

Velocity distributions of excited hydrogen atoms produced in dissociation of hydrogen molecules by electron impact

G. N. Polyakova, V. F. Erko, A. I. Ranyuk, and O. S. Pavlichenko

Physico-technical Institute, Ukrainian Academy of Sciences

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The velocity distributions of excited hydrogen atoms in states with principal quantum numbers $n = 3, 4, 5$, produced upon dissociation of hydrogen molecules bombarded by 90, 130, 300 and 1000 eV electrons, are studied. It is shown that the velocity distributions have two peaks at 0.6×10^6 cm/sec and $3/5 \times 10^6$ cm/sec and change only slightly in the electron energy range between 90 and 1000 eV.

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The study of the velocity distributions of excited hydrogen atoms produced upon dissociation of hydrogen molecules has been the subject of a number of papers.^[1-6] The velocity distributions were investigated principally for hydrogen atoms in the $2s$ state,^[1-4] and also in highly excited Rydberg states.^[5] In addition, in^[5,6] an estimate was presented of the possible velocities of the hydrogen atoms in states with principal quantum numbers $n = 3$ and $n = 4$. As shown by these results,^[1-6] knowledge of the velocity distributions of the dissociation fragments of the H_2 molecule permits a deeper understanding of the mechanisms that lead to the appearance of these fragments.

It was established as a result of the investigations of^[1-4] that when hydrogen molecules are dissociated by electron impact, two groups of excited hydrogen atoms in the $2s$ state are produced: fast atoms with a distribution maximum at $v \sim 3 \times 10^6$ cm/sec, and slow atoms with a maximum at $v \sim 0.75 \times 10^6$ cm/sec. To explain the processes that lead to appearance of these two groups of hydrogen atoms, the following experiments were performed: first, the thresholds for the appearance of fast and slow excited hydrogen atoms were determined and, second, the angular distributions of these atoms were investigated near the threshold. This has made it possible to determine the type of symmetry of the state of the H_2 molecule, the decay of which leads to the appearance of the investigated fragments.^[7] The investigations have shown also that the angular distribution is isotropic for slow hydrogen atoms in the $2s$ state, and corresponds to the symmetry Π_u or Δ_g of the dissociated state of the H_2 molecules in the case of the fast atoms. Finally, studies were made of the velocity distributions of the slow H ($2s$) atoms produced upon dissociation of hydrogen molecules cooled to 50 °K. It turned out that the distributions obtained in this manner had a structure that coincided with the positions of the vibrational levels of the states $D^1\Pi_u$, $d^3\Pi_u$, and a number of Rydberg states of the H_2 molecule.

The investigations have enabled the authors of^[1-4] to ascribe the group of slow H ($2s$) atoms to processes of predissociation of the states $D^1\Pi_u$ and $d^3\Pi_u$ into the states $B^1\Sigma_u^+$ and $e^3\Sigma_u^+$ of the H_2 molecule. The appearance of fast H ($2s$) atoms is attributed to the dissociation of the doubly excited state of the H_2 molecule with symmetry type $^1\Pi_u$.

For highly excited hydrogen atoms produced upon dissociation of hydrogen molecules, two groups of atoms are also observed: fast atoms with maximum velocity $v \sim 3 \times 10^6$ cm/sec, and slow ones with maximum at a velocity $v \sim 0.5 \times 10^6$ cm/sec.^[5] As in the preceding studies, the appearance of fast atoms is attributed to the decay of the doubly excited states of the H_2 molecule. The appearance of slow hydrogen atoms, in the authors' opinion, is due to Franck-Condon transitions to the repulsion branches of the bound highly excited states of the H_2 molecule. Since the potential curves of the highly excited states of the H_2 molecule differ little from the potential curve of the ground state of the molecular ion H_2^+ , we can compare the velocity distribution of the hydrogen atoms in highly excited states with the H^+ -ion velocity distribution calculated for the processes of dissociation via the repulsion branch of the potential curve of the ground state of the molecular ion H_2^+ . This comparison has shown good agreement between the experimental and the calculated distributions.

Thus, it follows from the considered studies that the principal and most complete investigations were carried out with H_2 -molecule dissociation fragments in metastable states. We know of only two studies^[5,6] in which attempts were made to estimate the velocities of the dissociation product in non-metastable states. Approximate measurements of the Doppler broadening of the H_β line ($n=4$), carried out in^[5], have shown that at low electron energies (< 26 eV), the line contour is narrow and corresponds to hydrogen atom velocities $v < 1.4 \times 10^6$ cm/sec. With increasing electron energy, the line contour broadens and corresponds to a hydrogen-atom velocity up to 3.5×10^6 cm/sec. In^[6], a study was made of the change of the intensity of the H_α ($n=3$) line as a function of the magnetic-field intensity. This has made it possible to estimate the velocity of the hydrogen atoms. Two groups of dissociation fragments were observed, with velocities $(8-9) \times 10^5$ and $(3-4) \times 10^6$ cm/sec.

In this study we have investigated the velocity distributions of hydrogen atoms in states with $n = 3, 4$, and 5, produced as a result of dissociation of hydrogen molecules by electrons with energies 90, 130, 300, and 1000 eV. The investigation of the velocity distribution of the excited hydrogen atoms was based on the Doppler broadening of the spectral lines H_α , H_β , and H_γ , the in-

tensity contours of which were measured by two methods—photoelectric and photographic. The optical part of the installation with photoelectric registration is illustrated in Fig. 1. The light 1 produced in the collision chamber by interaction of electrons with the hydrogen molecules was focused by lens 2 on slit 3 of the large-aperture monochromator MDR-2 (4). The lens 6 was located at a distance equal to its focal length from the exit slit 5 of the monochromator and directed a parallel light beam into a Fabry-Perot interferometer 7 placed in the pressure chamber 8. The central part of the interference pattern produced by the interferometer was projected by an achromatic objective 9 on diaphragm 10 and was registered by photomultiplier 11. To reduce the dark current, the photomultiplier was placed in a vacuum chamber and was cooled.

The intensity contour of the investigated spectral line was scanned by varying the pressure of the carbon dioxide in the pressure chamber 8. When this pressure was changed from 5 to 2 atm, and the distance between the interferometer mirrors was 0.6 mm, light extending over 2–3 orders of interference passes through the diaphragm. The free spectral range of the interferometer was 3.56, 1.97, and 1.57 Å for the lines H_α , H_β , and H_γ , respectively. The line intensity contours were recorded on the chart of an electronic potentiometer; the time required to record two neighboring orders was 15 minutes. Prior to each run of the measurements of the intensity contours of the lines H_α , H_β , and H_γ , the apparatus contour was measured with the aid of the mercury lines $\lambda = 6709.12$ Å, $\lambda = 5460.73$ Å and $\lambda = 4358.33$ Å. The measurement run consisted usually of five spectrograms, in each of which two interference orders were recorded.

Using the photographic method, the results were reduced in accordance with three neighboring interference rings; for each line we obtained likewise no less than five spectrograms. The distributions of the intensities in the contours of the H_α , H_β , and H_γ lines were registered at hydrogen pressures $(2-5) \times 10^{-3}$ Torr. Measurements of the dependences of the intensities of these lines on the hydrogen pressure in the collision chamber have shown that the pressure interval lies in the region of single collisions and amounts to $(2-5) \times 10^{-3}$ Torr. In addition, measurements of the intensity distributions in the contour of the H_α line at pressures $(2-7) \times 10^{-3}$ Torr has shown that these distributions do not depend on the hydrogen pressure in the indicated pressure region.

To convert the obtained experimental intensity distribution of the spectral line $f(\lambda')$ into the true distribution $\varphi(\lambda)$ we solved the integral equation

$$f(\lambda') = \int_{-\infty}^{\infty} a(\lambda, \lambda') \varphi(\lambda) d\lambda \quad (1)$$

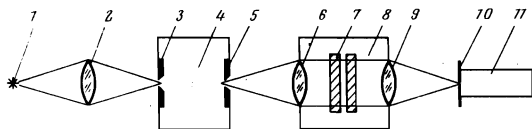


FIG. 1. Diagram of optical part of the installation.

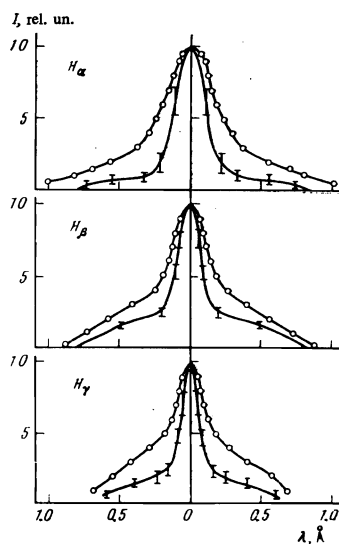


FIG. 2. Distributions of the intensities in the spectral-line contours: points—experimental distribution, solid curve—distribution with the apparatus distortions eliminated.

by the regularization method.^[8] The kernel $a(\lambda, \lambda')$ of the integral equation (1) is the apparatus function. In order to select the correct solution from among the set $\varphi(\lambda)$ allowed by the errors in the function $f(\lambda')$ it is necessary to resort to additional conditions concerning the form of the function $\varphi(\lambda)$. One such additional condition is the requirement that the sought solutions have a minimal structure. By starting from this requirement, we set up a computer program for the solution of Eq. (1), using the method described in^[9]. The values calculated with the aid of this program for the intensity distributions in the contours of the lines H_α , H_β , and H_γ excited upon dissociation of the molecules H_2 by electrons with energy 300 eV are shown in Fig. 2. The figure shows also the experimental distributions of the intensities for the corresponding lines.

To convert from the intensity distributions in the contour of the spectral line to the velocity distributions of the excited hydrogen atoms it is necessary to know their angular distribution. From measurements carried out in^[10] it follows that the lines H_α , H_β , and H_γ , emitted by the H^* atoms produced upon dissociation of the H_2 molecules by electron impact are very weakly polarized. Consequently, the angular distribution of the H^* atoms can be regarded as isotropic.^[11] In this case, the values of the intensities in the contour of the spectral line¹⁾ $\varphi(\lambda)$ or $\varphi(v_z)$ is connected with the velocity distribution function $\Phi(v)$ of the atoms by the relation

$$\varphi(v_z) \sim \int_{-\infty}^{\infty} \frac{\Phi(v)}{v} dv. \quad (2)$$

To solve this equation, we used a program similar to that used to solve Eq. (1), under the condition that $a(\lambda, \lambda') = 1$. The proportionality coefficients in (2) were chosen such that the area bounded by the $\Phi(v)$ curve was equal to the cross sections for the excitation of the lines H_α , H_β , and H_γ ^[10] at the specified values of the electron energies. Figure 3 shows the distributions obtained in this manner for the hydrogen-atom velocities at electron energies 90, 130, 300, and 1000 eV. The figure shows also the errors, which were determined from the

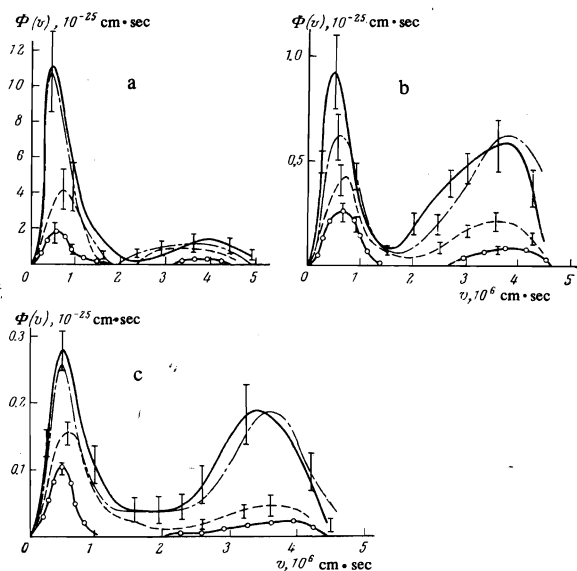


FIG. 3. Velocity distributions of hydrogen atoms in states with $n=3$ (a), $n=4$ (b), and $n=5$ (c) at electron energies 90 eV (solid curves), 130 eV (dash-dot), 300 eV (dashed), and 1000 eV (curve with light circles).

following series of calculations: with the aid of the functions $\Phi(v)$ shown in Fig. 3, we used Eq. (2) to solve the inverse problem, i. e., we obtain the intensity distribution $\bar{\varphi}(v_z)$ in the contour of the spectral line. Then, to imitate the errors, the points of the $\bar{\varphi}(v_z)$ dependence were randomly distributed in accordance with the normal law with specified variance. At these values of $\bar{\varphi}(v_z)$ with the errors obtained for the functions $\varphi(v_z)$ when solving Eq. (1) were substituted in Eq. (2). The values of $\bar{\Phi}(v)$ obtained in this manner were compared with the values of $\Phi(v)$, and this made it possible to estimate the errors of the rough velocity distributions.

As seen from Fig. 3, the obtained velocity distributions of the excited hydrogen atoms have two maxima, at velocities $v \sim 0.6 \times 10^6$ and $v \sim 3.5 \times 10^6$ cm/sec. In addition, as follows from the same figures, the velocity distributions $\Phi(v)$ vary insignificantly with changing electron energy.

To explain the obtained maxima we can advance the following considerations. We assume that the group of "fast" hydrogen atoms can be ascribed to the process of dissociation, when the hydrogen molecule goes via electron impact from the ground state to the repulsion autoionization states of the molecule H_2^* or of the molecular ion $(H_2^+)^*$. In^[12] are given curves of the repulsion states of the molecular ion H_2^+ , with the limits of the dissociation $H^+ + H^*$. Knowledge of these curves makes it possible to estimate the limits of the velocities of the excited hydrogen atoms. For a hydrogen atom in the state $n=3$, these limits are $(3.1-5.1) \times 10^6$ cm/sec, while for atoms in the states with $n=4$ and $n=5$ these values are $(3.5-4.9) \times 10^6$ cm/sec. The group of slower H^* atoms cannot be attributed to a transition to the repulsion

curves of the molecular ion H_2^+ .

The autoionization states of the H_2 molecule are much less known. Some autoionization repulsion states of the H_2 molecule were calculated in^[13,14]. However, a Franck-Condon transition into these states, followed by dissociation into $H + H^*$, cannot produce H^* atoms with velocities $v < 3.3 \times 10^6$ cm/sec. We have seen that the group of H^* atoms with velocities in the range $(1.5-3.3) \times 10^6$ cm/sec, which were observed in the present study, can be attributed to the process of dissociation via doubly excited autoionization states of the H_2 molecule.

One of the possible processes that leads to the appearance of the group of "slow" excited hydrogen atoms with a maximum at $v \sim 0.6 \times 10^6$ cm/sec can be the Franck-Condon transition to the repulsion branches of the bound electronic states of the molecule H_2 , located above the dissociation limit.²⁾ Another process may be the transition of the hydrogen molecule from its ground electronic state into highly excited electronic states with subsequent predissociation into dissociable states of the H_2 molecule. The probability of the predissociation process depends on the mass of the spreading fragments. Therefore analogous experiments with the D_2 molecule and a comparison of the velocity distributions of the atoms D^* and H^* can elucidate the relative role of the predissociation process in the formation of slow fragments.

- ¹⁾The value of λ is connected with the velocity v_z by the relation $v_z = \lambda c / \lambda_0$, where v_z is the projection of the velocity on the observation axis, c is the speed of light, and λ_0 is the wavelength at the center of the spectral line.
- ²⁾The potential curves of the bound states of the molecule H_2 , having a dissociation limit $H^*(n=3) + H$, are given in^[11].

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