Comments and Errata to the Article "Mean Amplitudes of Vibration in Molecules with Internal Rotation: Halogenated Ethanes"

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In the first article of the series on molecules with internal rotation [1] the following approximate formula was developed for the framework mean-square amplitude.

$$\langle \Delta\varrho^2 \rangle_{\mathrm{frm}} = (\alpha + \beta \cos\theta + \gamma \cos^2\theta)/\varrho^2 \quad (1)$$

one of the conclusions which have been reached.[2]

The coefficients $\alpha(\theta, T)$, $\beta(\theta, T)$ *and* $\gamma(\theta, T)$ *approach* θ*-independent values when* $T \to \infty$.

This theorem was derived from the known properties of classical limits of mean-square amplitudes.[3] In the present application to halogenated ethanes the above theorem has been verified numerically in the following way. The formula (1) with constant (θ-independent) coefficients was found to reproduce the rigorously calculated framework mean amplitudes with numerical exactness (within 5 to 6 significant figures) at 298°K, as was already stated in the previous paper.[1] At absolute zero on the other hand some deviations were detectable within the accuracy of the numerical computations. We have reached the conclusion that the approximation of constant α, β, and γ is perfectly sound for halogenated ethanes at room temperature, and even valid with a high degree of accuracy at absolute zero.

Table 1. α, β, and γ coefficients of eqn. (1) in Å^4 units.

	α		β		γ	
	$T = 0$	298°K	$T = 0$	298°K	$T = 0$	298°K
C_2F_6	0.03882	0.05978	0.00030	0.01194	−0.00029	−0.00037
C_2Cl_6	0.05261	0.12823	−0.00316	0.02454	−0.00436	−0.02131
C_2Br_6	0.04126	0.15023	−0.00386	0.03136	−0.00321	−0.02620

The mentioned article [1] should be consulted for explanation of the adopted symbols. In the application to halogenated ethanes unfortunately the coefficients of α and γ were given incorrectly. The reported coefficients [1] in fact apply to the form

$$\langle \Delta\varrho^2 \rangle_{\mathrm{frm}} = (\alpha' + \beta \cos\theta + \gamma' \cos 2\theta)/\varrho^2 \quad (2)$$

In Table 1 we give the correct coefficients, which are consistent with eqn. (1). They are given both at absolute zero and 298°K, and have been computed by means of an adjustment to the rigorous values at $\theta = 0°$, 90°, and 180°.

Some further studies have been made [2] on the nature of the inherent approximation of eqn. (1), including a consideration of the apparent constancy of the α, β, and γ coefficients. The following statement is

1. Cyvin, S. J., Elvebredd, I., Cyvin, B. N., Brunvoll, J. and Hagen, G. *Acta Chem. Scand.* **21** (1967) 2405.
2. Cyvin, S. J., Elvebredd, I., Hagen, G. and Brunvoll, J. *To be published.*
3. Decius, J. C. *J. Chem. Phys.* **39** (1963) 1130; Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo 1968.

Received March 29, 1968.