CALCULATION OF INTENSITY IN THE RESONANCE RAMAN AND TWO-PHOTON ABSORPTION SPECTRA OF POLYATOMIC MOLECULES

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A direct method for calculating the resonance Raman and two-photon absorption spectra of polyatomic molecules is described in detail. The method is based on the adiabatic model and uses Herzberg–Teller's approximation. Relations ruling out direct summation over vibrational quantum numbers of excited electronic states and representing the matrix elements of the Green function of a multidimensional oscillator as functions of vibration frequencies and Dushinsky transformation parameters are derived. The relations are convenient for constructing algorithms.

Basic relations describing resonance Raman (RR) and two-photon absorption (TPA) spectra were derived long ago but are scarcely used to describe particular spectra. The reason for this situation is the inconvenient form of these relations and the difficulty of calculating some of their quantities. These include the sums over vibrational quantum numbers of excited electronic states (matrix elements of the Green function of the multidimensional oscillator) and the matrix elements of the transient dipole moment. Development of methods for calculating these quantities will resolve the problem of quantitative description of intensity distribution in the spectra. Thus elaborating the theory and methods for calculating the RR and TPA spectra aims at obtaining simple relations for the necessary matrix elements using the minimal possible number of empirical parameters (ideally, only those that are necessary for calculating the electronic structure). Describing the intensity distribution in the spectra and agreement with experimental data as well as predictive ability are the main requirements to the method.

Based on the Kramers–Heisenberg formula for the Stokes line of RR spectra, which corresponds to the excitation of the vibrational level with quantum numbers \( \nu \) from the zero level in the ground state \( g \), the components of the scattering tensor may be represented as

\[
(R_{0\nu})_{\omega} = \frac{1}{\hbar} \sum_{\epsilon} \left\{ \langle g | p_\nu | \epsilon | p_\rho | g \rangle \sum_{\nu_\epsilon} \frac{\langle \nu | \nu_\epsilon \rangle \langle \nu_\epsilon | 0 \rangle}{\Delta \omega + \sum_{\alpha} \nu_\alpha \omega_\alpha} + \\
\sum_{m\omega} \sum_{E_m - E_\epsilon} \langle g | p_\nu | \epsilon | A_\lambda | m \rangle \sum_{\nu_\epsilon} \frac{\langle \nu | \nu_\epsilon \rangle \langle \nu_\epsilon | Q_\lambda | 0 \rangle}{\Delta \omega + \sum_{\alpha} \nu_\alpha \omega_\alpha} + \\
\sum_{n\omega} \sum_{E_n - E_\epsilon} \langle \epsilon | p_\nu | g \rangle \sum_{n\omega} \sum_{E_n - E_\epsilon} \langle \epsilon | A_\lambda | n \rangle \sum_{\nu_\epsilon} \frac{\langle \nu | Q_\lambda | \nu_\epsilon \rangle \langle \nu_\epsilon | 0 \rangle}{\Delta \omega + \sum_{\alpha} \nu_\alpha \omega_\alpha} + \\
\sum_{m,n\omega} (E_m - E_n) \sum_{\lambda} \langle e | A_\lambda | m \rangle \langle n | A_\lambda | e \rangle \sum_{\nu_\epsilon} \frac{\langle \nu | Q_\lambda | \nu_\epsilon \rangle \langle \nu_\epsilon | 0 \rangle}{\Delta \omega + \sum_{\alpha} \nu_\alpha \omega_\alpha} \right\},
\]

(1)


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where \(|e\rangle\) and \(E_e\) are the wave function and the energy of the \(e\)th electronic state, respectively; \(\nu\) and \(\nu^{(e)}\) are the vibrational quantum numbers in the ground and excited electronic states; \(\Delta \omega\) is the difference between the frequency of the 0–0 transition to the "resonance" electronic state and the frequency of exciting radiation; \(p_a\) is the component of the dipole moment; \(\omega^0_{e}\) is the frequency of the \(e\)th vibration in the \(e\)th electronic state; \((e|A_j|m)\) is the matrix element of the vibronic interaction operator; \(Q_j\) is the normal coordinate number \(\lambda\).

The first term in Eq. (1) is the component of the scattering tensor in the Condon approximation, and the other terms are corrections due to the Herzberg-Teller effect. From the form of Eq. (1) it follows that in the case of resonance between the frequency of exciting radiation and the frequency of a symmetry-forbidden transition the Herzberg-Teller effect is determining for the Raman spectrum. In the RR bands of symmetry-allowed transitions, the Herzberg-Teller effect may give rise to forbidden bands as it occurs in the electronic absorption and luminescence spectra. In particular, vibronic mixing of the "resonance" electronic state with other excited electronic states of appropriate symmetry explains the presence of bands corresponding to excitation of one-quantum nontotally symmetric vibrations, their odd overtones, and combinations in the RR spectra.

Using the representation of the matrix element of the transient dipole moment in Herzberg-Teller's approximation, one can express the band intensity of the TPA spectrum as a square of the value:

\[
R_{fg}^{(2)} = \sum_e \left\{ \langle f|\varepsilon_r|e\rangle \langle e|\varepsilon_r|g\rangle \sum_{\nu^{(e)}} \frac{\langle \nu^{(f)}|\varepsilon_r\rangle \langle \nu^{(f)}|\varepsilon_r\rangle \langle \nu^{(e)}|\varepsilon_r\rangle \langle \nu^{(e)}|\varepsilon_r\rangle}{\Delta \omega + \sum_{\alpha_{e}} \nu_{\alpha_{e}} \omega_{\alpha_{e}}} + \right. \\
\left. \sum_{m,e\neq f} \sum_{E_{m}-E_{f}} \langle m|\varepsilon_r|e\rangle \sum_{e} \langle e|A_{ae}|m\rangle \sum_{\nu^{(e)}} \frac{\langle \nu^{(f)}|\varepsilon_r\rangle \langle \nu^{(f)}|\varepsilon_r\rangle |Q_{ae}|\langle \nu^{(e)}|\varepsilon_r\rangle \langle \nu^{(e)}|\varepsilon_r\rangle}{\Delta \omega + \sum_{\alpha_{e}} \nu_{\alpha_{e}} \omega_{\alpha_{e}}} \right. \\
\left. \langle e|\varepsilon_r|g\rangle \sum_{n,e\neq f} \sum_{E_{n}-E_{f}} \langle n|\varepsilon_r|e\rangle \sum_{e} \langle e|A_{ae}|n\rangle \sum_{\nu^{(e)}} \frac{\langle \nu^{(f)}|Q_{ae}|\varepsilon_r\rangle \langle \nu^{(f)}|\varepsilon_r\rangle \langle \nu^{(e)}|\varepsilon_r\rangle \langle \nu^{(e)}|\varepsilon_r\rangle}{\Delta \omega + \sum_{\alpha_{e}} \nu_{\alpha_{e}} \omega_{\alpha_{e}}} \right\},
\]

where \(\varepsilon_r\) is the polarization vector of the photon. Importantly, all terms except the first one are related by the Herzberg-Teller effect. Due to the latter, we can explain the presence of bands corresponding to the excitation of one-quantum nontotally symmetric vibrations, their odd overtones, and combinations in the spectra and correct the values of the relative intensities of the bands corresponding to the excitation of other vibrations. Therefore, it is appropriate to describe the intensity distributions in the RR and TPA spectra of polyatomic molecules using Herzberg-Teller's approximation. This makes it possible to substantiate the spectra and reproduce or predict the intensity distributions.

It should be noted that for brevity in Eqs. (1) and (2) we omitted the vibronic mixing terms of the ground and excited states.

When these relations are applied to describe the intensity distributions in particular RR and TPA spectra, calculating the matrix elements of the transient dipole moment presents a difficulty. Here we suggest that one of the procedures for calculating these matrix elements, initially designed for describing one-photon absorption spectra, be extended to RR and TPA spectra. The author used the procedure of [1], which allows reliable quantitative description of intensity distribution in the one-photon absorption and luminescence spectra, at least for systems for which the \(p\)-electron approximation is valid.

Another difficulty is the impossibility of factorizing the scattering tensor components into factors relating to separate oscillators. This necessitates calculating the sums over vibrational quantum numbers of intermediate electronic states entering into Eqs. (1) and (2). Here we suggest a method for calculating such sums (matrix elements of the Green oscillator function in an energy representation) in general as functions of vibration frequencies, Dushinsky...