

Production of excited hydrogen atoms in photodissociation of the H_2 molecule

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(Submitted 4 July 1978)

Pis'ma Zh. Eksp. Teor. Fiz. **28**, No. 7, 446–448 (5 October 1978)

A new type of interaction between molecular states makes it possible to explain quantitatively the experimental data on the relative probability of production of the atoms $H(2s)$ and $H(2p)$ in photodissociation of the hydrogen molecule.

PACS numbers: 33.80.Gj

Experimental investigations have recently¹⁻³ been made of the photo-dissociation of the hydrogen molecule, wherein the first step was excitation of the $D^1\Pi_u^+$ state of H_2 . Predissociation leads next to a transition into the state $B^1\Sigma_u^+$ with subsequent breakup of the molecule along that term which corresponds, when the nuclei are separated, to the state $H(1s) + H(2s)$. According to the latest data of Mentall and Guyon³ excited hydrogen atoms in the states $2s$ and $2p$ are registered in experiment with approximate equal probability. Thus, there should exist a mechanism that ensures, when the nuclei move apart, population of the atomic state $2p$, i.e., effective transitions, corresponding at large internuclear distances R to one of the hydrogen atoms in degenerate states with principal quantum number $n = 2$, between the terms of the quasimolecule. (The fine structure of the levels with $n = 2$ is not resolved in experiment and is henceforth disregarded.) It must be borne in mind that the energy excess above the dissociation threshold in the experiments is several tenths of an electron volt, which makes transitions between adiabatic states of the molecule quite unlikely. The behavior of the terms at large internuclear distances is determined by the dipole—dipole potential in first-order perturbation theory.^{4,5} This interaction does not intermix the spherical states of the atom, thus excluding the interpretation given in Ref. 3 for the experimental data.

In the present paper we propose a qualitatively new mechanism that explains the appearance of hydrogen atoms in the $2p$ state as being due to the influence of the interaction of the covalent terms with the ionic diabatic term that corresponds to the system $H^- + H^+$ when the atoms move apart. At an internuclear distance $R_c = 11.1 a_0$, the ionic term crosses the diabatic terms corresponding to the H^* atom ($n = 2$); at this large distance these terms can be regarded with good accuracy as horizontal and degenerate. This makes it possible to analyze the problem completely by using Ovchinnikova's⁶ direct solution of the Landau–Zener model for the quantum motion of nuclei (the quantum description is necessary because of the very low velocity v at which the nuclei move apart). We shall not present here the general results of our calculations, and consider the limiting case when the probability of the non-adiabatic passage of the Landau–Zener pseudocrossing is very small. This, as shown by a simple estimate, corresponds precisely to the experimental situation. In this limit the result has a simple form and admits of a lucid interpretation.

Neglecting transitions due to rotation of the internuclear axis, we must consider two covalent electronic states of the molecule with zero projection of the electron angular momentum on the internuclear axes, namely $B'^1\Sigma_u^+$ and $B^1\Sigma_u^+$, which we shall designate $|B'\rangle$ and $|B\rangle$; the first of them is populated in the course of the predissociation. As $R \rightarrow \infty$ these states yield an H^* atom in states $2s$ and $2p$, respectively. The matrix elements of the interaction with the ionic diabatic state are designated V_s and V_p .

Bates and Lewis⁷ called attention to the fact that because of the degeneracy it is possible to change over to a basis of new states $|1\rangle$ and $|2\rangle$ such that the second of them interacts with the ionic term

$$|1\rangle = \frac{V_s}{V} |B'\rangle + \frac{V_p}{V} |B\rangle, \quad |2\rangle = \frac{V_p}{V} |B'\rangle - \frac{V_s}{V} |B\rangle, \quad V = (V_s^2 + V_p^2)^{1/2}.$$

Predissociation is accompanied by population of the state $|B'\rangle$, i.e., both states $|1\rangle$ and $|2\rangle$ with definite amplitudes. Under adiabatic conditions, the state $|1\rangle$ cannot lead to dissociation, since it correlates with the ionic term, for which the coming apart is energywise forbidden. Thus, the wave that describes the motion of the nuclei, following the state $|1\rangle$, is completely reflected backwards. To the contrary, following the state $|2\rangle$, the wave goes off completely to infinite internuclear distances, i.e., it leads to dissociation with a relative number $|V_p/V_s|^2$ of the atoms in the states $2s$ and $2p$. Using the data of Bates and Lewis⁷ for the matrix elements ($2V_s = 0.333$ eV, $2V_p = 0.407$ eV), we find that 59.9% of the excited atoms are in the state $2s$, and 40.1% are in the state $2p$ —in close agreement with the experimental values 57 and 43%.³ This result is stable with respect to the employed approximation and, in particular, is reproduced when V_s and V_p are calculated with the aid of zero-radius potentials (see, e.g., Ref. 8). At an energy 0.1 eV above the dissociation threshold, the Massey pseudo-precession parameter is very large: $2\pi V/v\Delta F = 2 \times 10^3$ a.u. (ΔF is the difference between the slopes of the terms). This corresponds to the deep adiabatic situation. We note finally that the state B of the H_2 molecule is populated at $R < R_c$. Observation of this effect, for example as revealed by radiative transition, could serve as the most direct experimental verification of the proposed mechanism. We note also that since only one component of the $2p$ state is populated, the emitted radiation is polarized if the directions in which the atoms move apart are registered by a coincidence technique.

Our problem deals with the case of interaction of three states, which may turn out to be important also in other situations. A qualitative feature of the problem, which makes it of fundamental interest for atomic physics, is that at a certain instant ($R = R_c$) there is turned on an interaction that classifies the degenerate states approximately in accord with their quantum numbers, which differ from those by which the detector classifies the system. The interaction is connected with a restructuring of the molecular orbitals at large distances, which differs in character from the most frequently encountered restructuring, described by Demkov's model,⁹ of molecular states into atomic states. Part of the flux propagating along the state $|1\rangle$ is reflected from the interaction region, and the transmitted part adds up with the wave that moves along the $|2\rangle$ state, producing in the general case an interference structure. In the considered concrete situation the reflection is complete, although there is no outflow of probab-

ity to the ionic term—the channel is energywise closed, but it is precisely because of the interaction with this term that the state $|1\rangle$ is “knocked out” of the dissociation process, and the remaining state $|2\rangle$ contains an appreciable admixture of the atomic state $2p$, the production of which cannot be explained otherwise.

The authors thank Yu. N. Demkov for a discussion of the results.

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