Remark on the Separation of High and Low Vibrational Frequencies *

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The approximate method of separation of high and low frequencies [1,2] in Wilson's treatment of molecular vibrations has been utilized by many investigators. In particular, the method is very useful in the case of hydrocarbons, where the high C—H stretching frequencies may be separated from the remaining frequencies with high degree of accuracy.

Separated product rule. As a consequence of the splitting of high and low frequencies, the Teller-Redlich product rule [2,3] splits into separate product rules for the high and low frequencies, respectively. This is true for the frequencies within a specific symmetry species, as well as the frequencies all together. In this connection the authors wish to formulate the following general theorem. When the (approximate) theoretical ratios from the separated product rule within one (or more) symmetry species are multiplied together, the *exact* frequency ratio is obtained.

Example. Ethylene and ethylene-d_4 (symmetry group D_{2h}) are assumed to have the same interatomic distances and interbond angles. Hence the product rule for the frequencies of the totally symmetric species (A_g) reads

$$\omega_1\omega_2\omega_3/\omega_1^*\omega_2^*\omega_3^* = \mu_\mathrm{H}/\mu_\mathrm{D} \qquad (1)$$

where μ_H and μ_D are the inverse masses of the H and D atoms, respectively. The frequencies of heavy ethylene are identified by an asterisk. From the G matrix of the molecular model in question (see, *e.g.*, Ref.[4]) the following separated product rules have been deduced.

$$\omega_1/\omega_1^* = (\mu_\mathrm{H} + 2\mu_\mathrm{C}\cos^2 A)^{1/2}/(\mu_\mathrm{D} + 2\mu_\mathrm{C}\cos^2 A)^{1/2} \qquad (2)$$

$$\omega_2\omega_3/\omega_2^*\omega_3^* = \mu_\mathrm{H}(\mu_\mathrm{H} + 2\mu_\mathrm{C}\cos^2 A)^{-1/2}/\mu_\mathrm{D}(\mu_\mathrm{D} + 2\mu_\mathrm{C}\cos^2 A)^{-1/2} \qquad (3)$$

The HCH (or DCD) interbond angle is designated $2A$. The exact relation (1) is seen to be reproduced by multiplying the approximate relations (2) and (3).

Proof of the theorem. Using the symbols of Wilson [2], the separated product rules may be written

$$\mathit{\Pi}\lambda(\text{high})/\mathit{\Pi}\lambda^*(\text{high}) = |\mathfrak{G}_{11}|/|\mathfrak{G}_{11}^*|$$

$$\mathit{\Pi}\lambda(\text{low})/\mathit{\Pi}\lambda^*(\text{low}) = |\mathfrak{G}^\circ|/|\mathfrak{G}^{\circ *}|$$

Here $|\mathfrak{G}^\circ| = |\mathrm{X}_{22}|^{-1}$. In order to prove

$$\mathit{\Pi}\lambda(\text{high})\mathit{\Pi}\lambda(\text{low})/\mathit{\Pi}\lambda^*(\text{high})\mathit{\Pi}\lambda^*(\text{low}) = \mathit{\Pi}\lambda/\mathit{\Pi}\lambda^* = |\mathfrak{G}|/|\mathfrak{G}^*|$$

it should be shown that

$$|\mathfrak{G}| = |\mathfrak{G}_{11}| \cdot |\mathfrak{G}^\circ|$$

Wilson [2] has given the relation

$$\mathfrak{G}^\circ = \mathfrak{G}_{22} - \mathfrak{G}_{21}\mathfrak{G}_{11}^{-1}\mathfrak{G}_{12}$$

Hence

$$\mathfrak{G}_{11}\mathfrak{G}^\circ = \mathfrak{G}_{11}\mathfrak{G}_{22} - \mathfrak{G}_{11}\mathfrak{G}_{21}\mathfrak{G}_{11}^{-1}\mathfrak{G}_{12}$$

Notice that $\mathfrak{G}_{21}$ is the transpose of $\mathfrak{G}_{12}$ (because $\mathfrak{G}$ is symmetric). In consequence, one obtains for the determinant:

$$|\mathfrak{G}_{11}\mathfrak{G}^\circ| = |\mathfrak{G}_{11}| \cdot |\mathfrak{G}^\circ| = |\mathfrak{G}_{11}| \cdot |\mathfrak{G}_{22}| - |\mathfrak{G}_{12}|^2 = |\mathfrak{G}|$$

q.e.d. In other words, it has been proved that the original $\mathfrak{G}$-matrix and the splitted $\mathfrak{G}$-matrix, *viz.*

$$\begin{bmatrix} \mathfrak{G}_{11} & \mathfrak{G}_{12} \\ \mathfrak{G}_{21} & \mathfrak{G}_{22} \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} \mathfrak{G}_{11} & 0 \\ 0 & \mathfrak{G}^\circ \end{bmatrix}$$

have identical determinants.

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