Ratios of Isotopic Frequencies Using HLFS Method

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Simple expressions involving elements of the kinetic energy matrix are obtained for the ratios of isotopic frequencies in the case of vibrational species, of order two and three, associated with small molecules by employing the high and low frequency separation method and the product rule. The applicability of the method is indicated.

The high and low frequency separation (HLFS) method developed by Wilson and others [1, 2] enables factoring out of the high and low frequencies associated with any particular vibrational species in a molecule. The applicability of the method in the analysis of normal coordinates and in the evaluation of force constants has been recently illustrated by Müller et al. [3–6]. The present discussion is intended to throw light on the applicability of the method in the evaluation of ratios of isotopic frequencies in the analysis of molecular vibrations.

In a case where the high frequency is to be separated, we use the secular equation

$$|F - G^{-1} \Lambda| = 0 \tag{1}$$

after dropping the row and column of G^{-1}, F and Λ matrices corresponding to the high frequency. In a case where the low frequency is to be separated, we use the secular equation

$$|GF - \Lambda E| = 0 \tag{2}$$

after dropping the row and column of G, F and Λ matrices corresponding to the low frequency. As usual, G^{-1} and F are the kinetic and potential energy matrices respectively and Λ is a diagonal matrix with its elements Λ_i proportional to the square of vibrational frequencies ω_i. E represents a unit matrix. The separation of any frequency in this manner means decoupling of the normal mode represented by that particular frequency and holds better correspondence to the true situation, the more the frequency concerned is spaced from the other ones.

In the second order vibrational problems, the separation of the high frequency would thus yield

$$F_{22} = G_{22}^{-1} \Lambda_2 , \tag{3}$$

and the separation of the low frequency would yield

$$G_{11} F_{11} = \Lambda_1 . \tag{4}$$

Referring by asterisks to the case after isotopic substitution and employing the condition of invariance of F_{ij} elements under isotopic substitution, these two equations lead to

$$\omega_1/\omega_1{}^* = (G_{11}/G_{11}^*)^{1/2} \tag{5}$$

and

$$\omega_2/\omega_2{}^* = (G_{22}^{*-1}/G_{22}^{-1})^{1/2} . \tag{6}$$

Equations (5) and (6) are the same as the ones obtained earlier [7] by splitting the normal coordinate transformation matrix L into two parts, one, a lower triangular matrix L_0 obeying the constraint $L_0 \tilde{L}_0 = G$ and the other, an orthogonal matrix C made up of a free parameter c such that $L = L_0 C$ and then setting the condition $c = 0$. Since the results thus obtained [7] correspond to separation of the high and low frequencies, as shown here, we may conclude that the matrix C takes charge of the mixing between the two normal modes in the actual case. (Some properties of the matrix C relevant to this context have been given earlier [8, 9].) The validity and usefulness of Eqs. (5) and (6) have already been established [7] by considering several examples.

In the third order vibrational problems, where ω_1 is well spaced from ω_2 and ω_3, separation of the high frequency would yield

$$\begin{vmatrix} F_{22} - G_{22}^{-1} \Lambda_2 & F_{23} - G_{23}^{-1} \\ F_{23} - G_{23}^{-1} & F_{33} - G_{33}^{-1} \Lambda_3 \end{vmatrix} = 0 . \tag{7}$$

Separation of high frequency ω_2 in the case of Eq. (7) would, in turn, yield [3]

$$F_{33} = G_{33}^{-1} \Lambda_3 . \tag{8}$$

In a similar way, subsequent separations of low frequencies would yield

$$\begin{vmatrix} G_{11} F_{11} - \Lambda_1 & G_{12} F_{12} \\ G_{12} F_{12} & G_{22} F_{22} - \Lambda_2 \end{vmatrix} = 0 \tag{9}$$

and

$$G_{11} F_{11} = \Lambda_1 \tag{10}$$

in turn. The conditions of invariance of F_{ij} elements can now be evoked upon Eqs. (10) and (8) to get

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ratios of isotopic frequencies as

$$\omega_1/\omega_1{}^* = (G_{11}/G_{11}^*)^{1/2} \tag{11}$$

and

$$\omega_3/\omega_3{}^* = (G_{33}^{*-1}/G_{33}^{-1})^{1/2}\,. \tag{12}$$

Alongwith the product rule [1], we can now get the remaining ratio as

$$\frac{\omega_2}{\omega_2{}^*} = \left(\frac{|G|}{|G^*|}\,\frac{G_{11}^*}{G_{11}}\,\frac{G_{33}^{-1}}{G_{33}^{*-1}}\right)^{1/2}. \tag{13}$$

An illustration of the applicability of the present approach is given in Table 1 where the frequency ratios in the case of isotopic substitution H → D in Methyl fluoride are evaluated using Eqs. (11), (12) and (13) and are compared with the experimental results [10]. It may be noted that the calculated ratios bear better comparison with those corresponding to the harmonic frequencies (ω_i) rather than the observed ones (ν_i) requiring anharmonicity correction.

The Eqs. (11), (12) and (13) warrant large separation between the three frequencies. The spacings between the three frequencies are [10] around 1600 cm^{-1} ($\omega_1 - \omega_2$) and 350 cm^{-1} ($\omega_3 - \omega_4$) for CH_3F and 1100 cm^{-1} ($\omega_1{}^* - \omega_2{}^*$) and 160 cm^{-1} ($\omega_2{}^* - \omega_3{}^*$) for CD_3F for both the vibrational species A and E. There are many examples in literature where three frequencies contained in a vibrational species are reasonably well separated as in the present example. It may be noted that even the ratios $\omega_2/\omega_2{}^*$ and $\omega_3/\omega_3{}^*$ in Table 1, compare tolerably well with the actual values for both the vibrational species, even though the spacing between the two low frequencies is much smaller than their spacing with the high frequency. In this context, it is worthwhile to note that the Eqs. (8) and (10) emerging from the HLFS method contain the Λ_i elements, and evaluation of the frequency ratios in the next step involves getting the square root of the kinetic energy matrix elements which, however, brings in considerable reduction in the disparity between the calculated and actual values.

Table 1. Frequency ratios for Methyl fluoride due to H → D isotopic substitution.

Vibrational species	i	Frequency ratio		
		Present method	From reported frequencies [10]	
		($\omega/\omega_i{}^*$)	harmonic ($\omega_i/\omega_i{}^*$)	anharmonic ($\nu_i/\nu_i{}^*$)
A	1	1.396	1.398	1.389
	2	1.301	1.293	1.289
	3	1.053	1.062	1.040
E	1	1.347	1.347	1.331
	2	1.374	1.379	1.369
	3	1.311	1.317	1.309

The excellent agreement of the calculated and experimental value in the case of $\omega_1/\omega_1{}^*$, in the table, indicates that separation of the two lower frequencies is preferable to separation of the two higher frequencies. This, in fact, is also very evident from the spacing between the vibration frequencies obtained experimentally. Conversely, from a look at the relative spacing between the different frequencies in a vibrational species, one can make a reasonable guess as to which of the frequency ratios would be calculated with better accuracy. In cases, where values of $\omega_i/\omega_i{}^*$ terms calculated are expected to be of high accuracy, the anharmonicity correction α_i can be directly evaluated using the equation [11]

$$\alpha_i = [(\nu_i/\nu_i{}^*) - (\omega_i/\omega_i{}^*)]/[1 - (\nu_i/\nu_i{}^*)] \tag{14}$$

and the harmonic frequencies ω_i and $\omega_i{}^*$ evaluated [12] employing Dennison's relations $\omega_i = \nu_i(1 + \alpha_i)$ and $\omega_i{}^* = \nu_i{}^*[1 + \alpha_i(\omega_i{}^*/\omega_i)]$.

[1] E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill; New York 1955.

[2] B. C. Crawford and J. T. Edsall, J. Chem. Phys. **7**, 223 (1939).

[3] A. Müller, N. Mohan, K. H. Schmidt, and I. W. Levin, Chem. Phys. Letters **15**, 127 (1972).

[4] K. H. Schmidt and A. Müller, J. Mol. Structure **18**, 135 (1973).

[5] A. Müller and S. N. Rai, J. Mol. Structure **24**, 59 (1975).

[6] A. J. P. Alix, H. H. Eysel, B. Jordanov, R. Kebabcioglu, N. Mohan, and A. Müller, J. Mol. Structure **27**, 1 (1975).

[7] T. R. Ananthakrishnan and G. Aruldhas, J. Mol. Structure **23**, 316 (1974).

[8] T. R. Ananthakrishnan, Z. Naturforsch. **32a**, 337 (1977).

[9] T. R. Ananthakrishnan, Acta Chim. Acad. Sci. Hung. **92**, 395 (1977).

[10] J. Aldous and I. M. Mills, Spectrochim. Acta **18**, 1073 (1962).

[11] T. R. Ananthakrishnan and G. Aruldhas, Aust. J. Chem. **28**, 2727 (1975).

[12] D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).