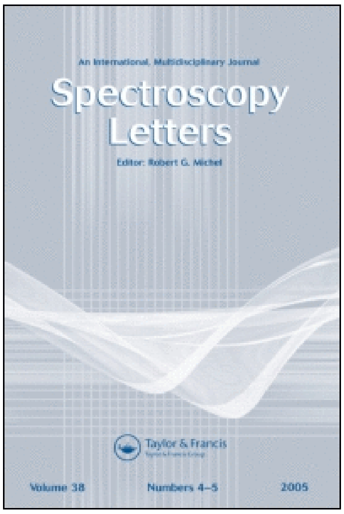

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On the Application of the Method of Moments to the Investigation of Molecular Structureless Electronic Spectra

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ON THE APPLICATION OF THE METHOD OF MOMENTS TO THE INVESTIGATION OF MOLECULAR STRUCTURELESS ELECTRONIC SPECTRA

Key words: Electronic spectrum, Optically active vibration, Vibrational progression, Central moment.

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INTRODUCTION

It is well known that in the course of an electronic transition a molecule undergoes a structural change usually along a single one of its normal coordinates /1-3/(the corresponding vibration is called optically active). This change is given by the dimensionless parameter X, defined as the shift of the equilibrium position of the relevant oscillator in the transition. Optically active vibrations are known in the theory of radiationless transitions as accepting modes (as they accept most of the electronic energy which is released in the transition). Knowledge of the relevant parameters X is of utmost importance for the correct calculation of radiationless transition rates /4,5/.

Optically active vibrations are prominent in molecular electronic absorption and emission spectra as they form progressions. Thus from structurally resolved spectra it is no special problem to determine the parameters X. However structural spectra of complex molecules are often not obtainable, especially in the particular conditions required. In the present letter we shall outline a procedure which makes possible the determination of the shift X of the optically active vibration in the electronic transition from structurally unresolved absorption or emission spectra, which are typical for polyatomic molecules.

Much attention in literature has also received the problem of the determination of the frequency ω_{00} of the zero electronic transition from continuous electronic spectral bands. The methods applied to this end have been discussed in /6/. Our procedure, described below, proves efficient in the determination of ω_{00} too.

THEORETICAL CONSIDERATIONS

The molecular model on which the derivation of the subsequent formulas is based was described in /7/

Here we shall only give the basic features. The molecular normal modes are classified into two groups : a high frequency (ω_0) vibration and shift parameter X_0 which (its progression) determines the general contour of the spectral band and a multitude of low frequency vibrations of equal frequency ω_1 ($\omega_1 = \omega_0/m$, m - integer) and shift parameters X_i. The latter vibrations are responsible for the broadening of the components of the progression of the vibration ω_0 . The superposition of those broadened components yields a structureless band, which is the object of our investigation.

Using the general formulas from /8/ for our special model we can write the folloing expression, describing the absorption coefficient

$$W_a(\omega) = W_0 \sum_{v_1, v_0 = -\infty}^{\infty} W_{v_0 v_1} \cdot \delta(\omega_{00} + \omega_0 v_0 + \omega_1 v_1 - \omega) \quad , \qquad (1)$$

where $W_{v_0 v_1} = \exp\left[-X_0^2 \cdot cth(mB) - a \cdot cth B\right] \times$

$$\times \exp\left[\frac{\hbar}{2kT}(v_0\omega_0 + v_1\omega_1)\right] \cdot I_{v_0}\left(\frac{X_0^2}{sh(mB)}\right) \cdot I_{v_1}\left(\frac{a}{sh B}\right) ,$$

$W_0 = const.$

Here I_ν - modified Bessel function; $a = \sum X_i^2$ (summation is over the group of low frequency modes);

$B = \hbar\omega_1/2kT$. The moments of the distribution (1) are given by the following formulas :

$$S_\ell = \omega_1 \sum_{p=-\infty}^{\infty} W_\alpha(p\omega_1)(p\omega_1)^\ell \qquad \text{- moments,}$$

$$M_\ell = S_\ell / S_0 \qquad \text{- normal moments,} \tag{2}$$

$$\bar{M}_\ell = \sum_{k=0}^{\ell} (-1)^k \binom{\ell}{k} \left(\frac{S_1}{S_0}\right)^k M_{\ell-k} \qquad \text{- central normal moments}$$

Using the expression for the generating function of the modified Bessel functions from (1) and (2) can be obtained following formulas for the first three moments of the distribution (1) :

$$M_1 = \omega_1 (m X_0^2 + \alpha) \quad ,$$

$$\bar{M}_2 = \omega_1^2 [m^2 X_0^2 \, cth(mB) + cth\, B] \, , \tag{3}$$

$$\bar{M}_3 = \omega_1^3 (m^3 X_0^2 + \alpha) \quad .$$

M_1 as calculated from (3) is given with respect to the zero electronic transition ω_{00} of the spectrum (1), while $\bar{M}_2$ and $\bar{M}_3$, being central moments, are given with respect to M_1. Formulas (3) can also be used for the description of emission spectra by just changing the signs of the first and third moments.

DISCUSSION

The values of the three moments (3) are enough to characterize the shape of the structureless spectral band ($\bar{M}_2$ and $\bar{M}_3$) and its spectral position (M_1). Using relations (3) is concluded that the spectrum is equally well characterized by the parameters X_0, a, m and M_1(when ω_0 and T are known). X_0 determines the overall width of the spectrum while a is characteristic of the widths of the components of the progression in ω_0 . Thus the spectrum is structureless only when a exceeds certain minimum value, otherwise the spectrum reveals structure.

It was shown in /7/ that the shape of the spectrum W_a does not depend on the values of the parameters a and m(or $\omega_1 = \omega_0/m$) separately but varies only with the ratio a/m. Using this fact we take the limit $m \to \infty$ in expressions (3) and define $\alpha = \lim_{m\to\infty}(a/m)$. We obtain :

$$M_1 = \omega_0 (X_0^2 + \alpha) , \qquad (4a)$$

$$\bar{M}_2 = X_0^2 \cdot \omega_0^2 \cdot \mathrm{cth}\, \beta + 2 \cdot \omega_0 \, \alpha \, kT , \qquad (4b)$$

$$\bar{M}_3 = \omega_0^3 X_0^2 \qquad (4c)$$

Formulas (4) are the principal result of this work. They do not contain either ω_1 or m which characterize the group of low frequency vibrations. Thus we may argue that the relations (4) are applicable to a more general class of spectra than originally considered, namely those, for which the broadening of the components of the high frequency progression is not due to low frequency vibrations but to some other mechanism /6,9/.

Now let us describe the procedure by which spectroscopic information may be gained from a given structureless (continuous) spectrum using formulas (4). We note that the described method does not yield the values of T and ω_0 (T is the temperature at which the spectrum is recorded) so that their values have to be known. From the experimental band are obtained (by graphical integration) the values of the moments M_1, $\bar{M}_2$ and $\bar{M}_3$ and the last two are then substituted in eqs.(4 b,c); from eq.(4c) is then determined X_0; with X_0 known from eq.(4b) is obtained α ; knowing $\dot{X}_0$ and α from eq.(4a) is determined the value of the first moment which is then subtracted from the value of M_1, determined from the experimental curve, thus obtaining the value of the frequency ω_{00} of the zero electronic transition.

As an illustration of the procedure described above, let us consider the spectrum of 3-acetamidophtalymid at T = 200 K published in /10/. In the calculations we use the value $\omega_0 = 1050$ cm^{-1}. The obtained results are shown in first three columns of the following table :

TABLE

X_0	α	ω_{00}/cm^{-1}/	ω'_{00}/cm^{-1}/
1.33	1.27	27122	27105

In the last column of the table is displayed the value of ω_{00}, obtained by the method of crossing of the fluorescence and absorption spectral bands. It is seen that the determined value for ω_{00} is in good aggreement with that obtained by the procedure outlined above.

In conclusion we note that the techniques described above for the extraction of spectroscopic information continuous electronic spectral bands can be readily generalized to spectra, where more than one high frequency vibration is involved. In such cases higher order moments will have to be introduced in the description.

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