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Abstract

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ALLOWANCE FOR ANHARMONICITY IN MOLECULAR VIBRATIONS USING GENERAL FORMULAS FOR TRANSITION FREQUENCIES BY SUCCESSIVE APPROXIMATIONS

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The general formula for the vibrational energy levels of a polyatomic molecule, first obtained by quantum-mechanical methods in (^{1}) (see also (^{2})), has the form

$$(E_v/hc) = (E_0/hc) + \sum_s \omega_s (v_s + g_s/2) + \\ + \sum_{ss'} X_{ss'} (v_s + g_s/2)(v_{s'} + g_{s'}/2) + \sum_{t \le t'} X_{l_t l_{t'}} l_t l_{t'}, \tag{1}$$

where E_0/hc is a constant quantity, which is usually omitted, since only level differences are of interest; ω_s are zero-order frequencies; v_s are vibrational quantum numbers; g_s is a factor taking into account the degree of degeneracy of ω_s; l_t is a quantum number taking, for degenerate zero-order levels, the values $v_t, v_t - 2, \dots, 1$ or 0. If vibrational-rotational interactions are neglected, then

$$X_{ss} = \frac{1}{4}\{6k_{ssss} - 15(k^2_{sss}/\omega_s) - \sum_{s'} (k^2_{sss'}/\omega_{s'})(8\omega_s^2 - 3\omega_{s'}^2)/(4\omega_s^2 - \omega_{s'}^2)\},$$

$$X_{ss'} = \frac{1}{2}\{k_{sss's'} - 6(k_{sss}k_{ss's'}/\omega_s) - 4k^2_{sss'}[\omega_s/(4\omega_s^2 - \omega_{s'}^2)] - \\ - \sum_{s''} (k_{sss''}k_{s's's''}/\omega_{s''}) - \sum_{s''} (k_{ss's''}/2)\omega_{s''}(\omega_{s''}^2 - \omega_s^2 - \omega_{s'}^2)/[(\omega_s + \omega_{s'} + \omega_{s''}) \times \\ \times (\omega_s + \omega_{s'} - \omega_{s''})(\omega_s - \omega_{s'} + \omega_{s''})(\omega_s - \omega_{s'} - \omega_{s''})]\}, \tag{2}$$

$$X_{l_t l_t} = -\frac{1}{4}\{2k_{tttt} + \sum_{s'} k_{tts'}^2 [\omega_{s'}/(4\omega_t^2 - \omega_{s'}^2)]\},$$

$$X_{l_t X_{l_{t'}}} = 0,$$

where $k_{sss'}$ and $k_{sss's''}$ are force constants in the anharmonic part of the potential energy (in terms of third- and fourth-degree terms), expressed in normal coordinates; t denotes values of s for which the vibrations are twice degenerate.

The usually used method for determining the vibrational constants ω_s and $X_{ss'}$ (see, for example, ([3,4])) by means of (1) has, in our opinion, the following shortcomings: a) to determine the quadratic force constants in natural coordinates (or symmetry coordinates), it is necessary to know in advance the transformation from natural coordinates (symmetry coordinates) to normal ones; b) to determine all vibrational constants ω_s and $X_{ss'}$, knowledge of a considerable number of experimental transition frequencies is required; if the number of such frequencies is limited, then, for an approximate solution of the problem, it is necessary to introduce certain relations between the $X_{ss'}$ (or between the $k_{sss'}$), which leads to difficulties in choosing such relations.

The purpose of this article is to present the results of work aimed at overcoming the above-mentioned difficulties in the approximate solution of the problem of allowing for anharmonicity in molecular vibrations. In doing so, we shall use the expression for the potential energy in natural coordinates (or symmetry coordinates) q^i in the following form:

$$V = \frac{1}{2}\sum_{ij} F_{ij} q^i q^j + \sum_{ijk} F_{ijk} q^i q^j q^k + \sum_{ijkl} F_{ijkl} q^i q^j q^k q^l. \tag{3}$$

Then the following relations hold:

$$\begin{aligned}
k_{sss} &= 2.10865 \cdot 10^{-2} (1/\omega_s^3)^{1/2} \sum_{ijk} x_s^i x_s^j x_s^k F_{ijk}, \\
k_{sss'} &= 6.32595 \cdot 10^{-2} (1/\omega_s^2 \omega_{s'})^{1/2} \sum_{ijk} x_s^i x_s^j x_{s'}^k F_{ijk}, \\
k_{ss's''} &= 12.65190 \cdot 10^{-2} (1/\omega_s \omega_{s'} \omega_{s''})^{1/2} \sum_{ijk} x_s^i x_{s'}^j x_{s''}^k F_{ijk}, \\
k_{ssss} &= 1.57766 \cdot 10^{-3} (1/\omega_s^2) \sum_{ijkl} x_s^i x_s^j x_s^k x_s^l F_{ijkl}, \\
k_{sss's'} &= 9.46596 \cdot 10^{-3} (1/\omega_s \omega_{s'}) \sum_{ijkl} x_s^i x_s^j x_{s'}^k x_{s'}^l F_{ijkl}.
\end{aligned} \tag{4}$$

Here x_s^i are forms normalized according to

$$\sum_{ij} T_{ij} x_s^j x_s^j = 1 \quad \text{or} \quad \sum_{ij} F_{ij} x_s^i x_s^j = \lambda_s, \qquad \lambda_s = (2\pi c)^2 \omega_s^2, \tag{5}$$

where T_{ij} are the coefficients of inertia in natural coordinates (or symmetry coordinates). In this case, the quantities used above are expressed in the following units:

$$\begin{gathered}
(2\pi c)^2 - 10^{22}\ \text{cm}^2/\text{sec}^2, \qquad F_{ij} - 10^5\ \text{dyne/cm}, \qquad k_{ss's''} - 10^3\ \text{cm}^{-1}, \\
\lambda_s - 10^{28}\ \text{sec}^{-2}, \qquad F_{ijk} - 10^{13}\ \text{dyne/cm}^2, \qquad k_{sss's''} - 10^3\ \text{cm}^{-1}, \\
x_s^i - 10^{11}\sqrt{10}\ \text{g}^{-1/2}, \qquad F_{ijkl} - 10^{21}\ \text{dyne/cm}^3, \qquad \omega_s - 10^3\ \text{cm}^{-1}.
\end{gathered} \tag{6}$$

The calculation procedure we propose is based on the following fundamental propositions:

1) the calculation is carried out by the method of successive approximations, which makes it possible to eliminate shortcoming a), since the necessary transformation from natural coordinates or symmetry coordinates to normal coordinates (determined by the normalized forms x_s^i) is obtained in the course of the successive approximations;

2) the main role in the process of successive approximations is assigned to the force constants in natural coordinates (harmonic and anharmonic) indicated in (3); this makes it possible partially to eliminate shortcoming b), since, in our opinion, there is more basis for introducing relations between anharmonic force constants in natural coordinates than in normal ones. In addition, this makes it possible simultaneously to use the transition frequencies of isotopic modifications of the molecule, since it is assumed that their force fields are identical.

The scheme of the proposed procedure is now as follows.

1) The quadratic force constants of the zeroth approximation are determined. This may be done, for example, by using the fundamental frequencies of isotopic modifications of molecules according to the commonly applied procedure. Other methods are also possible.

2) From the quadratic force constants of the zeroth approximation, the zero frequencies and the corresponding forms of the zeroth approximation are determined. The latter are normalized by one of relations (5); here ω_s is the zero frequency of the approximation.

3) Relations are introduced between F_{ijk} and F_{ijkl}, in such a way that the total number of unknowns in the final equations (which will be discussed below) does not exceed the number of equations.

4) All the quantities and expressions obtained above are substituted into (4), which, in turn, are substituted into (2). In both (4) and (2), ω_s are the zero frequencies of the zero approximation indicated in the second point of the scheme.

Table 1

Quadratic force constants
(10^5 dyn/cm)

K_q	K_α	h	a	Source
8.4580	0.7713	-0.075	0.328	Our calculation
8.4537	0.7608	-0.101	0.230	(^{3})

Table 2

Zero frequencies (cm^{-1})

H_2O ω_1	H_2O ω_2	H_2O ω_3	D_2O ω_1'	D_2O ω_2'	D_2O ω_3'	Source
3840	1646	3938	2766	1205	2885	Our calculation
3832	1648	3942	2764	1206	2889	(^{3})

5) According to $\nu = (E_\nu - E_{\nu'})/hc$, from (1) one finds expressions for those transition frequencies for which experimental values are known. Substitution into them of the expressions for $X_{ss'}$ obtained above leads to equations that we call final equations.

Table 3

Some overtones and combination frequencies

	(200)	(020)	(002)	(110)	(101)	(011)	Source
H_2O	7212	3148	7429	5260	7240	5323	Our calculation
H_2O	7201	3152	7445	5235	7250	5331	(^{4})
D_2O	5290	2333	5532	3858	5369	3952	Our calculation
D_2O	5292				5374	3956	(^{3})

Further solution is possible in two variants:

a) In the final equations the unknowns are ω_s, obtained from (1), and F_{ijk} and F_{ijkl}, left as unknowns. If, in doing this, the transition frequencies of different isotopic modifications of the molecule are used, then product rules may be added to the final equations. Solving all these equations gives zero frequencies of the first approximation, from which the quadratic force constants of the first approximation are found, and the calculation is repeated until complete agreement is obtained.

6) In the final equations, the following expressions are substituted for the corrections to the zero frequencies:

$$\Delta\omega_s = [{}^1/_2\,(2\pi c)^2\omega_s] \sum_{ij} \Delta F_{ij} x_s^i x_s^j \tag{7}$$

(here ω_s in the denominator is the zero frequency of the zero approximation, and x_s^i are the normalized forms of the zero approximation). Now, in the final equations, the unknowns are the corrections to the quadratic force constants ΔF_{ij} and the previously selected F_{ijk} and F_{ijkl}. Solving these equations leads to the first approximation of the quadratic force constants, which makes it possible to repeat the calculation.

It is quite obvious that the method proposed by us makes it possible to obtain a result that is the more accurate, the greater the number of experimental transition frequencies that can be used in the calculation and the closer to the true values the chosen relations between F_{ijk} and between F_{ijkl} are.

As an illustration, we present the results of a calculation for a pair of molecules H_2O and D_2O, carried out according to variant a). As the zero approximation of the zero frequencies, the fundamental frequencies for these molecules (cm^{-1}) were taken from ([3]): $\nu_1 = 3656.65$; $\nu_2 = 1594.59$; $\nu_3 = 3755.79$; $\nu_1' = 2671.46$; $\nu_2' = 1178.33$; $\nu_3' = 2788.05$. The overtones and combination frequencies were not used as initial data for the calculation.

The following relations were adopted between the anharmonic force constants in natural coordinates:

$$F_{111} = F_{222}, \qquad F_{1111} = F_{2222}\text{—by virtue of symmetry;}$$

$$F_{123} = F_{333} = 0, \qquad \text{the remaining } F_{ijk} = 0.05F_{111}, \text{ the remaining } F_{ijkl} = 0 \tag{8}$$

(indices 1 and 2 refer to changes in bond lengths, and index 3 to a change in the valence angle).

After 4 approximations the results given in Tables 1-3 were obtained; for comparison, data taken from ([3],[4]) are also indicated.

It is seen that the calculation results may be regarded as satisfactory, despite the small amount of initial data and the rather simple assumptions (8).

In conclusion, we note that one can show the connection between the method proposed in the present communication and the method of effective parameters described in (^{5}).

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