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Abstract

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ACCOUNTING FOR THE VIBRATIONAL STRUCTURE OF THE LEVELS OF ELECTRONIC EXCITATION OF MOLECULES IN THE QUANTUM THEORY OF LIGHT SCATTERING

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1. In work (1) it was shown that the classical theory is applicable for describing the spectra of combination scattering (c. s.) over the entire range of exciting frequencies only at very large damping constants γ_{ev} of the corresponding electron-vibrational oscillators. At smaller γ_{ev}, decisive importance is acquired by taking into account the vibrational structure of the excitation level, which can therefore be done only in the quantum theory.

A central place in the quantum theory of light scattering by molecules (2) is occupied by the analysis of the distribution of the contributions of vibrational sublevels to the matrix elements of the polarizability, which determine the intensities of lines in the spectrum. We shall call the contribution of the v-th sublevel of the electronic excitation level under consideration to the matrix element of the polarizability a^{mn} (corresponding to the vibrational transition $m \to n$) the quantity

$$A_v^{mn} = F(\nu, v)\langle v|M_{0e}(r)|m\rangle\langle v|M_{0e}(r)|n\rangle, \tag{1}$$

where

$$F(\nu, v) = \frac{2\nu_{ev} - \nu_k + 2i\gamma_{ev}}{\nu_{ev}^2 - \nu^2 - \gamma_{ev}^2 + 2i\gamma_{ev}\nu_{ev} - \nu_k(\nu_{ev} - \nu - i\gamma_{ev})}$$

is the frequency factor (ν_{ev} is the transition frequency to the v-th sublevel of the excited state from the m-th sublevel of the ground state; γ_{ev} is the width of the v-th sublevel; ν_k is the change in the photon frequency upon scattering; ν is the frequency of the exciting light; $M_{0e}(r)$ is the matrix element of the transition moment, constructed from the electronic wave functions; r is the internuclear distance). Obviously,

$$a^{mn} = \frac{1}{hc} \sum_{v} A_v^{mn}. \tag{2}$$

Relation (2) can be obtained from the Kramers—Heisenberg formula if the complete wave function of a (diatomic) molecule is considered in the adiabatic approximation. For simplicity we restrict ourselves to a single excitation level and consider only the diagonal elements of the polarizability tensor.*

2. Expression (1) is considerably simplified in the Condon approximation, which assumes that $M_{0e}(r) = \text{const}$. In this case $A_v^{mn} = F(\nu, v) M_{0e}^2 B_v^{mn} = F(\nu, v) M_{0e}^2 (v, m)(v, n)$, where for the overlap integrals of the vibrational wave functions the notation $(v, m) = \langle v | 1 | m \rangle$ has been adopted.

The overlap integrals are most simply calculated by using the wave functions of the harmonic oscillator, especially in the particular case when the potential curves of the ground and excited states have the same shape but are displaced relative to one another one another. Using a method close to that described by Rhone (3), one can show that in this case*

$$\begin{aligned}
B_v^{00} &= [(v,0)]^2 = \frac{1}{v!} \exp\left(-\frac{\alpha\Delta^2}{2}\right)\left(\frac{\alpha\Delta^2}{2}\right)^{v};\\
B_v^{01} &= (v,0)(v,1) = \frac{1}{v!} \exp\left(-\frac{\alpha\Delta^2}{2}\right)\left(\sqrt{\frac{\alpha}{2}}\,\Delta\right)^{2v-1}\left(\frac{\alpha\Delta^2}{2} - v\right);\\
B_v^{02} &= (v,0)(v,2) = \frac{1}{v!} \exp\left(-\frac{\alpha\Delta^2}{2}\right)\frac{\sqrt{2}}{2}\left(\frac{\alpha\Delta^2}{2}\right)^{v-1} \times\\
&\times \left[\left(\frac{\alpha\Delta^2}{2}\right)^2 - 2v\frac{\alpha\Delta^2}{2} + v(v-1)\right],
\end{aligned} \tag{3}$$

where $\alpha = 4\pi^2 c\mu\omega_0/h$ is a parameter characterizing the form of the potential curves (μ is the reduced mass, ω_0 is the frequency of nuclear vibrations); $\Delta = r_0' - r_0''$ is the difference between the equilibrium internuclear distances of the excited and ground states.

The quantities B_v^{0n} possess the following important property:

$$\sum_{v=0}^{\infty} (v,m)(v,n) = \begin{cases} 1, & \text{if } m = n,\\ 0, & \text{if } m \neq n. \end{cases} \tag{4}$$

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* The results obtained below are not difficult to generalize also to nondiagonal elements that are important in the study of resonance scattering.

Fig. 1

Figure 1: Fig. 1

Fig. 1

This result is valid for any choice of vibrational wave functions, provided only that they form a complete orthonormal system.

Obviously, if $M_{0e}(r) = \text{const}$, then $a^{01} = a^{02} \equiv 0$ for $\Delta = 0$. By contrast, unshifted scattering also exists for $\Delta = 0$, owing to the contribution of the sublevel with $v = 0$.

The distribution of the contributions of the sublevels to the matrix element a^{00} (without taking into account the frequency factor) copies the structure of the absorption band and is characterized by a single maximum, introduced by the Franck-Condon sublevel

$$v^* = \mathrm{E}(\alpha\Delta^2/2)$$

(the symbol $\mathrm{E}(s)$ denotes the integer nearest to s). All $B_v^{00} > 0$, and, in agreement with (4), $\sum_v B_v^{00} = 1$. The Franck-Condon sublevel v^*, however, makes a zero (close to zero) contribution to a^{01} (and at the same time the largest, in absolute value, negative contribution to a^{02}). The quantities B_v^{01} for groups of sublevels lying above and below v^* have opposite signs; in agreement with (4), $\sum_v B_v^{01} = 0$. Two sublevels (v_1 and v_2) correspond to the extreme values of B_v^{01} (and to values of B_v^{02} close to zero); for sufficiently large Δ they are located symmetrically with respect to v^*:

$$v_{1,2} = \mathrm{E}\left[\frac{1}{2}(2x^2 \pm 2x + 1)\right], \qquad x = \sqrt{\alpha/2}\,\Delta. \tag{5}$$

The distribution B_v^{02} is characterized by three extrema (two maxima and one minimum).

* Without loss of generality one may assume that $m = 0$; $n = 0, 1, 2, \ldots$, corresponding respectively to unshifted scattering, the fundamental tone, the first overtone in the Raman spectrum, etc.

Under nonresonant excitation of the spectrum ($\nu \ll \nu_{e0}$), taking the frequency factor into account practically does not change the character of the distribution of the contributions of the sublevels; under resonant excitation, on the contrary, it plays a decisive role (for small damping constants, a sharp predominance of the contributions of one or two sublevels must be observed and, at the same time, a considerable enhancement of the overtones, i.e., an approach to the intensity distribution characteristic of resonant fluorescence).

3. It is not difficult to show that the qualitative conclusions obtained are preserved also in the case when the shapes of the potential curves of both electronic states are different. Analysis of the dependences obtained by the Manneback method (4) leads to the conclusion that a change in the shape of the potential curve upon electronic excitation is not reflected in the number of sublevels giving extremal and zero contributions, but only somewhat changes their positions. A typical example of the distribution of the contributions of sublevels to the matrix elements of the polarizability is shown in Fig. 1.

4. Experimental data (5) show that a theory which neglects deviations from the Condon approximation (i.e., the dependence of M_{0e} on r) cannot correctly explain the dependence of the intensity of combination-scattering lines on the frequency of the exciting light at considerable distances from the absorption band. In the first approximation one may assume that

$$M_{0e}(r) = M_{0e}^{0}(1+\eta r). \tag{6}$$

Formula (1) then takes the form

$$A_{\nu}^{mn} = F(\nu,\nu)(M_{0e}^{0})^2[(\nu,m)+\eta(\nu,rm)][(\nu,n)+\eta(\nu,rn)], \tag{7}$$

where $(\nu, rm) = \langle \nu|r|m\rangle$.

Let us consider the influence of the dependence (6) in the case when the form of the potential curves (parabolas) is the same in the ground and excited electronic states. The calculations lead to the following formulas for the contributions of the sublevels (without taking the frequency factors into account)*:

$$\begin{aligned}
B_{\nu}^{00} &= \frac{1}{\nu!}\left(\frac{\alpha\Delta^2}{2}\right)^{\nu}\exp\left(-\frac{\alpha\Delta^2}{2}\right)\left[(1+\eta\bar{r}_0)-\frac{\eta}{\alpha\Delta}\nu\right]^2;\\
B_{\nu}^{01} &= \frac{1}{\nu!}\left(\frac{\alpha\Delta^2}{2}\right)^{\nu-1/2}\exp\left(-\frac{\alpha\Delta^2}{2}\right)\left(\frac{\alpha\Delta^2}{2}-\nu\right)\times\\
&\quad\times\left[(1+\eta\bar{r}_0)\left(1+\eta\bar{r}_0+\frac{\eta}{\alpha\Delta}\right)-\frac{\eta}{\alpha\Delta}\left(2+2\eta\bar{r}_0+\frac{\eta}{\alpha\Delta}\right)\nu+\frac{\eta^2}{\alpha^2\Delta^2}\nu^2\right];\\
B_{\nu}^{02} &= \frac{\sqrt{2}}{2}\frac{1}{\nu!}\left(\frac{\alpha\Delta^2}{2}\right)^{\nu-1}\left[\left(\frac{\alpha\Delta^2}{2}\right)^2-2\nu\frac{\alpha\Delta^2}{2}+\nu(\nu-1)\right]\exp\left(-\frac{\alpha\Delta^2}{2}\right)\times\\
&\quad\times\left[(1+\eta\bar{r}_0)\left(1+\eta\bar{r}_0+\frac{\eta}{\alpha\Delta}\right)-\frac{2\eta}{\alpha\Delta}\left(1-\eta\bar{r}_0+\frac{\eta}{\alpha\Delta}\right)\nu+\frac{\eta^2}{\alpha^2\Delta^2}\nu^2\right].
\end{aligned} \tag{8}$$

(in these formulas $r_0 = \frac{1}{2}(r_0' + r_0'')$, $\Delta \neq 0$).

Let us note that the representation of $M_{0e}(r)$ in the form (6) is permissible only in a small interval of r, which, however, is sufficient for the calculation of (ν, rm). If the function $M_{0e}(r)$ does not change its sign in it, then the principal features of the distribution of the contributions of the sublevels remain the same as in the Condon approximation. In the opposite case the distribution of the contributions changes more or less noticeably (the appearance of additional "irrelevant" sublevels and extrema). In this case a splitting of the absorption band must take place: at $\nu = \mathrm{E}[(\alpha\Delta/\eta)(1+\eta r_0')]$, $B_\nu^{00} \cong 0$.

Taking the dependence $M_{0e}(r)$ (in any form) into account leads to a violation of the total compensation of the contributions A_ν^{01} and A_ν^{02}, even if one neglects the differences in the frequency factors of the individual sublevels. If one starts from (8), it is not difficult to show that

$$\sum_v B_v^{00} = 1 + 2\eta r_0'' + \eta^2 \left(r_0''^2 + \frac{1}{2\alpha} \right);$$

$$\sum_v B_v^{01} = \frac{2\eta}{\sqrt{2\alpha}}(1+\eta r_0''); \qquad \sum_v B_v^{02} = \frac{\sqrt{2}}{2\alpha}\eta^2, \tag{9}$$

i.e., one may assume that at very large distances from the resonance region (the Placzek region of excitation) the appearance of lines of combination scattering of the 1st and 2nd orders is determined by deviations from the Condon approximation, whereas near the resonance region, in most cases, the main role is played by differences in the frequency factors of the individual sublevels, which violate the total compensation of the contributions.

5. Calculations by the method of perturbation theory show* that allowance for anharmonicity of the nuclear vibrations does not affect the general structure of the distribution of contributions of the sublevels, but it does significantly change the intensity of the combination-scattering lines. Anharmonicity of the vibrations in the excited state is most important near and in the resonance region. Its influence is manifested both through a change in the shape of the potential curve (reflected in the magnitudes of the contributions and the positions of the extremal sublevels), and through convergence of the sublevels (which significantly changes the frequency factors). Conversely, in the Placzek region the anharmonicity of the excited state may be neglected. Anharmonicity of the vibrations in the ground state in the resonance region introduces small corrections; in the Placzek region its allowance is more important, but does not change the order of magnitude of the intensity of the combination-scattering line.

6. In the Placzek region of exciting frequencies, summation of the contributions of the sublevels (7) leads to the following formula for a^{02}:

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* The integrals (ν, rm) were calculated by the Wagner method (^{6}).

$$a^{02} = \frac{2}{hc}\frac{\nu_e}{\nu_e^2 - \nu^2}(M_{0e}^0)^2\left[2\eta r^{02} + (\eta^2 + 2\zeta)(r^2)^{02}\right] \tag{10}$$

(ν_e is the frequency of the maximum of the absorption band; we assume that $M_{0e}(r) = M_{0e}^0(1 - \eta r + \zeta r^2)$). For harmonic vibrations of the nuclei $r^{02} = 0$, $(r^2)^{02} = \sqrt{2}(q^{01})^2$, where q^{01} is the zero-point amplitude. Therefore

$$a^{02} = \frac{2}{hc}\frac{\nu_e}{\nu_e^2 - \nu^2}(M_{0e}^0)^2(\eta^2 + 2\zeta)\sqrt{2}(q^{01})^2, \tag{11}$$

$$a^{01} = \frac{2}{hc}\frac{\nu_e}{\nu_e^2 - \nu^2}(M_{0e}^0)^2 2\eta(1 + \eta r_0'')q^{01}. \tag{12}$$

The ratio calculated from formulas (11) and (12), $(a^{02}/a^{01})^2 \sim 10^{-3}$ for typical cases, agrees with experiment. Allowance for anharmonicity affects the values r^{01}, r^{02}, etc., which is especially important for a^{02}; however, the order of magnitude of a^{01} and a^{02} is not changed thereby. In another limiting case, when deviations from the Condon approximation may be neglected (near the absorption band), numerical calculations show that $(a^{02}/a^{01})^2 \sim 10^{-2} \div 10^{-1}$; this ratio grows very rapidly with increasing Δ (for comparable values of the remaining parameters).

Let us note that in both cases mechanical anharmonicity by itself cannot be the cause of the appearance of an overtone in combination scattering.

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* In the perturbation operator the most important term is the one proportional to the cube of the vibrational coordinate.

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