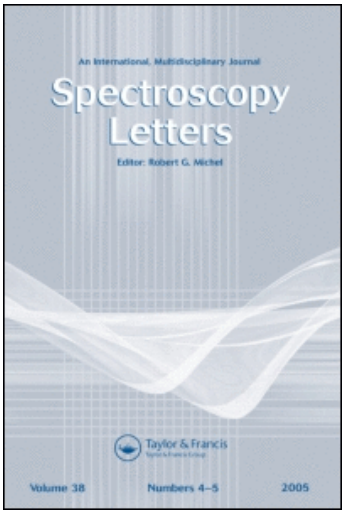

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An Original Approach to the Calculation of Mean-Square Amplitudes

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AN ORIGINAL APPROACH TO THE CALCULATION OF MEAN-SQUARE AMPLITUDES

Keywords: Mean-square amplitude matrix, Σ matrix

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ABSTRACT

A new method of calculating the Σ matrix is based on a polynomial fitted point-wise to the function $\coth(hc\,\omega_k/2kT)$. Equations in closed form are deduced for the two-dimensional case and for T = 0 in particular. The method is applied to derive in closed form the mean-square amplitude at absolute zero for the bond distance in a water-type molecule.

Many properties of the mean-square amplitude matrix,[1-3] Σ, in the theory of molecular vibrations[4] have been described. Most of them are treated in the cited book,[3] and more recent publications[5-14] may be consulted

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for further development. In the present work an original method of computing the Σ matrix is given, which is closely connected with the various expansions of Σ into series.[2,3,7,11,12,15] The basic expansion[3,15] is derived from the power series of $x \coth(x)$. The approach has the deficiency of not being applicable to cases corresponding to $|x| > \pi$, for which the series diverges. This occurs for medium (and high) frequency regions and moderate (and low) temperatures. Other approaches[2,16,17] originate from empirical functions trying to fit $\coth(x)$ within certain ranges of x. All these approaches have been critically reviewed by Ra.[11] He made it clear that a point-wise fit to $\coth(x)$ for the x values corresponding to the actual normal frequencies and a given temperature is essential, rather than an over-all fit.

The present method is based on a polynomial of the form

$$f(\omega) = \sum_k a_k \left(\frac{hc\,\omega_k}{2kT} \right)^n , \qquad (1)$$

where $n = -1, 1, 3, 5, \ldots$ (occasionally $-3, -5, \ldots$) and has as many terms as the number of normal frequencies (ω_k). The coefficients a_k should be determined in such a way that

$$f(\omega_k) = \coth \frac{hc\,\omega_k}{2kT} \qquad (2)$$

for a given absolute temperature, T. In these equations h is Planck's constant, c the velocity of light, and k the Boltzmann constant.

In the following we are restricting the exposition to the case of a two-dimensional Σ matrix, which seems to be sensible for several reasons. (1) It gives a good illustration of the method. (2) The method is hardly

believed to be of practical importance for large molecules with Σ-matrix blocks considerably greater than 2×2. (3) The two-dimensional case is especially interesting inasmuch as it leads to closed expressions for the Σ elements.

The a_1 and a_2 coefficients are found from the linear set of equations:

$$\coth \frac{hc\omega_k}{2kT} = \frac{2kT}{hc\omega_k} a_1 + \frac{hc\omega_k}{2kT} a_2 \; ; \; k = 1, 2. \qquad (3)$$

The frequency parameters

$$\delta_k = \frac{h}{8\pi^2 c \omega_k} \coth \frac{hc\omega_k}{2kT} \qquad (4)$$

may consequently be written

$$\delta_k = \frac{kT}{\lambda_k} a_1 + \frac{h^2}{16\pi^2 kT} a_2 \; , \qquad (5)$$

where

$$\lambda_k = 4\pi^2 c^2 \omega_k^2 \qquad (6)$$

Hence for the diagonal matrix $\boldsymbol{\delta}$ one obtains:

$$\boldsymbol{\delta} = kT \, a_1 \boldsymbol{\lambda}^{-1} + \frac{h^2}{16\pi^2 kT} a_2 \mathbf{E} \; , \qquad (7)$$

and for the mean-square amplitude matrix ($\boldsymbol{\Sigma} = \mathbf{L} \boldsymbol{\delta} \tilde{\mathbf{L}}$):

$$\boldsymbol{\Sigma} = kT \, a_1 \mathbf{N} + \frac{h^2}{16\pi^2 kT} a_2 \mathbf{G} \; . \qquad (8)$$

Here $\mathbf{N}$ is the compliance matrix, and $\mathbf{G}$ is the familiar inverse kinetic energy matrix.[3,4] Finally on inserting the solutions for a_1 and a_2 obtained from Eq. (3) the formula (8) reads:

$$\Sigma = \frac{hc\,\omega_1\,\omega_2}{2(\omega_1^2 - \omega_2^2)}\left[\omega_1 \coth\frac{hc\,\omega_2}{2kT} - \omega_2 \coth\frac{hc\,\omega_1}{2kT}\right]\mathbf{N} + \frac{h}{8\pi^2 c(\omega_1^2 - \omega_2^2)}\left[\omega_1 \coth\frac{hc\,\omega_1}{2kT} - \omega_2 \coth\frac{hc\,\omega_2}{2kT}\right]\mathbf{G}. \tag{9}$$

This equation becomes considerably simplified for $T = 0$. On inserting unity for the hyperbolic-cotangent function it is deduced:

$$\Sigma(0) = \frac{h}{\omega_1 + \omega_2}\left[\frac{c\,\omega_1\,\omega_2}{2}\mathbf{N} + \frac{1}{8\pi^2 c}\mathbf{G}\right]. \tag{10}$$

The intermediate steps (3)-(8) do not permit $T = 0$. We should therefore check the validity of Eq. (10), for instance in the following way. On inserting $\mathbf{N} = \mathbf{L}\boldsymbol{\lambda}^{-1}\tilde{\mathbf{L}}$ and $\mathbf{G} = \mathbf{L}\tilde{\mathbf{L}}$ it is obtained

$$\Sigma(0) = \mathbf{L}\left[\frac{hc\,\omega_1\,\omega_2}{2(\omega_1 + \omega_2)}\boldsymbol{\lambda}^{-1} + \frac{h}{8\pi^2 c(\omega_1 + \omega_2)}\mathbf{E}\right]\tilde{\mathbf{L}}, \tag{11}$$

in which the nonvanishing elements of the diagonal matrix $\boldsymbol{\lambda}^{-1}$ are $1/(4\pi^2 c^2 \omega_1^2)$ and $1/(4\pi^2 c^2 \omega_2^2)$ in accordance with Eq. (6). Hence it is easily verified that Eq. (11) is equivalent to $\Sigma(0) = \mathbf{L}\,\boldsymbol{\delta}(0)\tilde{\mathbf{L}}$, where the nonvanishing elements of $\boldsymbol{\delta}(0)$ are

$$\delta_k(0) = \frac{h}{8\pi^2 c\,\omega_k} \tag{12}$$

for $k = 1, 2$.

The present approach may be used to deduce mean-square amplitudes of vibration for simple molecules in closed form. Here we give the mean-square amplitude at T = 0 for the X-Y (bond) atom pair in a bent symmetrical XY_2 (water-type) model:

$$l^2_{X-Y}(0) = \frac{hc\,\omega_1\,\omega_2}{4(\omega_1+\omega_2)}\,N_{11}(A_1) + \frac{h}{16\pi^2 c}\left(\frac{2\mu_X\cos^2 A+\mu_Y}{\omega_1+\omega_2} + \frac{2\mu_X\sin^2 A+\mu_Y}{\omega_3}\right). \quad (13)$$

Here μ_X and μ_Y denote as usual the inverse masses of the atoms X and Y, respectively, and 2A is the equilibrium YXY angle.

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