Comments and Addenda

Comments on "Multiphoton processes in homopolar diatomic molecules," "Perturbation theory in closed form for heteronuclear diatomic molecules," and "Multiphoton processes in heteropolar diatomic molecules"

M. V. Fedorov, V. P. Makarov, and A. A. Samokhin

P. N. Lebedev Physical Institute, Academy of Sciences of the USSR, Moscow, USSR
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It is argued that the method proposed in recent papers by Bunkin and Tugov is not adequate for calculation of the multiphoton transition probabilities in diatomic molecules.

The general expression for the amplitude A_{fi} for multiphoton transitions in a quantum system in the framework of time-dependent perturbation theory contains a summation over all intermediate states of the system. In molecules such a summation involves intermediate electronic, vibrational, and rotational states (if the Born-Oppenheimer approximation is used). Bunkin and Tugov[1-3] recently proposed a method for the calculation of such sums in diatomic molecules. We should like to make the following comments.

A general approach for calculation of A_{fi} in molecules at optical frequencies based on the Born-Oppenheimer approximation is well known (see, e.g., Ref. 4). According to this method the electronic problem should be considered first at a fixed nuclear configuration q, which gives $A_{fi}(q)$ depending parametrically on q. The final result is obtained then by calculation of the matrix element

$$A_{fi} = \int \psi_f^*(q) A_{fi}(q) \psi_i(q) \, dq$$

which takes into account the nuclear motion in the initial $[\psi_i(q)]$ and final $[\psi_f(q)]$ states of the nuclei.

This specific character of multiphoton transitions in molecules has not been included in Refs. 1–3. In these papers no procedure is given for calculating the electronic sums, while for the summation over intermediate vibrational states it is proposed that the Green's functions for some simple model potentials be used. No justification for this approach, as well as no actual calculation

of A_{fi}, is given in Refs. 1–3. It is clear, however, that disregarding the electronic structure can lead to serious errors in the calculation of A_{fi}. Such an error is made in Ref. 5, which is cited by Bunkin and Tugov[1-3] without any discussion.

The use of the vibrational Green's function would be necessary if a wide range of intermediate vibrational states (in energy scale) contributed essentially to the final result. In this case, however, the model curves should give a correct description of the real electronic terms over the wide range of internuclear distances R. In Refs. 1–3 this point is not discussed at all, while it is evident that the simple model curves used in Refs. 1–3 are unable to give such a description in the region of interest. One of these curves is the well-known Morse curve (see, for example, Ref. 6, where many other model curves are also discussed) and the other is the Coulomb energy with a degeneracy-breaking term, combined with a hard core at $R_c \cong \frac{1}{2} R_0$, where R_0 is the equilibrium distance. As shown in Ref. 7, the latter curve deviates considerably from the real-potential curves of alkali-halide molecules and the statement in Ref. 2 that it "ensures better agreement with the experimental data than the Rittner potential"[8] is not correct.

It should also be noted that for experimental observation of multiphoton transitions in molecules at optical frequencies, large radiation intensities are required ($I \cong 10^{12}$ W/cm^2). The validity of the lowest-order calculation of A_{fi} becomes questionable for such intensities. This aspect

is also missing in Refs. 1-3.

It seems to us that in fact Refs. 1-3 do not contain a constructive method for the calculation of multiphoton transition probabilities.

Note added in proof. The usual approach[4] was applied recently to the calculation of nonresonant two-photon transition probabilities in H_2, HD, and H_2^+ in Ref. 9. It was shown in particular that the corrections due to the nuclear motion in the intermediate states are negligible. The nuclear motion becomes more important if resonance at some vibrational-rotational level occurs, but in this case the use of the nuclear Green's function[1-3] in the corresponding electronic term is superfluous. The lowest-order perturbation theory used in Refs. 1-3 breaks down at large intensi-

ties of resonant radiation field, and the usual Born-Oppenheimer approximation should be replaced by a different approach.[10]

In their reply Bunkin and Tugov report a new value of the cross section for the two-photon dissociation which is smaller than the previous result,[5(a)] the change being about 44 orders of magnitude. This small value just shows that the one-electronic-state approximation[5] is not adequate and other electronic terms should be taken into account. We should like to emphasize also that the ground electronic state for many alkali-halide molecules is not purely ionic. In particular, the potential curve for NaI drawn in Ref. 2 differs considerably from the real curve (see, e.g., Ref. 11).

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