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Abstract

Full Text

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ON THE CALCULATION OF THE SPECTROSCOPIC MASSES OF HYDROGEN AND DEUTERIUM

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This article reports the derivation of an "equivalence equation," which offers interesting possibilities for the development of the method of spectroscopic masses ([1–3]).

The anharmonicity of the vibrations of the atoms of hydrogen and deuterium within the framework of the nonquantum theory of molecular vibrations can be taken into account in two ways: a) by the zero-frequency method proposed in ([4]), and b) by the spectroscopic-mass method proposed in ([1]). In case a), the correction for anharmonicity is contained in the value of the fundamental frequency ω (the zero frequency), and the secular equation (34) of ([5]) may be written in the form*

$$|U_{ij}\omega^2 - B_{ij}| = 0, \tag{1}$$

where B_{ij} contain the actual masses of the atoms. When b) is applied, the secular equation (1) should be rewritten in the form

$$|U_{ij}\nu^2 - \overline{B}_{ij}| = 0, \tag{2}$$

where ν is the fundamental frequency**, and the anharmonicity is taken into account by introducing the spectroscopic mass of hydrogen $\overline{m}$ instead of the actual mass of hydrogen m into the expressions $\overline{B}_{ij}$.

Let us consider two isotopic molecules of the same symmetry, RH_n and RD_n, where R is a group of atoms containing neither hydrogen nor deuterium. Starting from equations (1) and (2), we write the expressions for the squares of the partial frequencies ([7]) for one of the hydrogen vibrations of the molecule RH_n

$$\tilde{\omega}_i^2 = \frac{B_i}{U_i}, \tag{3}$$

$$\tilde{\nu}_i^2 = \frac{\overline{B}_i}{U_i}, \tag{4}$$

where $B_i, \overline{B}_i, U_i$ are the diagonal elements of the corresponding matrices; $\tilde{\nu}_i$ is the partial fundamental frequency, and $\tilde{\omega}_i$ is the partial zero frequency.

We express the influence coefficient U_i from (3) and (4) and impose the equivalence requirement on the resulting equalities

$$U_i = \frac{\overline{B}_i}{\tilde{\nu}_i^2} = \frac{B_i}{\tilde{\omega}_i^2},$$

which gives, for the original modification,

$$\overline{B}_i \tilde{\omega}_i^2 = B_i \tilde{\nu}_i^2. \tag{5}$$

* The choice of the form of the secular equation is due to the known invariance property ([2,3]) of the elements of the matrices of kinetic coefficients (mobility coefficients) $\|B_{ij}\|$ and of the matrices of influence coefficients $\|U_{ij}\|$. Reduction by symmetry is assumed to have been performed.

** The terms "zero"and "fundamental"frequencies are used in the sense described, for example, in ([6]).

For the corresponding vibration of the molecule RD_n one can write, by analogy,

$$\overline{B}_i' \omega_i'^2 = B_i' \tilde{\nu}_i'^2, \tag{6}$$

where B_i' and $\overline{B}_i'$ contain the actual (m') and spectroscopic ($\overline{m}'$) mass of deuterium, respectively.

The relation between the zero and fundamental partial frequencies can be represented in the form

$$\begin{aligned} \tilde{\nu}_i &= \tilde{\omega}_i(1-\alpha_i), \\ \tilde{\nu}_i' &= \tilde{\omega}_i'(1-\alpha_i'), \end{aligned} \tag{7}$$

where α_i and α_i' are anharmonicity corrections for the partial frequencies. Then expressions (5) and (6) take the form

$$\begin{aligned} \overline{B}_i &= B_i(1-\alpha_i)^2, \\ \overline{B}_i' &= B_i'(1-\alpha_i')^2. \end{aligned} \tag{8}$$

It is known that the methods proposed in ([1,4]) are based on the use of the following hypothesis:

$$\frac{x_i'}{x_i} = \frac{\omega_i'}{\omega_i}, \tag{9}$$

where x_i and x_i' are anharmonicity corrections for the natural frequencies, analogous in meaning (see, for example, ([6])) to α_i and α_i'. Equality (9) is rigorous for diatomic molecules; it is assumed ([1,4]) that it is approximately satisfied for polyatomic molecules. We shall slightly change the notation of the hypothesis, namely, let

$$\frac{\alpha_i'}{\alpha_i} = \frac{\tilde{\omega}_i'}{\tilde{\omega}_i}. \tag{10}$$

Now, on the basis of (3) and the analogous equality for RD_n, one may write

$$\frac{\tilde{\omega}_i'}{\tilde{\omega}_i} = \left(\frac{B_i'}{B_i}\right)^{1/2}. \tag{11}$$

Next, eliminating α_i and α_i' from (8) by means of (10) and (11), we obtain the equality

$$B_i'(\sqrt{B_i} - \sqrt{\overline{B}_i}) = B_i(\sqrt{B_i'} - \sqrt{\overline{B}_i'}), \tag{12}$$

which we shall call the equivalence equation.

Equality (12) makes it possible to separate the problem of calculating spectroscopic masses from the problem of calculating force constants (cf. ([3])). The use of the quantities $\overline{m}$ and $\overline{m}'$, calculated on the basis of the equivalence equation, instead of the standard spectroscopic masses ([1]), improves the agreement between experimental and calculated frequencies, as was shown for the example of tetrahedral hydrides and their deutero derivatives ([8]). In addition, in ([8]) it was shown that the use of nonstandard $\overline{m}$ and $\overline{m}'$ makes it possible to avoid the use of overdetermined systems of equations in calculating force constants, which considerably simplifies the calculations (cf. ([2,3])).

At present there exist some experimental data that allow a direct verification of hypothesis (10). Thus, in ([9]), on the basis of a complete analysis of the spectra, sufficiently reliable values of the natural fundamental and zero frequencies of the molecules H_2O and D_2O have been determined.

From these data, by known methods ([2,3]), one can calculate the influence coefficients and also, applying the method described in ([10]), determine the "experimental" values of the spectroscopic masses. Further, from formulas (3) and (4) one can

find the partial zero and fundamental frequencies and, using formulas (7), calculate the anharmonicity corrections for the partial frequencies of the molecules indicated above. The ratio of these corrections is given in Table 1, where, for comparison, the ratios of the anharmonicity corrections (which are calculated by formulas (1) and (2) from (6)) for the proper frequencies are also given.

Table 1.

Character of vibration	Hypothesis (9) $\frac{x_i'}{x_i} \approx \frac{\omega_i'}{\omega_i}$	Hypothesis (9) $\frac{x_i'}{x_i} \approx \frac{\omega_i'}{\omega_i}$	Hypothesis (10) $\frac{\alpha_i'}{\alpha_i} \approx \frac{\tilde{\omega}_i'}{\omega_i}$	Hypothesis (10) $\frac{\alpha_i'}{\alpha_i} \approx \frac{\tilde{\omega}_i'}{\omega_i}$
Valence symmetric A_1	0.729	0.721	0.728	0.723
Valence symmetric B_1	0.736	0.733	0.736	0.733
Deformation symmetric A_1	0.712	0.732	0.689	0.733

It is evident from Table 1 that writing the hypothesis in the form (9) and (10) is equivalent, since the discrepancies between the right- and left-hand parts begin in one and the same order. Unfortunately, for the remaining triatomic nonlinear symmetric hydrides and deuterides, determination of "experimental" spectroscopic masses is impossible, since experimental values of the zero frequencies of D_2S, H_2Se, and D_2Se are lacking. For more complex objects, the quantities ω are, as a rule, determined with the use of additional assumptions of type (9).

In ([10]) it was shown that the force constants of pyramidal hydrides, calculated by applying method (a) and hypothesis (10), agree, within the possible errors, with the force constants determined on the basis of the method of nonstandard spectroscopic masses and hypothesis (9). This once again indicates that writing the hypothesis in the forms (9) and (10) is equivalent.

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Note: Figure translations are in progress. See original paper for figures.