_1 is associated with the lighter atom in the asymmetric species.

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The general expression for the distortion effects are given in Ref. (*1*) in matrix form

$$\langle \mathbf{R} \rangle_{\text{cent}} = \mathbf{F}_R^{-1}\mathbf{G}_R^{-1}\mathbf{B}\Phi\mathbf{X}, \tag{1}$$

where

$$\langle \mathbf{R} \rangle_{\text{cent}} = \begin{pmatrix} \Delta r_1 \\ \Delta r_2 \\ (r_1 r_2)^{\frac{1}{2}}\Delta\alpha \end{pmatrix} \tag{2}$$

and $\mathbf{X}$ is, in the case of the bent triatomic molecule, a nine component vector describing the position of the three nuclei in a body fixed Cartesian coordinate system which is parallel to the molecular inertial axes. $\mathbf{F}_R$, $\mathbf{G}_R$, $\mathbf{B}$, and Φ are defined in Ref. (*1*). As was shown by the authors of Ref. (*1*), it is convenient to rewrite Eq. (1) as

$$\langle R \rangle_{\text{cent}} = \rho_a\langle P_a^2\rangle + \rho_b\langle P_b^2\rangle + \rho_c\langle P_c^2\rangle, \tag{3}$$

where a, b, and c designate the molecular inertial axes and $\langle P_a^2\rangle$, etc., are the expectation values of the angular momentum component operators along the molecular equilibrium axes. These values may be easily calculated for any specific rotational level of a given molecule (*2*). The vector coefficients ρ_a, ρ_b, and ρ_c of Eq. (3), which are defined in Ref. (*1*), have been evaluated and are presented in Table I for water and hydrogen sulfide. Coefficients for H_2O and D_2O have been recalculated for completeness.

The force constants used are those of Cook, De Lucia, and Helminger (*3*, *4*). As noted by the authors of Refs. (*3*) and (*4*), model errors produce significant uncertainties in the values of the force constants. The constants used are those obtained from infrared data with equal weighting. These uncertainties are the primary limitation to the accuracy of the coefficients of this work and those of Ref. (*1*). Symmetric forms of water and hydrogen sulfide distort symmetrically and only one coefficient is necessary to describe the change in bond length. In the case of the asymmetric forms, changes in both bonds must be specified. In Table I, r_1 refers to the bond extending from the apex atom to the atom of least mass.

REFERENCES

1. M. Toyama, T. Oka, and Y. Morino, *J. Mol. Spectrosc.* **13**, 193 (1964).
2. W. Gordy and R. L. Cook, "Microwave Molecular Spectra," Wiley-Interscience, New York, 1970.
3. R. L. Cook, F. C. De Lucia, and P. Helminger, *J. Mol. Spectrosc.* **53**, 62 (1974).
4. R. L. Cook, F. C. De Lucia, and P. Helminger, *J. Mol. Struct.* **28**, 237 (1975).

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