PHYSICAL REVIEW A VOLUME 11, NUMBER 5 MAY 1975

Reply to "Comments on 'Multiphoton processes...in diatomic molecules' "

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(Received 19 November 1974)

The critical comments by Fedorov, Makarov, and Samokhin on a treatment of multiphoton vibronic transitions in diatomic molecules are discussed and are shown to be unsubstantiated at all points.

There are few theoretical[1-5] and experimental[6-8] works on the problem of multiphoton dissociation and excitation of diatomic molecules under laser radiation. So even a very short discussion[9] of some related points is of interest. Our reply to the comments by Fedorov *et al.* (see Ref. 9) on a treatment[1-3] of multiphoton transitions in diatomic molecules is as follows.

(i) The semiclassical approximation considered by Fedorov *et al.* as a general approach to calculating multiphoton transition amplitudes A_{fi} in molecules does not apply to real diatomic molecules, where the quasiresonances and resonances at vibrational-rotational levels of electronic bands play the most important part in the process of multiphoton dissociation and ionization.[6-8]

(ii) The necessity of taking into account the intermediate states structure requires that the motion of the nuclei during the excitation process be treated explicitly. The usual perturbation-theory approach[1-3] includes the effect of nuclear motion in a rigorous manner within the Born-Oppenheimer (BO) approximation. Using the semiclassical procedure one considers[9] the molecule to be nonrotating and nonvibrating during the multiphoton excitation process.

(iii) Having applied the method given in Refs. 1-3 to calculations of the probabilities of the three-photon and two-photon processes in a hydrogen molecular ion and its isotopes, as well as in alkali-halide molecules,[4,5] we have found that there are sets of successive intermediate electronic bands ("electronic channels") which predominantly contribute to the sums over intermediate states. In these cases a procedure for calculation of partial amplitudes of electronic channels exhausts the problem. We think that such a situation is of rather a general character.

(iv) In Refs. 1-3 a method for calculating partial amplitudes is given and a number of homopolar and ionic molecules to which this method may be successfully applied are indicated. Fedorov *et al.* take for granted that the model potential-energy (PE) functions proposed in Refs. 1 and 2 for the ground and excited electronic terms cannot give a correct description of the real curves. As a matter of fact, however, the straightforward evaluation of the errors due to the use of these PE functions for calculating multiphoton vibronic transition amplitudes in the molecules mentioned in Refs. 1 and 2 shows that these errors are small.[4,5] For example, such errors in cross-section maxima of the three-photon dissociation of the ground and excited vibrational levels of H_2^+ $1s\sigma_g + 3E_p \to 2p\sigma_u$ are under 1%.

(v) In Ref. 9 it is believed that there is a "serious error" in Ref. 10 which is attributed to "disregard of electronic structure." But in Ref. 10 a purely nuclear (ionic) two-photon transition was treated (see Refs. 11-16), which by its definition has no electronic structure. Indeed, there was an error in Ref. 10, but it was a miscalculation of a cross section, not associated with any neglect of electronic structure at all.[14] It was due to the lack of a reliable method for calculating the Appel functions $F_1(\alpha; \beta, \beta'; \gamma; x, y)$; later we developed such a method.[17]

(vi) A set of PE curves for the ground and excited terms $|i\rangle$ of heteropolar diatomics $V_i(r) = A_i(r-r_i)^{-2} - B_i(r-r_i)^{-1} + C_i$ was proposed in Ref. 2, which gives a very good representation of the ground ionic states of alkali halides MX. In Ref. 9 it is thought that such a ground-state PE curve ($B_0 = e^2$) "deviates drastically from the real ground-state potential curve of MX at $r \gtrsim r_x = e^2/[I(M) - E(X)]$" [where $I(M)$ is the ionization potential and $E(X)$ is the electron affinity],[9b] because the authors of Ref. 9 do not consider the ground states of MX to be ionic. This conclusion may very well have been deduced by Fedorov *et al.* by extending "the noncrossing rule" to the electronic terms of the same species of the ground (ionic) and first excited (atomic) states of the alkali-halide molecules. However, the alkali halides are the classic example of molecules in which the noncrossing rule is violated.[18]

Consider the first point in more detail. The semiclassical approximation (known for a long time in Rayleigh and Raman scattering), neglecting structure in the electronic absorption bands, does not consider the nuclear motion in any rigorous manner and so fails to describe a number of effects which can be treated within the BO approximation. A misunderstanding of this fact could lead to the conclusion that the semiclassical approximation is a "well-known general approach for calculation of A_{fi} in molecules at optical frequencies based on the BO approximation".[9] In fact, it is common knowledge that the semiclassical procedure in Raman-scattering theory is applicable only far away from resonance.[19] But in the experimental investigation of multiphoton dissociation and ionization of hydrogen molecules with Nd-glass laser radiation at 10590 and 5293 Å, it has been found that the multiphoton processes proceed via a number of nearly resonant intermediate states.[6-8] There are grounds to expect that the quasiresonances in the multiphoton optical transitions in molecules are no less important than in multiphoton processes in atoms.

Consider also the formal possibility of extending the semiclassical procedure to calculations of the N-photon absorption amplitudes, as proposed in Ref. 9. This procedure would lie in "collapsings" of partial amplitudes (1.10) [i.e., Eq. (10) of Ref. 1],

$$M(n_1, \ldots, n_{N-1} | E_p) = \left\langle v_f \middle| d_N \sum_{v_{N-1}} \frac{|v_{N-1}\rangle\langle v_{N-1}|}{E_0 - E_{N-1} + (N-1)E_p} \cdots d_2 \sum_{v_1} \frac{|v_1\rangle\langle v_1| d_1}{E_0 - E_1 + E_p} \middle| v_0 \right\rangle , \tag{1}$$

determining the total amplitude (1.8), over the vibrational functions $|v_1\rangle, |v_2\rangle, \ldots, |v_{N-1}\rangle$ with the help of the closure identity $\sum_{v_n} |v_n(r)\rangle\langle v_n(r')| = \delta(r - r')$. It is possible if one neglects the v_n dependence of the intermediate-state energies E_{n,v_n} $(n = 1, 2, \ldots, N-1)$ and restricts oneself in Eq. (1) to the first terms of expansions[20]

$$\frac{1}{E_0 - E_n + nE_p} = \frac{1}{\mathcal{E}_0(r) - \mathcal{E}_n(r) + nE_p} [1 + q_n(r) + q_n^2(r) + \cdots] \quad (n = 1, 2, \ldots, N-1) , \tag{2}$$

where $\mathcal{E}_0(r)$ and $\mathcal{E}_n(r)$ are the "electronic energies" of the ground and of the nth intermediate states, respectively,

$$q_{n,v_n}(r) = [\Delta_n(r) + E_{0,v_0} - E_{n,v_n}][\Delta_n(r) - nE_p]^{-1}, \quad \Delta_n(r) = \mathcal{E}_n(r) - \mathcal{E}_0(r) .$$

Within a given absorption band the range of values E_{n,v_n} at which expansion (2), depending parametrically on r, holds,

$$- |\Delta_n(r) - nE_p| < E_{n,v_n} - E_{0,v_0} - \Delta_n(r) < |\Delta_n(r) - nE_p| , \tag{3}$$

is narrower when r goes to the local "electronic" resonance position r_{res} for the nth intermediate transition $\Delta_n(r_{\text{res}}) = nE_p$. If $E_0 + nE_p < E_{\text{thr}}$ (where E_{thr} is the electronic excitation threshold for the nth intermediate transition), expansion (2) is not defined [$|q_{n,v_n}(r)| \geq 1$] for all electronic absorption bands at every value of r for which $\Delta_n(r) < nE_p$. As long as such divergences are nonphysical, one can omit the range of $\Delta_n(r) < nE_p$ in the semiclassical approach, though at high v_0 this "cutting off" can lead to considerable errors.

But when $E_0 + nE_p > E_{\text{thr}}$, expansion (2) is defined in interval (3) *over* the intermediate transition energy $E_0 + nE_p$ if $\Delta_n(r) > nE_p$ and *under* this value if $\Delta_n(r) < nE_p$. Hence, at every internuclear distance r expansion (2) diverges for the levels near $E_0 + nE_p$, i.e., for "near-resonance" levels.

Thus, the "general approach," as offered in Ref. 9, may fail in treating multiphoton dissociation and ionization of molecules proceeding via the quasiresonances and resonances at specific vibrational-rotational levels.

In contrast to the semiclassical approach our treatment[1-3] of multiphoton vibronic transitions makes it possible to take into account the quasiresonant and resonant intermediate states, including the continuous spectrum within the terms of vibrational-rotational Green's functions of electronic absorption bands.

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[14] The procedure of taking a vibrational-rotational structure of intermediate states into account using the Green's functions of the corresponding terms has been initially considered in Ref. 10 by a simple example: the two-photon purely nuclear (ionic) transition (see also Refs. 11–13). The correct numerical value of the cross section given in the last paragraph of Ref. 10 is $\sigma = 10^{-44}(I/I_0)$ cm^2, $I_0 = 14\times10^{16}$ W/cm^2, $e_{\text{eff}} = e$. This minute value is due to the fact that it refers to a bound-free vibrational transition from the ground level. Such purely nuclear transitions are observable in the infrared. In the optical range such transitions naturally have not been found (see Refs. 15 and 16). We thank M. V. Fedorov, V. P. Makarov, and A. A. Samokhin, who have drawn our attention to the "surprisingly large" numerical value of the cross section in our earlier paper (Ref. 10). We are greatful to Yu. L. Schitikov and V. P. Sokolov for numerical calculations.

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