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ELEMENTARY PROCESSES OF CHANGE OF CHARGE STATES IN THE INTERACTION BETWEEN PROTONS AND HYDROGEN MOLECULES

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The cross sections for elementary changes of the charge states in $H^+ - H_2$ interactions are measured by simultaneously analyzing the charge states of fast atomic particles and of particles produced from target molecules. Particles that are partners of the same collision are separated by delayed coincidences. By a simultaneous analysis of the kinetic energies of the protons produced in the dissociation of molecular H_2^+ ions, the cross sections are determined for elementary processes that possess identical charge-state variation patterns but are connected with the dissociation of the H_2^+ ion from the lower ($1s\sigma_g$) and higher electron states. Cross section measurements performed for incident proton energies $T_0 = 5 - 50$ keV showed that for $T_0 \lesssim 30$ keV electron capture by the incident proton (charge exchange) is the major process of H_2^+ formation. With increase of T_0 the role of ionization in which one electron is removed from the H_2 molecule becomes greater and for $T_0 \approx 45$ keV the capture and ionization cross sections become equal. The major process of proton formation from H_2 molecules is electron capture by the incident proton with subsequent dissociation of the H_2^+ ions from the repulsive $2p\sigma_u$ state and excited electron states. The cross section for capture involving ionization is also quite large. In this process one electron of the H_2 molecule is captured by the incident proton and the other is removed into the continuous spectrum. The processes of ionization with dissociation and two-electron capture possess smaller cross sections. An analysis of the dissociation probability in H_2^+ ion formation in the $1s\sigma_g$ state shows that electron transitions in the target molecule in $H^+ - H_2$ collisions obey the Franck-Condon principle for all incident proton energies.

INTRODUCTION

We have undertaken an investigation of the simplest case of ion-molecular collisions between H^+ and H_2. However, even for this case, the picture of the elementary processes whereby the charge states of the interacting particles are changed is more complicated than in ion-atom collisions. This is connected with the possible realization not only of processes in which an electron is removed from the shell of the target particle or is captured by the incoming ion, but also of various dissociation processes. An experimental investigation of the schemes of the elementary processes and a determination of the cross sections of these processes is of great interest for the purpose of obtaining information concerning the mechanism of collisions in which molecules take part. A study of the processes for the simplest $H^+ - H_2$ case is important both in connection with its practical significance, and also because in this case it is apparently possible to analyze most fully the experimental data, since the possible states of the molecule and molecular ion of hydrogen are relatively few and are well known. We can expect that the theoretical calculations of the cross sections of the elementary processes whereby the charged states are changed in ion-molecular collisions will likewise be performed first for the simplest $H^+ - H_2$ case. At present there are no such calculations, if we disregard the estimating calculation of the capture of two electrons by a proton in a collision with an H_2 molecule[1].

The scheme of the possible changes of the charge state of the incoming particle upon collision is exceedingly simple. As a result of the collision, the proton may retain its charge state or be transformed into a fast atom by capturing one electron, or into a fast negative ion by capturing two electrons.

The scheme of the possible transitions that lead to the formation of ions from the hydrogen molecule is somewhat more complicated, and it is convenient to consider it by using the well known diagram of the interaction potential-energy curves for this system[2]. Figure 1 shows such curves for the ground state of the H_2 molecule ($^1\Sigma_g^+$), the ground state of the molecular H_2^+ ion ($1s\sigma_g$), the repulsion state of the H_2^+ ion ($2p\sigma_u$), and the Coulomb interaction of two protons ($H^+ + H^+$). Between the $2p\sigma_u$ and $H^+ + H^+$ curves there exist also many repulsion curves, corresponding

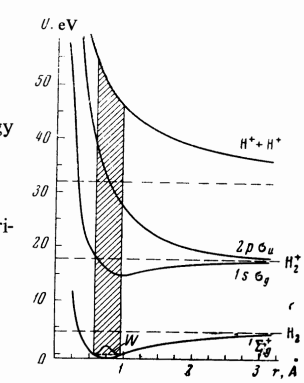

FIG. 1. Plots of the potential energy of the interaction against the internuclear distance for the hydrogen molecule H_2, the molecular hydrogen ion H_2^+, and two protons $H^+ + H^+$. The horizontal dashed lines show the energies of the states of H_2, H_2^+, and $H^+ + H^+$ at $r = \infty$.

to different excited electron states of the H_2^+ ion. However, for a qualitative analysis of the picture of the transitions connected with the realization of processes of the change of charge states, it is sufficient to consider the four curves shown in Fig. 1. Actually, the transition to any of the curves corresponding to electronic excitation of H_2^+ ion, just as a transition to the $2p\sigma_u$ curve, leads to dissociation of the H_2^+ ion into a hydrogen atom and a proton[1)]; the difference lies in the state of the hydrogen atom. Therefore, when considering the schemes and the cross sections of the processes in which the charge states are changed, we shall arbitrarily designate by the symbol $2p\sigma_u$ transitions not only to that state, but also to all the excited electronic states of the H_2^+ ion.

When the Franck-Condon law is satisfied, the electronic transitions are realized in the region of internuclear distances corresponding to the ground vibrational state of the H_2 molecule. In Fig. 1 this region is shown as a shaded strip, and the distribution function of the internuclear distances, calculated in the harmonic-oscillator approximation, is represented by the curve W(r).

Figure 1 illustrates transitions that lead to the formation of the ions H_2^+ and H^+ from the molecule target, and makes it possible to estimate the kinetic energies which these ions should acquire as a result of such transitions. The transition ${}^1\Sigma_g^+ \rightarrow 1s\sigma_g$ leads mainly to the formation of molecular ions H_2^+ in different vibrational states, and practically without transfer of kinetic energy. In the same transition, however, dissociation of the H_2^+ ion with formation of a hydrogen atom and a proton with very small kinetic energy, should occur on the part of the $1s\sigma_g$ curve which lies above the limit of the dissociation of the H_2^+ ion, and which corresponds to the smallest internuclear distances within the limits of the shaded region of Fig. 1. Another transition, ${}^1\Sigma_g^+ \rightarrow 2p\sigma_u$, is connected with the formation of a hydrogen atom and a proton, having an average kinetic energy $\sim$ 7 eV (at the maximum of the energy distribution). Finally, the transition ${}^1\Sigma_g^+ \rightarrow (H^+ + H^+)$ leads to the formation of two protons with average kinetic energy $\sim$9 eV. The schemes of the possible processes in which the charge states are changed in $H^+ - H_2$ collisions are listed in the table. In the designations for the cross sections of the processes indicated in the table, the upper indices correspond to the initial (1) and to the final (1, 0, or −1) charge states of the incoming particle, and the lower indices to the initial charge state of the target molecule (0) and to the particles produced from the molecule as a result of the collision (H_2^+, H, and H^+). It is seen from the table that in processes (1−3) the fast protons retain their charge state, in processes 4−6 they are transformed into fast atoms, and in process 7 they are transformed into fast negative ions. As a result of processes 1 and 4, slow molecular ions H_2^+ are produced in the gas, and realization of any of the remaining processes is connected with the formation of one or simultaneously two protons in the gas.

Processes in which the charge states change in H^+-H_2 collisions.

Number of process	Scheme of process*	Final state of the molecular system	Energy of slow ions, eV	Designation of the cross section of the process	Name of process
1	$\vec{H}^+ + H_2 \rightarrow \vec{H}^+ + H_2^+ + e$	$1s\sigma_g$	$\sim$0	$\sigma^{11}_{0H_2^+}$	Pure ionization
2a, 2b	$\vec{H}^+ + H_2 \rightarrow \vec{H}^+ + H + H^+ + e$	$\{1s\sigma_g$, $2p\sigma_u\}$	$\{\sim$0, $\sim$7$\}$	$\sigma^{11}_0(H, H^+)$	Ionization with dissociation
3	$\vec{H}^+ + H_2 \rightarrow \vec{H}^+ + H^+ + H^+ + e$	$H^+ + H^+$	$\sim$9	$\sigma^{11}_0(H^+, H^+)$	Double ionization
4	$\vec{H}^+ + H_2 \rightarrow \vec{H} + H_2^+$	$1s\sigma_g$	$\sim$0	$\sigma^{10}_{0H_2^+}$	Pure capture (charge exchange)
5a, 5b	$\vec{H}^+ + H_2 \rightarrow \vec{H} + H + H^+$	$\{1s\sigma_g$, $2p\sigma_u\}$	$\{\sim$0, $\sim$7$\}$	$\sigma^{10}_0(H, H^+)$	Capture with dissociation
6	$\vec{H}^+ + H_2 \rightarrow \vec{H} + H^+ + H^+ + e$	$H^+ + H^+$	$\sim$9	$\sigma^{10}_0(H, H^+)$	Capture with ionization
7	$\vec{H}^+ + H_2 \rightarrow \vec{H}^- + H^+ + H^+$	$H^+ + H^+$	$\sim$9	$\sigma^{1-1}_0(H^+, H^+)$	Double capture

*The fast particles $\vec{H}^+$, $\vec{H}$, $\vec{H}^-$ are marked with a superior arrow to distinguish them from the slow particles produced from the H_2 molecules.

The $H^+ - H_2$ collisions connected with a change of the charge states of the particles have been investigated before by many workers. However, all investigations, without exception, were based on registration of one of the particles, which changed its charge state after the collision: fast ($\vec{H}$, $\vec{H}^-$) or slow (H_2^+, H^+). This is why relatively little is known as yet concerning the cross sections of the elementary processes with change of the charge states in $H^+ - H_2$ collisions. Direct measurements were made only on the cross section of the double capture process (process 7 in the table). This process is the only way of producing fast negative $\vec{H}^-$ ions, and its cross section coincides with the total cross section for double capture σ^{1-1}, determined by measuring the total number of fast $\vec{H}^-$ ions. All other presently known cross sections—the total cross section σ^{10} for capture of one electron by a fast proton, the total cross sections $\sigma_{H_2^+}$ and σ_{H^+} for the production of H_2^+ ions and protons in the gas—are sums of cross sections of various elementary processes in which the charge states are changed[2)].

Much greater possibilities may be afforded by a method of investigating elementary collision acts, which ensures a simultaneous analysis of the final charge states of the fast particles and of the slow ions. The particles taking part in the same collision act are separated with the aid of coincidences. Such a procedure of investigating the elementary collisions of ions and atoms was introduced first in our paper[3]. In the present investigation this procedure was improved, making it possible to use it for the study of collisions in which molecules take part.

1)The potential-energy curves of certain excited electronic states of H_2^+ ion have rather shallow minima ($\lesssim$ 0.2eV) in the region of large internuclear distances ($r \gtrsim 5$Å) [2]. However, in the considered transitions from the initial state ${}^1\Sigma_g^+$ of the H_2 molecule ($r_0 \approx 0.8$Å) the probability of formation of a stable H_2^+ ion in an excited electronic state is negligibly small.

2)Together with the processes indicated in the table, one more elementary process is possible: $\vec{H}^+ + H_2 \rightarrow \vec{H}^+ + H^+ + H^-$; its cross section can be determined directly by registering one of the particles—the slow negative ions H^-, since the dissociation $H_2 \rightarrow H^+ + H^-$ is the only source of the H^- ions in $H^+ - H_2$ collisions. Experimental estimates of the total cross section σ_{H^-} for the production of slow H^- ions, given in the present paper, have shown that σ_{H^-} does not exceed 3×10^{-20} cm^2, which is lower by more than one order of magnitude than the cross section of any of the processes listed in the table (see Figs. 4 and 5 below).

MEASUREMENT PROCEDURE

It is seen from the table that in order to determine the cross sections of processes that differ in the scheme whereby the charge states of the particles are changed, it is necessary to be able to mass-analyze and register all the atomic particles produced in each act of collision $H^+ - H_2$. To separate the processes having the same scheme of charge-state variation, but connected with transitions of the target molecule to different final electronic states ($1s\sigma_g$ or $2p\sigma_u$ and other excited states of the H_2^+ ion, see processes 2a and 2b, 5a and 5b), it is necessary in addition to analyze the kinetic energies of the protons, which are the products of the dissociation of H_2^+. Experiments aimed at solving the foregoing problems were performed with a setup described in our paper[4]. In this setup, a narrow monokinetic beam of fast protons was directed to a collision chamber filled with hydrogen. After passing through the collision chamber, the fast particles ($\vec{H}^+$, $\vec{H}$, $\vec{H}^-$) were charge-analyzed and counted. The slow ions (H_2^+, H^+) produced in the gas were extracted from the collision chamber by an electric field, mass-analyzed in a magnetic field, and also counted. The fast and slow particles—partners of the same collision act—were separated with the aid of a delayed-coincidence circuit, which made it possible to compensate for the difference between the times of flight of the fast and slow particles from the place of collision to the corresponding detectors.

The cross sections of the different elementary processes with change of charge states were determined as follows. First, the method described in[5] for the analysis of the composition of the slow ions produced in the gas (without the use of coincidences) was used to determine the total cross sections for the production of the molecular ions H_2^+ and the protons $\sigma_{H_2^+}$ and σ_H^+. Coincidences were then used to resolve the total cross section $\sigma_{H_2^+}$ into its component parts, namely the cross section for the pure ionization process (process 1) and the pure capture process (process 4):

$$\sigma_{H_2^+} = \sigma_{0H_2^+}^{11} + \sigma_{0H_2^+}^{10} \tag{1}$$

The ratio of the cross sections of processes 1 and 4 was determined directly from the number of coincidences of the slow ions H_2^+ with the fast protons $\vec{H}^+$ and with the fast atoms $\vec{H}$, respectively.

The total cross section for the production of the slow protons, σ_H^+, cannot be resolved into components in such a simple manner. The reason is that the cross sections of the elementary processes in which one proton (processes 2 and 5) and two protons (processes 3, 6 and 7) are produced enter in the cross section σ_H^+ with different coefficients:

$$\sigma_{H^+} = \sigma_{0\,(H,\,H^+)}^{11} + 2\sigma_{0\,(H^+,\,H^+)}^{11} + \sigma_{0\,(H,\,H^+)}^{10} + 2\sigma_{0\,(H^+,\,H^+)}^{10} + 2\sigma_{0\,(H^+,\,H^+)}^{1-1}. \tag{2}$$

Thus, the contribution of the cross sections of the different elementary processes to the cross section σ_{H^+} depends on the number of the protons produced in these processes. On the other hand, in the investigation of processes by a coincidence technique, the process in which either one or two protons are formed leads to the registration of only one coincidence with the corresponding fast particle. Therefore the first problem that can be solved with the aid of coincidences is the determination of the ratio of the cross sections of the processes leading to the formation of protons in the gas but corresponding to different charge states of the fast particles after the collision (1, 0, and −1):

$$[\sigma_{0\,(H^+,\,H^+)}^{11} + \sigma_{0\,(H,\,H^+)}^{11}] : [\sigma_{0\,(H,\,H^+)}^{10} + \sigma_{0\,(H^+,\,H^+)}^{10}] : \sigma_{0\,(H^+,\,H^+)}^{1-1}. \tag{3}$$

The next problem is the separation of the processes corresponding to the same charge state of the fast particles, but leading to the formation of one and two protons. Such processes, in ionization, are processes 2 and 3, and in capture of an electron by an incoming proton—processes 5 and 6. The sums of the cross sections of processes 2, 3 and 5, 6 form respectively the first and second terms of (3). The separation of these processes is best carried out on the basis of an analysis of the amplitude spectrum of the pulses produced at the output of the slow-ion detector in the registration of one proton and simultaneously two protons. As the standard spectrum for the registration of the individual protons we used the spectrum produced in the presence of a weak drawing electric field in the collision chamber ($\lesssim$ 3V/cm), when only single protons separated by the mass analyzer can fall on the detector. The pulse amplitude spectrum in the registration of proton pairs was obtained by registering the coincidences between the protons extracted from the collision chamber and the fast negative hydrogen ions $\vec{H}^-$. The $\vec{H}^-$ ions appear as a result of the double capture of electrons (process 7), which is known to lead to the formation of only proton pairs in the gas. In this case, the pulse-amplitude spectrum was measured in the presence of a strong drawing electric field (300 V/cm), which ensured, owing to the high-aperture ion-optical system, the extraction of all the protons produced in the chamber, and prevented growth of the number of registered coincidences with further increase of the drawing field.

The separation of the processes 2 and 3 in ionization and of the processes 5 and 6 in capture of one electron by an incoming proton was carried out in the presence of a drawing field of 300 V/cm in the collision chamber. Measurement of the number of coincidences of the slow protons with the fast protons in ionization and with fast atoms in capture was carried out at two levels of pulse discrimination in the channel registering the slow protons. The lower discrimination level was chosen such as to ensure practically the same efficiency of registration of single protons and of proton pairs. The higher discrimination level was chosen in that region of the pulse amplitude spectrum, in which the efficiency of registration of the proton pairs exceeded noticeably (by not less than a factor of two) the efficiency of registration of the single protons. A comparison of the actually measured ratio of the number of coincidences at different discrimination levels with the known ratios for the standard spectra has made it possible to determine the ratio of the cross sections of processes 2 and 3 or of the cross sections of processes 5 and 6. Thus, the described procedure made it possible to determine the cross sections of all the processes that have different variations of the charge states of the colliding particles and enter in the total cross section σ_{H^+} for the production of slow protons, (expression (2)).

One more methodological problem was to determine the cross sections of processes that have the same scheme of variation of the charge states, but are connected with transitions to different final electronic states of the molecular system—$1s\sigma_g$ and $2p\sigma_u$ (processes 2a and 2b, and also 5a and 5b). The solution of this problem is facilitated by the fact that the kinetic energy of the protons produced as a result of the dissociation of the H_2^+ ion in the transition to the state $1s\sigma_g$ differs strongly from the energy corresponding to the dissociation in the transition to $2p\sigma_u$ and higher electronic states of the H_2^+ ion (~ 0 and ~ 7 eV, see the table). The difference of the kinetic energies causes practically all the protons produced in transitions in the state $1s\sigma_g$ to be extracted from the collision chamber even at electric drawing fields 1—3 V/cm, and to enter the detector. This is manifest by the presence of a plateau on the plot of the slow-proton line intensity against the drawing field in the 1—3 V/cm region. In such electric fields, only a small fraction of the protons produced in transitions to other electronic states of H_2^+ fall into the detector. (The growth of the proton-line intensity, which is connected with the efficient extraction from the collision chamber of the protons produced as a result of the transitions to $2p\sigma_u$ and higher excited states, begins with fields ~ 10 V/cm and stops only in fields ~ 250 V/cm.) The intensity of the line of molecular ions H_2^+, the overwhelming part of which has very low kinetic energies, saturates likewise in electric fields 1—3 V/cm. The total cross section for the production of protons that appear in transitions to the state $1s\sigma_g$, $\sigma_{H^+ | 1s\sigma_g}$, was determined by comparing the intensity of the proton line, which saturates in drawing fields 1—3 V/cm, with the line intensity of the H_2^+ ions, whose production cross section $\sigma_{H_2^+}$ was measured by analyzing the composition of the slow ions. The division of the cross section $\sigma_{H^+ | 1s\sigma_g}$ into components connected with transitions to the state $1s\sigma_g$ with subsequent dissociation in ionization (process (2a)), $\sigma^{11}_{0(H, H^+) | 1s\sigma_g}$ and in electron capture (process 5a), $\sigma^{10}_{0(H, H^+) | 1s\sigma_g}$, was effected by measuring the number of coincidences of the slow protons extracted by the 3 V/cm field with the fast protons and fast atoms. In a drawing field of 3 V/cm, the protons produced in the transition to the $1s\sigma_g$ state may be separated from the protons produced in transitions to higher electronic states of the H_2^+ ions, by using their time of flight from the collision chamber to the detector. Figure 2 shows the dependence of the number of coincidences, N_{12}, on the delay time τ_3 introduced into the channel that registered the fast particles after the collision. The maximum of the curve, which lies at larger delay times, corresponds to protons with initial energy ~ 0 eV. As expected, this maximum vanishes practically completed in the case of a weak decelerating field 1 V/cm (dashed line in Fig. 2), whereas the maximum connected with the protons having an initial energy 7—9 eV remains practically unchanged. The arrows in Fig. 2 show the limits of the "time window" separated by the coincidence circuit; this window was used to measure the relative values of the cross sections of the processes 2a and 5a with the

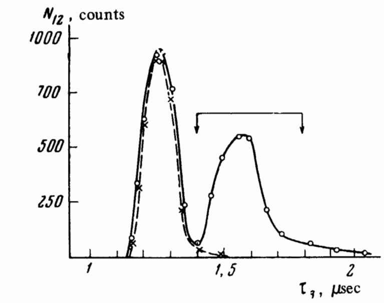

FIG. 2. Dependence of the number of coincidences between slow protons and fast hydrogen atoms on the pulse delay time in the channel for the registration of the fast atoms. The electric field drawing the protons in the collision chamber is 3 V/cm (solid curve), and that decelerating the protons is 1 V/cm (dashed curve). The energy of the fast incoming particles is $T_0 = 20$ keV. The resolving time of the coincidence circuit is $\tau_p = 0.1$ μsec.

aid of coincidences (the width of this window is 0.4 μsec). The cross section of the process 2b was determined as the difference between the cross section of the process 2, which enters in expression (2), and the cross section of the process 2a. Analogously, the cross section of the process 5b was determined as the difference between the cross section of the process 5, which also enters in expression (2), and the cross section of the process 5a.

Thus, the procedure described above made it possible to determine the absolute values of the cross sections of all the processes indicated in the table. Cross sections exceeding 1×10^{-18} cm^2 were measured with an accuracy $\pm 10\%$, while smaller cross sections were accurate to $\pm 20\%$.

MEASUREMENT RESULTS AND THEIR DISCUSSION

1. Total Cross Sections for the Production of Slow Ions

Figure 3 shows the total cross sections for the production of molecular ions $\sigma_{H_2^+}$ and protons σ_{H^+}, obtained by analyzing the composition of the ions produced in the gas. The cross section $\sigma_{H_2^+}$ has a maximum at an incident-proton energy $T_0 \approx 6$ keV; this maximum reaches $\sim 9 \times 10^{-16}$ cm^2. The cross section for proton production, determined by the dissociation processes, is smaller in the entire investigated energy interval. The maximum of the cross section σ_{H^+} lies at a higher energy of the incoming protons ($T_0 \approx 15$ keV). This is natural, inasmuch as the processes connected with dissociation of the molecular ion H_2^+ or with the formation of two protons require a larger energy consumption than processes involving the formation of H_2^+ ions in the stable state. The total cross

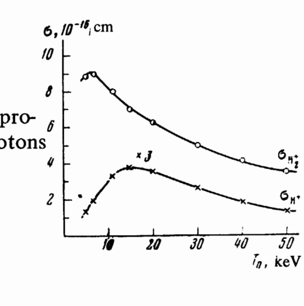

FIG. 3. Total cross sections for the production of molecular ions ($\sigma_{H_2^+}$) and protons (σ_{H^+}).

sections for the production of molecular ions, $\sigma_{H_2^+}$, shown in Fig. 3, are in good agreement with the cross sections obtained in[6,7]. The dependence of the total proton-production cross section σ_{H^+} on the energy of the incoming protons is similar to that given in[6,7]. However, the value of the cross section σ_{H^+} greatly exceeds that obtained in[6,7], and in the maximum at $T_0 = 15$ keV it reaches 1.2×10^{-16} cm^2, amounting to $\sim 15\%$ of the cross section $\sigma_{H_2^+}$. This discrepancy with the data of[6,7] is apparently connected with the insufficient efficiency, with which the produced protons having appreciable kinetic energies as a result of dissociation of the molecular ion from different collisional electronic states were gathered in[6,7].

2. Cross Sections of the Elementary Processes in which the Charge States are Changed

a) Production of molecular ions H_2^+. The cross sections of the pure-capture processes (charge exchange, process 4 in the table), $\sigma^{00}_{1H_2^+}$ and of pure ionization with removal of one electron (process 1), $\sigma^{11}_{0H_2^+}$, which are components of the total cross section for the production of the molecular ions $\sigma_{H_2^+}$, are shown in Fig. 4. This figure shows that in the greater part of the investigated energy interval the main process leading to the formation of molecular ions H_2^+ is pure capture. This process turns out to predominate in the region $T_0 \lesssim 30$ keV and determines the position of the maximum of the total cross section $\sigma_{H_2^+}$ at $T_0 \approx 6$ keV. However, with increasing energy of the incoming protons, the role of the ionization process increases, and at $T_0 \approx 45$ keV the cross sections of both processes become the same. It should be expected that the cross section of pure ionization $\sigma^{1}_{01H_2^+}$ reaches a maximum value at an incoming-proton energy $T_0 \approx 70$ keV, at which the total cross section for the production of free electrons for the collisions $H^+ - H_2$ has a maximum[6,7].

b) Proton production. The cross sections of the elementary processes leading to the production of protons are shown in Fig. 5. Of all the proton-production processes, the largest cross section is possessed by capture of one electron with dissociation of the molecular system into a hydrogen atom and a proton. The principal role is played here by the dissociation accompanying the transitions to repulsive states of the H_2^+ ion ($2p\sigma_u$ and the excited states lying above it), namely process 5b. It is interesting to note that the

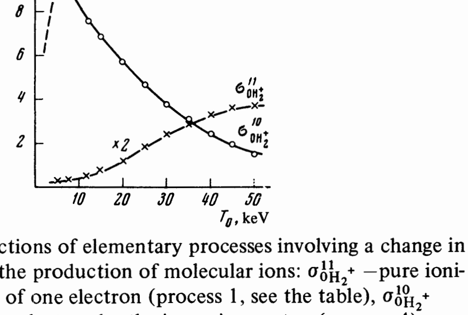

FIG. 4. Cross sections of elementary processes involving a change in the charge states in the production of molecular ions: $\sigma^{11}_{0H_2^+}$ —pure ionization with removal of one electron (process 1, see the table), $\sigma^{10}_{0H_2^+}$ —pure capture of one electron by the incoming proton (process 4).

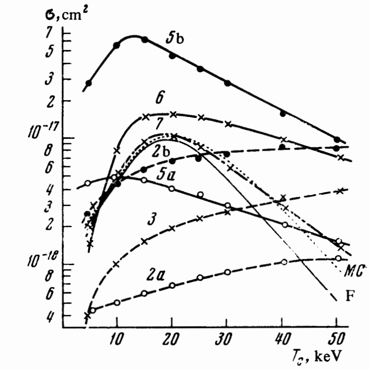

FIG. 5. Cross sections of elementary processes involving a change of the charge states in production of protons. The solid curves denote processes connected with the capture of one electron by an incoming proton, dashed—process connected with the capture of two electrons by the incoming proton (double capture), dotted—processes connected with ionization. The electronic states of the molecular target after the collision are: ○—$1s\sigma_g$; ●—$2p\sigma_u$ and the excited electronic states of the ion H_2^+; ×—$H^+ + H^+$. Data on the cross sections of the double-capture process: F—by Fogel' et al. [12], MC—by McClure [13]. The figures next to the curves correspond to the numbers of the processes in the table.

cross section for the process of dissociation in capture of one electron with a transition to the state $1s\sigma_g$ (process 5a), $\sigma^{10}_{0(H,H^+)|1s\sigma_g}$, is smaller by practically one order of magnitude than the cross section of the analogous process with transition to repulsive states (process 5b), $\sigma^{10}_{0(H,H^+)|2p\sigma_u}$. The next in the size of the cross section is the capture of one electron with ionization (process 6), which leads to simultaneous production of two protons. The processes of capture with ionization were first observed experimentally in our investigations[8-11], by the coincidence method, in collisions between ions and atoms of a gas. It was established that in ion-atom collisions the processes of capture with ionization play a predominant role in the production of multiply charged ions from target atoms. The results of the present investigation show that the process of capture with ionization plays a predominant role in the formation of protons in ion-molecular collisions, at least in the incident-proton energy region $T_0 \gtrsim 30$ keV. Indeed, although the cross section for the capture with ionization $\sigma^{10}_{0(H^+,H^+)}$ at $T_0 \gtrsim 30$ keV is approximately 1.5 times smaller than the cross section for capture with dissociation $\sigma^{10}_{0(H^+,H^+)|2p\sigma_u}$, each act of capture with ionization leads to the formation of two protons, whereas a capture with dissociation leads to the formation of one proton.

The next process in order of decreasing cross section, which also leads to formation of two protons, is double capture (process 7). As noted above, the capture of two electrons by a proton in hydrogen is the only process whose cross section can be measured without using coincidences. Figure 5 shows the cross sections of this process, measured in[12,13] by registering fast negative hydrogen ions produced as a result of capture of two electrons by the incoming proton in $H^+ - H_2$ collisions. The values of the cross section $\sigma^{1-1}_{0(H^+,H^+)}$, obtained in the present paper, are in satisfactory agreement with the values given by McClure[13] in the entire investigated energy interval, and with the data obtained by Fogel' et al.[12] in the energy region $T_0 < 30$ keV. A theoretical calculation of the cross section of the double capture process[1] leads to a discrepancy with the experimental data by a factor of several times in the entire interval $T_0 = 5-50$ keV.

The slow-proton production processes considered above, which are connected with the capture of one or two electrons by the incoming fast proton, have cross section-maxima at relatively low energies $T_0 = 12-16$ keV. The appreciable contribution of these processes to the total proton-production cross section σ_{H^+} causes the cross section σ_{H^+} also to have a maximum at $T_0 \approx 15$ keV.

Among the pure ionization processes, the largest cross section is possessed by the process of ionization with dissociation into a hydrogen atom and a proton from the repulsive states (process 2b)—$\sigma^{11}_{0(H,\,H^+)|2p\sigma_u}$. In pure ionization, as in the capture of one electron, the dissociation of the H_2^+ ion in transitions to the state $1s\sigma_g$ (process 2a) makes a relatively small contribution. The cross section for ionization with removal of two electrons, $\sigma^{11}_{0(H^+,\,H^+)}$ (process 3) turns out to be smaller by two or three times than the cross section for the ionization with dissociation, $\sigma^{11}_{0(H,\,H^+)|2p\sigma_u}$ (process 2b) in the entire investigated incoming-proton energy interval. All the processes of pure ionization have a maximum of the cross section at an incoming-proton energy $T_0 > 50$ keV, and therefore the contribution of these processes to the production of slow protons increases with increasing T_0 in the investigated interval.

The obtained data on the cross sections make it possible to assess the relative role of the elementary processes connected with pure ionization, with capture of one electron, and with capture of two electrons in the formation of slow protons in $H^+ - H_2$ collisions. Figure 6 shows the relative probabilities of the processes of production of protons from H_2 molecules in pure ionization (11), capture of one electron (10), and of two electrons (1 – 1) by an incoming fast proton. We see that, just as in the production of molecular ions H_2^+, the role of the pure ionization processes increases with increasing T_0 in the case of proton production. However, the probability of proton production in the capture of an electron by a fast proton remains a maximum in the entire investigated T_0 interval.

3. Probabilities of Transitions of the Molecular System to Different Electronic States

As shown by the experimental data given in Figs. 4 and 5, the largest cross sections are possessed by those charge-change processes which are connected with the production of the molecular ions H_2^+. This means that the most probable transition in $H^+ - H_2$ collisions is the transition ${}^1\Sigma_g^+ \rightarrow 1s\sigma_g$. Some of the transitions on the $1s\sigma_g$ curve correspond, at the smallest internuclear distances in the target molecule, to cases in which the energies of the produced H_2^+ ions exceed the limit of H_2^+ dissociation. In this case, the

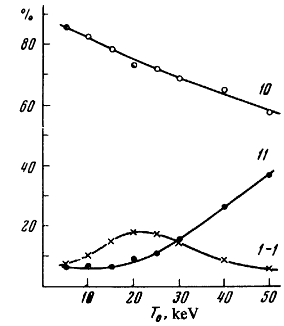

FIG. 6. Relative probability of proton production from hydrogen molecules in pure ionization (11), capture of one electron (10), and capture of two electrons (1 – 1) by a fast incoming proton.

H_2^+ ion dissociates and protons having a very small kinetic energy are produced. The relative probability of the dissociation of the H_2^+ ion in transitions to the $1s\sigma_g$ state, within the framework of the Franck-Condon principle, was calculated by Dunn[14] and should amount to 2.8%. Measurements of the relative yield of the atomic and molecular ions, H^+ and H_2^+ in the ionization of hydrogen molecules by electrons having an energy 30 eV, in which only ionization transitions to the $1s\sigma_g$ state are possible, yielded a smaller value, namely 0.58% in the paper of Bauer and Beach[15] and 1.3% in the paper of Shaeffer and Hastings[16]. It is of interest to compare these data with data on the ratio of the proton and H_2^+ ion yield obtained in the present paper for the transitions ${}^1\Sigma_g^+ \rightarrow 1s\sigma_g$ in $H^+ - H_2$ collisions. In spite of the noticeable discrepancy between the data of different experiments for electron impact and the calculated data, such a comparison can be used to determine qualitatively whether the Franck-Condon principle holds in ion-molecular collisions. Indeed, it should be expected that in ${}^1\Sigma_g^+ \rightarrow 1s\sigma_g$ transitions with violation of the Franck-Condon principle, the relative probability of the dissociation should increase greatly.

Figure 7 shows the ratio of the yield of the protons and of H_2^+ ions in the $H^+ - H_2$ collisions connected with the transition ${}^1\Sigma_g^+ \rightarrow 1s\sigma_g$. This ratio, as shown by Fig. 7, depends little on the energy of the incoming protons in the investigated interval. The ratio amounts to ~0.8%, which is close to the mean value of the ${}^1\Sigma_g^+ \rightarrow 1s\sigma_g$ transitions in electron impact, which follows from the experimental data[15,16], and is also smaller than the calculated value obtained in[14]. This result gives grounds for assuming that in the investigated interval of incoming-proton energies the transitions between the electronic states of the target molecule in $H^+ - H_2$ collisions satisfy the Franck-Condon principle.

The availability of data on the cross sections of all the elementary processes in which the charge states

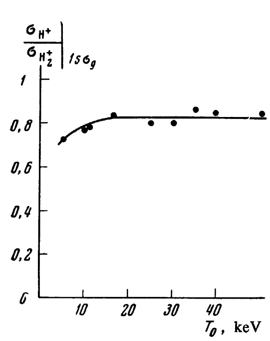

FIG. 7. Ratio of the probabilities of proton and molecular-ion (H_2^+) production in collisions with the electronic transition ${}^1\Sigma_g^+ \rightarrow 1s\sigma_g$ (in percent).

change makes it possible to determine the total cross sections of the transitions to different electronic states of the molecular system. These data are shown in Fig. 8. As expected, the probability of the transition decreases with increasing energy loss needed for its realization, and turns out to be smallest for the state $H^+ + H^+$. It is interesting to note that the relative probability of the transitions to higher electronic states (Fig. 8b) reaches a maximum value in the incoming-proton energy region $T_0 = 15-25$ keV, when the velocities of the protons are close to the velocities of the electrons in the molecule $v \approx e^2/\hbar$. This effect is analogous to the presence of maxima of the relative probability of production of multiply charged ions in collisions of protons with multi-electron atoms in the velocity region $v \approx e^2/\hbar$ [10,11]. A general conclusion that can be drawn from the indicated data on the positions of the maxima of the relative probability of the inelastic processes is that the average excitation energy of the quasimolecule produced in the collision is maximal when the nuclei have a velocity close to the velocities of the electrons in the shells of the interacting particles.

The results show that an investigation of the elementary collision acts with simultaneous analysis of the fast and slow particles, separated by a coincidence procedure, makes it possible to expand qualitatively the amount of information regarding processes in which the charge states are changed, even in such a simple case as $H^+ - H_2$. Instead of the procedure used in numerous investigations performed to date, that of measuring the total cross sections, which characterize a summary effect of a large number of elementary processes in which the charge states change, it becomes possible to study directly the schemes of each of these processes and to determine their cross sections. In addition, the analysis of the kinetic energies of the dissociation products, introduced in the present paper, makes it possible to determine the probabilities of the transitions of the molecular target into various electronic states resulting from the realization of any given elementary process connected with ionization of the target or with capture of an electron by an incoming fast particle.

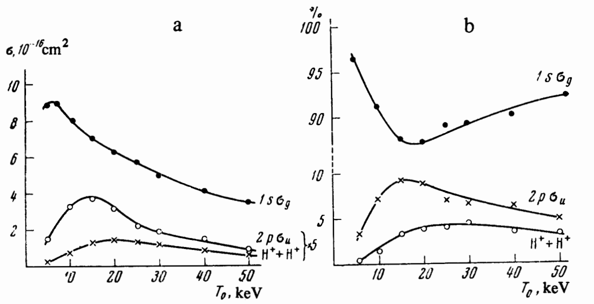

FIG. 8. Total probabilities of the transition of a molecular target, after collision, to various electronic states: a—absolute cross sections, b—relative probabilities.

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