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EFFECT OF A STRONG OPTICAL-FREQUENCY ELECTROMAGNETIC FIELD ON THE HYDROGEN MOLECULE

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An experimental study has been carried out of the effect of a strong electromagnetic field in the beam produced by a neodymium glass laser on the hydrogen molecule at photon energies ($\hbar\omega = 1.18$ eV) much smaller than the ionization and dissociation potentials of the molecule. It was found that at field strengths $E \approx 5 \times 10^7$ V/cm the leading process was the ionization of the molecule leading to the formation of the H_2^+ ion ($H_2 + 14\hbar\omega \rightarrow H_2^+ + e$) and not the dissociation process ($H_2 + 5\hbar\omega \rightarrow H + H$). Data have been obtained on the ionization probability for the H_2 molecule and its dependence on the radiation intensity.

INTRODUCTION

A strong optical-frequency electromagnetic field may give rise to the excitation, ionization, and dissociation of a molecule. The probabilities of these processes as functions of frequency, field strength, and type of molecule are unknown at present. Only the first experimental[1-3] and theoretical[4,5] steps have been taken in the study of the dissociation and ionization of molecules by optical-frequency radiation. For all molecules the dissociation energy and even more so the ionization energy are several times greater than the photon energy in the optical frequency range. Accordingly, these two processes can occur only as a result of absorption of a number of photons, i.e., we are dealing with a multiphoton process.

Although the dissociation of a molecule necessitates the absorption of a smaller number of photons than ionization, it is not obvious that the dissociation probability must be greater than the ionization probability. Molecular dissociation may occur as a result of nuclear vibrations. Such vibrations are efficiently excited in the case of a resonance between the natural vibrational frequency of the molecule and the frequency of the radiation field. However, the natural vibration frequencies are usually much smaller than the optical frequencies. Dissociation may occur as a result of a preliminary excitation of electrons in the molecule. The essential point then is that the dissociation energy in the excited electronic state is lower than in the ground state. When the minima of the potential curves for the ground and excited states correspond to different distances between the nuclei, the excited electronic state corresponds to a highly excited vibrational state which requires relatively little energy for dissociation. Finally, dissociation may occur as a result of electronic transition to a repulsive term.

When the possible interactions between molecules and optical-frequency fields are considered it is important to bear in mind the structural differences between different molecules and differences between the dipole moments. Thus, heteropolar molecules may dissociate as a result of the interaction between the mean dipole moment and the radiation field[4]. In the case of homeopolar molecules the interaction occurs only between the field and the induced dipole moment produced as a result of the polarization of the molecule by the radiation field[5].

Analysis of multiphoton ionization of molecules is additionally complicated (in comparison with the analogous problem for multiphoton ionization of an atom) by the necessity of taking into account the vibrational and rotational states. In particular, new phenomena, for example, the violation of the Franck-Condon principle may arise in the case of multiphoton ionization of molecules.

From our point of view, the basic questions that must be answered are as follows:

1) Which process, dissociation or ionization of molecules, has the greater probability in the optical frequency range? 2) Does the probability of these proces-

ses depend on the dipole moment of the molecule?
3) Which transitions predominate during dissociation (between electronic or vibrational states)?

We have chosen the hydrogen molecule as the first object for experimental studies because it has been relatively well investigated and is amenable to theoretical analysis. A strong electromagnetic field of optical frequency acting on a hydrogen molecule may result in the following three reactions:

1) dissociation, $H_2 + 4.5\ \text{eV} \rightarrow H + H$;
2) ionization, $H_2 + 15.4\ \text{eV} \rightarrow H_2^+ + e$;
3) double ionization, $H_2 + 48\ \text{eV} \rightarrow H^+ + H^+ + e + e$.

As in the case of a homeopolar molecule, the excitation of vibrations in the hydrogen molecule can occur only through the interaction with the induced dipole moment. Estimates based on the results obtained by Askar'yan[5] have shown that nonresonant dissociation of the hydrogen molecule through the interaction with the induced dipole moment can occur only at field strengths that are higher than the field strength in the atom.

The process of multiphoton ionization of the hydrogen molecule has been analyzed by L. V. Keldysh and N. A. Medvedeva (private communication) by analogy with the process of multiphoton ionization of an atom[6], carried out by Keldysh in 1964. In the new analysis the solution of the problem of ionization of the hydrogen molecule was replaced by the solution of a model problem involving ionization from a short-lived potential well whose depth was equal to the ionization potential of the molecule. The effect of the field on the initial state and the existence of intermediate excited electronic states were neglected. In the optical frequency range the formula for the ionization probability of the hydrogen molecule has a form analogous to the well-known formula for atoms[6]:

$$W = AE^{2K_0}, \qquad K_0 = \langle I/\hbar\omega + 1\rangle,$$

where W is the ionization probability, E is the electric field, I is the ionization potential, and K_0 is the number of photons whose absorption is necessary to conserve energy. Estimates based on this formula yield the observed values of the ionization probability for electric fields $E \approx 10^8$ V/cm. It also follows from[6] that there are two competing ionization channels, namely, transitions in which the Franck-Condon principle is satisfied and a large number of photons is absorbed, and transitions to the minimum on the potential curve of the molecular ion in which the Franck-Condon principle is violated and a smaller number of photons is absorbed.

In our first experiment on the hydrogen molecule we have used the beam from a ruby laser[1]. In this case, the dissociation of the hydrogen molecules requires the absorption of three photons, whereas ionization requires five photons. We have observed the ions produced by the laser radiation in gaseous molecular hydrogen. The main results of this experiment may be summarized as follows.

1. The H_2^+ and H^+ ions are observed at electric fields of the order of 10^7 V/cm.
2. Molecular ions are produced preferentially: $N(H_2^+)/N(H^+) \lesssim 100$.
3. The probability of formation of molecular ions is $W(H_2^+) = 10^{6.3 \pm 1.7}\ \text{sec}^{-1}$ at a field strength $E = (1.1 \pm 0.3) \times 10^7$ V/cm.
4. For the same electric field the dependence of the probability of formation of molecular ions on the field strength is of the form $W = AE^{2K}$, where $K = 7.7 \pm 0.4$.

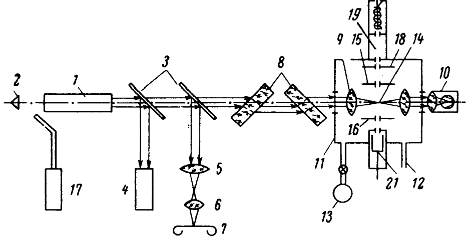
The preferential formation of molecular ions suggested that the dissociation probability was not greater than the ionization probability. In fact, if the dissociation probability for the hydrogen molecule were much greater than the ionization probability, all the molecules would dissociate into atoms and no molecular ions could be produced.

The present work is a continuation of the above study of the probability ratios for dissociation and ionization of the hydrogen molecule. The experiment was performed at a different radiation frequency.

EXPERIMENTS AT $\lambda = 1.06\ \mu$

In the new series of experiments we used the beam from a neodymium glass laser ($\hbar\omega = 1.18$ eV, $\lambda = 1.06\ \mu$). In this case, dissociation of the hydrogen molecule requires the absorption of four photons, whereas ionization requires fourteen photons.

The experimental arrangement is illustrated in the figure. A Q-switched laser was employed, the switching being achieved by a rotating prism. The laser pulse length was ~30 nsec and the energy per pulse was about 3 J. The laser radiation was focused inside a vacuum chamber by a composite objective of focal length $f \approx 27$ mm. The radiation field strength in the focal region was measured with the aid of a linear attenuator at the entrance to the chamber. The energy of the radiation reaching the focal region was measured with a calorimeter located behind the chamber. The radiation field strength in the focal region was established through an independent determination of the spatial distribution $\varphi(x, y, z)$ of the radiation integrated over the length of the giant pulse, the time distribution $\psi(t)$ integrated over the entrance aperture of the objective, and the energy Q in the radiation pulse[8]. For this purpose a portion of the radiation was removed from the main beam by a separating wedge. The FÉK-09 coaxial photocell was placed in one of the beams and was used with the I2-7 oscillograph to determine the time distribution with a 1 nsec resolution. An objective similar to the main objective and placed at the same distance from the laser was placed in the other beam. The radiation distribution in the focal region of the objective was photographed through a microscope with a magnification



Experimental arrangement: 1, 2 – laser; 3 – beam splitters; 4 – photocell; 5 – objective similar to the focusing objective 9 in the chamber; 6 – microscope; 7 – camera; 8 – linear attenuator; 9 – focusing objective; 10 – calorimeter; 11 – vacuum chamber; 12 – pumping system; 13 – gas reservoir; 14 – focal region; 15, 16, 18 – ion extraction system; 17 – photomultiplier; 19 – flight gap of mass spectrometer; 20 – electron multiplier of mass spectrometer; 21 – probe.

of about 100. This ensured spatial resolution of a few microns.

The vacuum chamber was filled with hydrogen, and ions produced in the region in which the laser radiation was focused were recorded. The pressure in the chamber was chosen so that there were no secondary effects during the ionization of the molecules and the detection of the generated ions. Under our particular experimental conditions the maximum pressure of the molecular hydrogen was about 10^{-3} Torr. The experiments were carried out at a pressure of $10^{-5}-10^{-4}$ Torr. Ions produced in the region in which the radiation was focused were accelerated by a constant field and were then passed through an ion-optical system of slits. They were then mass-separated in the flight gap and finally detected by an electron multiplier. The mass resolution in the case of H_2^+ and H^+ ions was $m/\Delta m \sim 2.6$.

We have measured three parameters, namely, the mass of the resulting ions, the functional dependence of the ion production probability on the density of the radiation in a certain range of intensity values, the absolute ionization probability, and the corresponding absolute electric field strength.

The ion production probability was measured by observing the saturation of the ion signal. As the radiation intensity was increased, the probability of ion production increased until the relation

$$W\tau = 1,$$

was satisfied, where τ is the radiation pulse length. If the radiation intensity is increased further the number of ions does not increase because all the molecules (atoms) are then ionized. The uncertainty in the measured absolute probability was only partly determined by the uncertainty in the measured laser pulse length which was about 20%. The main uncertainty in the determination of the probability is connected with the fact that the curve $W = AF^K$ reaches saturation over a finite range of intensities. This is due to the nonuniform distribution of the field in the ionization volume and the spread of the signal due to laser instability. Analysis of experimental data has shown that the ionization probability was subject to an uncertainty of $\Delta \log W = 1$.

EXPERIMENTAL RESULTS

Our main data on ions produced as a result of the interaction between the alternating electromagnetic field of wavelength $\lambda = 1.06\ \mu$ and the hydrogen molecules may be summarized as follows.

1. Ions are observed at electric fields $E = 5 \times 10^7$ V/cm.
2. There is a preferential production of molecular ions: $N(H_2^+)/N(H^+) \sim 10^3$.
3. The probability of formation of H_2^+ ions in fields of $E = 10^{7.8 \pm 0.15}$ V/cm is $W(H_2^+) = 10^{7.8 \pm 1.0}$ sec^{-1}.
4. At the above field strength, the probability of the formation of molecular ions as a function of the electric field is

$$W(H_2{}^+) = AE^{2K} \quad \text{where } K = 10.5 \pm 2.8.$$

Comparison of these results with the data obtained earlier with the ruby laser[1] (see the table) shows that the results at the two frequencies are very similar.

$\hbar\omega$, eV	E_{exp}, V/cm	W^*_{theor}, sec^{-1}	K^*_{theor}	W_{exp}, sec^{-1}	K_{exp}
1.78[1]	$10^{7.05 \pm 0.15}$	10^3	9	$10^{6.3 \pm 1.7}$	7.7 ± 0.4
1.16	$10^{7.8 \pm 0.15}$	10^4	14	$10^{7.8 \pm 1.0}$	10.5 ± 2.8

*L. V. Keldysh and N. A. Medvedeva (private comm.).

H_2^+ ions are produced preferentially, the probability of formation of molecular ions is a power function of the electric field, and the exponent in this relation is much less than K_0.

DISCUSSION OF EXPERIMENTAL DATA

In order to deduce any conclusion about the ratio of dissociation to ionization probabilities, let us first consider the various processes which lead to the appearance of H_2 and H_2^+ ions, and let us estimate the corresponding probabilities.

The molecular ion H_2^+ is produced during the ionization process $H_2 + 15.4\text{ eV} \rightarrow H_2^+ + e$. The H^+ ions are produced as a result of the double ionization process $H_2 + 48\text{ eV} \rightarrow 2H^+ + 2e$ and subsequent secondary processes, i.e., the dissociation of the molecule with subsequent ionization of the hydrogen atoms $H_2 + 4.5\text{ eV} \rightarrow H + H$, $H + 13.6\text{ eV} = H^+ + e$; dissociation of the molecular ion $H_2^+ + 2.6\text{ eV} = H^+ + H$; and ionization of the molecular ion $H_2^+ + 32\text{ eV} = 2H^+ + e$.

Double ionization of the molecule and ionization of the molecular ion have low probabilities because they require the absorption of a considerable amount of energy. The ionization probability of the hydrogen atom and the dissociation probability of the H_2^+ ion in a strong optical-frequency field are unknown. However, experimental data on the multiphoton ionization of inert-gas atoms[8], and data on the role of the spectrum of the atom during multiphoton ionization[9,10], suggest that for optical-frequency fields of the order of 10^7-10^8 V/cm, and laser pulse lengths $\tau \sim 10^{-8}$ sec, the ionization probability of the hydrogen atom is such that $W\tau \sim 1$. Accordingly, each dissociation of the hydrogen molecule should lead to the appearance of atomic ions. The probability that atomic ions are observed will, in this case, provide an upper limit for the dissociation probability of hydrogen molecules. The dissociation probability can be smaller only if the atomic ions are also efficiently produced as a result of the process $H_2 + 15.4\text{ eV} \rightarrow H_2^+ + e$, $H_2^+ + 2.6\text{ eV} \rightarrow H^+ + H$. Therefore, the dissociation probability of the hydrogen molecule in a strong optical-frequency field is lower by a factor of 100–1000 than the corresponding ionization probability.

Let us consider the multiphoton ionization of hydrogen molecules in greater detail. From our point of view, the fact that the ionization process predominates over the dissociation process is in agreement with the known properties of the H_2 molecule whose dipole moment is zero and transition to the repulsive term is highly forbidden owing to the weak spin-orbit interaction.

The table gives data on the probability of multiphoton ionization of the hydrogen molecule. We note that at both radiation frequencies $K < K_0$ and the absolute probability is lower than the value predicted by the Keldysh-Medvedeva theory.

The potential curve minima for the H_2^+ ion and the H_2 molecule correspond to different distances between the nuclei. It follows that the ionization process associated with the minimum absorption of energy should occur with violation of the Franck-Condon principle. However, under our experimental conditions this process was not realized because the energy of 13 photons from the neodymium laser and 8 photons from the ruby laser is insufficient for the transition from the minimum of the H_2 curve to the minimum of the H_2^+ curve, and the energies of 14 and 9 photons are sufficient for the realization of the transition without violation of the Franck-Condon principle.

The fact that in the multiphoton ionization of the hydrogen molecule $K < K_0$ and the absolute probability is greater than the calculated value obtained from the quasiclassical model by L. V. Keldysh and N. A. Medvedeva is analogous to the typical situation observed for the multiphoton ionization of atoms[8]. In the case of multiphoton ionization of atoms, it has been established that when there is a resonance between the energy of a number of photons and the energy of a particular electronic excited state in the atom there is a reduction in the exponent of the power-function dependence and an increase in the ionization probability[9]. It is still difficult to determine the role of the resonances during multiphoton ionization of the hydrogen molecule, because the electronic spectrum of the molecule is smeared out by vibrational and rotational degrees of freedom.

It is obvious that further experimental and theoretical studies will be required before a sufficiently complete description of the interaction between a strong electromagnetic field and the molecules will become possible. If we confine ourselves to the problem formulated above, i.e., to the elucidation of the conditions under which either ionization or dissociation predominates, then significant information can be obtained by varying the type of the molecule under investigation. It will be interesting to determine which processes will appear during the interaction between a strong electromagnetic field and a heteropolar molecule or a molecule having an allowed transition to a repulsive term. The elucidation of factors affecting the probability and its dependence on the field strength during multiphoton ionization of the hydrogen molecule is of interest in itself.

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91