Forbidden vibrational-rotational transitions in multiatomic molecules

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A mechanism for the onset of forbidden vibrational-rotational transitions in the absorption spectra of multiatomic molecules is investigated. The possible role of forbidden transitions in the multiphoton absorption of IR radiation by molecules is examined.

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Two models,[2–5] which take into account the weak or forbidden vibrational-rotational transitions, have recently been proposed to explain a number of singularities in the spectra of multiphoton absorption of strong IR laser emission and the collision-free dissociation of molecules.[1] It was suggested[2–4] that multiphoton excitation of molecules such as SF_6 or OsO_4 occurs with the participation of weak transitions with $\Delta R > 0$; Blok *et al.*[5] favor the transitions with $\Delta J > 1$, which are allowed because of the external field. However, the mechanism for that makes these transitions no longer forbidden has not been explained. This paper is devoted to the solution of this problem for cubic molecules such as SF_6 and OsO_4, for which most of the experiments have been performed.

The excited vibrational levels of the dipole-active vibrations of cubic molecules are split because of anisotropic anharmonicity. For example, the level with $v_3 = 5$ for SF_6 is split into eight sublevels and the level with $v_3 = 6$ is split into 15 sublevels with an overall spread of more than 100 cm^{-1} ($v_3 = 6$). If the splitting of the rotational levels due to anisotropic vibrational-rotational interaction is neglected, then each vibrational sublevel has a rotational structure characterized by the quantum number $R = J$ (for the A and E sublevels) and $R = J + 1$, J, and $J - 1$ (for the F sublevels).[1)] According to simple selection rules,[6] the transition between the vibrational levels Γ and Γ' is allowed if $\Gamma \times \Gamma'$ has a symmetry of the $\Gamma\mu$ vector, which for rotational transitions $\Delta J = 0 \pm 1$ and $\Delta R = 0$. However, the selection rules $\Gamma \times \Gamma' \subset \Gamma\mu$ and $\Delta R = 0$ is weakened greatly when the vibrational-rotational interaction and anharmonicity are taken into account. Thus, the dipole moment $\tilde{\mu}$ (relative to the laboratory coordinate system) is replaced by a sum of polynomials $\tilde{\mu}_{mn}$, which are functions of the m-th power of vibrational (q_k, p_k) operator and the n-th power of the rotational $(J_\alpha, \lambda_{A\alpha})$ operator. Each of the operators $\tilde{\mu}_{mn}$ characterizes certain transitions, including forbidden transitions. Thus the transition probabilities in the fundamental band $v + 1 \leftarrow v$ are determined by the matrix elements of the sum of the operators $\mu_{11} + \tilde{\mu}_{12} + \tilde{\mu}_{13}$, where μ_{11} characterizes the allowed transitions, $\tilde{\mu}_{12}$ as a pseudoscalar relative to the angular momentum **R** contributes only to the allowed transitions with $\Delta R = 0$ (or removes the exclusion of inactive E-type oscillations), and the exclusion of transitions $\Delta R > 0$ is removed by the operator $\tilde{\mu}_{13}$:

$$\tilde{\mu}_{13} = \frac{1}{2} \sum_{k} \sum_{\alpha\beta\gamma} \theta_k^{\alpha\beta,\gamma} q_k [J_\alpha J_\beta, \lambda_\gamma]_+ , \tag{1}$$

where

$$\theta_k^{\alpha\beta,\gamma} = -\sum_{l\ (\omega_k=\omega_l)} \left(\frac{\partial\mu^\gamma}{\partial q_l}\right) \left[\frac{a_{kl}^{\alpha\beta}}{\omega_k} + 4B^2 \sum_{m\ (\omega_k\neq\omega_m)} \frac{\omega_m^2(\zeta_{km}^\alpha \zeta_{lm}^\beta + \zeta_{km}^\beta \zeta_{lm}^\alpha)}{(\omega_k^2-\omega_m^2)^2} \right]$$

$$+ 4 \sum_{i\ (\omega_k\neq\omega_l)} \left(\frac{\partial\mu^\gamma}{\partial q_l}\right) \frac{\omega_l a_{kl}^{\alpha\beta}}{(\omega_k^2-\omega_l^2)} - \sum_l \left(\frac{\partial^2\mu^\gamma}{\partial q_k \partial q_l}\right) \frac{B_l^{\alpha\beta}}{\omega_l} , \tag{2}$$

and the notations of the parameters are the same as those in Ref. 7: $\alpha_{kl}^{\alpha\beta}$ are coefficients of the operator $\tilde{\mathbf{H}}_{22}$. In contrast to the angular momentum $\mathbf{R}$, the operator μ_{13} is an irreducible tensor operator of the third rank. Therefore, the operator $\tilde{\mu}_{13}$ activates the transitions with $\Delta R = 0, \pm 1, \pm 2$, and ± 3. Thus, it should be borne in mind that the matrix elements of the operator $\tilde{\mu}_{13}$ must be computed in its own Hamiltonian basis that differs from the basis $|RK_R\rangle$. The nondiagonal elements of the Hamiltonian in the $|RK_R\rangle$ basis also contributes to the dipole moments of the transitions with $\Delta R > 0$; this contribution is proportional to $(\alpha/B\zeta)J$,[8] which may be the dominant value for small J.

Exact calculations based on Eqs. (1) and (2) for molecules such as SF_6 or OsO_4 are not possible at this time because of the lack of data for many parameters in Eq. (1). However, approximate calculations show that the ratio of the probability of transitions with $\Delta R > 0$ to that for the allowed transitions with $\Delta R = 0$ is $\sim(10^{-4}-10^{-6})\,J^4$ for light molecules (CH_4, SiH_4) and $(10^{-8}-10^{-10})J^4$ for heavy molecules (SF_6,UF_6); for resonances ($\omega_k \approx \omega_m$ or $\zeta \approx 0$) this ratio may be much higher. Since in heavy molecules the rotational levels with very high J are populated at room temperature, the contribution of the transitions with $\Delta R > 0$ to the multiphoton excitation of molecules may be rather large. At the same time, the probability of transitions with $\Delta J > 1$, which are allowed because of the field, decreases greatly with increasing J.[5] Therefore, it is reasonable to assume that at least for large J the contribution from the transitions with $\Delta R > 0$, which are allowed because of intramolecular interactions, to the multiphoton excitation and dissociation of molecules in a field of strong IR laser emission[1-4] is a dominant.

The fully symmetric oscillations of cubic molecules (e.g., ν_1 of CH_4) are forbidden in the $\mu_{11} + \tilde{\mu}_{12}$ approximation; but become active due to $\tilde{\mu}_{13}$, in which the nonvanishing parameter θ is given by

$$\theta_s^{xy,z} = \theta_s^{yz,x} = \theta_s^{zx,y}$$

$$= 4 \sum_{t \subset F_2} \left[\left(\frac{\partial \mu_z}{\partial q_{t_c}} \right) \frac{\omega_t a_{stc}^{xy}}{(\omega_s^2 - \omega_t^2)} - \left(\frac{\partial^2 \mu_z}{\partial q_s \partial q_{t_c}} \right) \frac{B_{t_c}^{xy}}{\omega_t} \right]. \quad (3)$$

The ν_1 band was observed in the IR spectrum of SiH_4,[9] for which the estimates from Eq. (3) give the correct order of magnitude for the strength of the lines. In heavy molecules (OsO_4) the ν_1 band coincides with the ν_3 band. Therefore, absorption by the oscillation ν_1 should be taken into account in the analysis of multiphoton excitation of molecules.

[1)]It was assumed that the anharmonic splitting is greater than the Coriolis splitting, consistent with the high vibrational states of most molecules.

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