ELECTRON CAPTURE AND LOSS BY FAST HYDROGEN ATOMS PASSING THROUGH MOLECULAR GASES

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The cross sections for electron loss σ_{01} and capture σ_{0-1} by hydrogen atoms in CO, H_2, N_2, and O_2 gases were measured. The structure of the energy dependence curves, $\sigma_{01}(\epsilon)$ and $\sigma_{0-1}(\epsilon)$, is explained using the adiabatic Massey criterion.

INTRODUCTION

ELECTRON capture and loss on collisions of 5—40 keV hydrogen atoms with inert-gas atoms and molecules of H_2, N_2, and O_2 were dealt with in our earlier papers.[1-2] No structure was found in the energy dependences of the cross sections, $\sigma_{01}(\epsilon)$ and $\sigma_{0-1}(\epsilon)$, for any of the atom-atom and atom-molecule pairs. Some of the $\sigma_{0-1}(\epsilon)$ curves had a maximum whose position was determined by the adiabatic Massey criterion. The quantity a which occurs in this criterion had a value of ≈ 3 Å for $H^0 \rightarrow H^-$ processes in various gases. A similar value of a for electron capture by other fast atoms was found by Fogel'.[3]

Electron loss and capture by hydrogen atoms in CO and H_2 gases have also been investigated by American workers.[4-6] They measured the cross section σ_{01} accurately (error of 2—3%) and used small energy intervals (about 1 keV) in their work. These authors found structure in the $\sigma_{01}(\epsilon)$ curves for CO and H_2 and suggested a reason for this. Their explanation is based on the assumption that electron loss by hydrogen atoms in collisions with gas molecules is a two-stage process. In the first stage an electron is removed from a hydrogen atom and carries away an energy proportional to the hydrogen atom energy. In the second stage the free electron is captured by a gas molecule, forming a stable or unstable negative molecular ion. Since capture of free electrons by gas molecules obeys the Franck-Condon principle, the dependences of the cross sections for such capture on the electron energy are of resonance type. According to the American writers the structure of these curves is due to superposition of resonance curves $\sigma''_{01}(\epsilon)$, representing capture of free electrons by gas molecules, on smooth $\sigma'_{01}(\epsilon)$ curves representing electron loss and the electron transition to states with a continuous energy spectrum. To check this hypothesis the American workers used a mass spectrometer to analyze slow negative ions formed on passage of fast hydrogen atoms through carbon monoxide. CO^- ions were found, as well as O^- and C^- ions formed by dissociation of excited CO^- ions.

Bukhteev et al[7] studied electron loss by fast K, Rb, and Cs atoms in O_2 and Cl_2 gases. Mass-spectrometric analysis of the slow negative ions showed the presence of O_2^- ions and a few O^- ions in the oxygen and mainly Cl^- ions with a very small amount of Cl_2^- in the chlorine. Bukhteev et al explained the presence of negative ions by electron capture from fast alkali atoms.

The physical meaning of the American workers' hypothesis is not clear and the present authors favor the explanation given by Bukhteev et al.

The present paper reports measurements of the cross sections σ_{01} for electron loss by hydrogen atoms in CO, H_2, N_2, and O_2 gases. The observed structure of the $\sigma_{01}(\epsilon)$ curves is explained using the adiabatic Massey criterion and assuming that the electrons are captured by gas molecules. The cross sections σ_{0-1} for electron capture by hydrogen atoms in CO, N_2, and O_2 gases were also measured and the structure of the $\sigma_{0-1}(\epsilon)$ curves accounted for, again on the basis of the adiabatic Massey criterion. The apparatus and experimental technique have been described in detail in earlier work.[1,2]

RESULTS AND DISCUSSION

a) Electron loss. Figure 1 gives the $\sigma_{01}(\epsilon)$ curve for the process $H^0 \rightarrow H^+$ in CO. Each experimental point represents an average of five measurements. The random errors ranged from

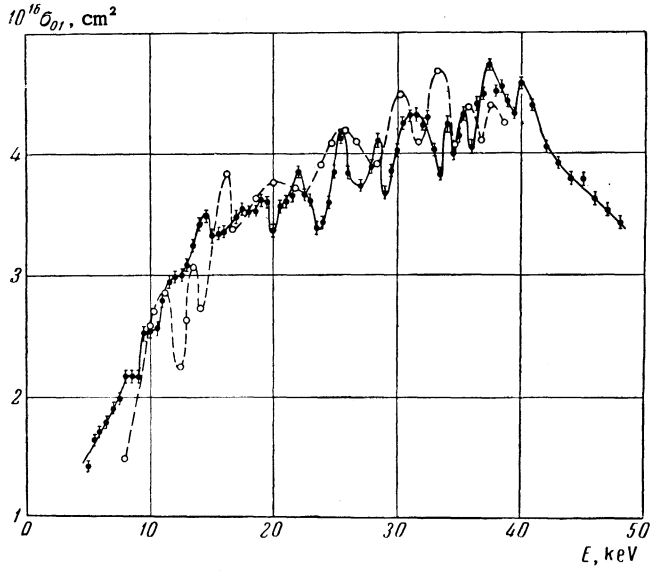

FIG. 1. Cross sections for electron loss in CO: ●—our results; o—Donahue and Hushfar's data.[4]

1 to 3%, depending on the current in the primary beam, pressure in the collision chamber, and the magnitude of the cross section. The same figure shows the $\sigma_{01}(\epsilon)$ curve obtained by Donahue and Hushfar.[4] Although the structure details of the two curves do not coincide there is no doubt about the reality of the structure itself.

To explain the structure of the $\sigma_{01}(\epsilon)$ curve for CO we shall assume that some of the electrons are lost by hydrogen atoms in the process

$$H + CO \rightarrow H^+ + CO^-, \quad (I)$$

which produces stable CO^- ions.

Apart from the above process, electrons can be captured by CO molecules and the resultant unstable CO^- ions may dissociate:

$$H + CO \rightarrow H^+ + CO^{-*} \rightarrow H^+ + C^* + O^-, \quad (II)$$
$$H + CO \rightarrow H^+ + CO^{-*} \rightarrow H^+ + C^- + O^*, \quad (III)$$
$$H + CO \rightarrow H^+ + CO^{-*} \rightarrow H^+ + C^* + O^* + e. \quad (IV)$$

In the above three processes the neutral products (O and C atoms) can be formed in both the ground and the excited states. Resonance defects of these processes can be calculated from

$$\Delta E_1 = S(CO) - V_I(H), \quad (1)$$
$$\Delta E_2 = -[V_I(H) + D(CO) - S(O) + E(C)], \quad (2)$$
$$\Delta E_3 = -[V_I(H) + D(CO) - S(C) + E(O)], \quad (3)$$
$$\Delta E_4 = S(CO) - [V_I(H) + D(CO) + E(C) + E(O)], \quad (4)$$

where S(CO), S(C), and S(O) are the electron affinities of the CO molecule and the C and O atoms; $V_I(H)$ is the ionization potential of the hydrogen atom; D(CO) is the dissociation energy of the CO molecule;[8] E(C) and E(O) are the excitation energies of the C and O atoms.[9]

According to the adiabatic Massey criterion, a maximum on the $\sigma(v)$ curve for an atomic collision process occurs at a velocity v_{max} given by

$$a|\Delta E|/hv_{max} \approx 1, \quad (5)$$

where a is the distance over which interaction forces between the colliding particles are acting; ΔE is the resonance defect; h is Planck's constant. Assuming that the quantity a is the same for processes I—IV, we find from Eq. (5) that $v_{max} \sim |\Delta E|$.* For all maxima on the $\sigma_{01}(\epsilon)$ curve in Fig. 1 we can find the ratios of the velocities corresponding to the i-th maximum and that corresponding to the first maximum, $v_{i\,max}/v_{1\,max}$. The adiabatic criterion and the constancy of a for all the four processes I—IV give

$$v_{i\,max}/v_{1max} = \Delta E_i/\Delta E_1, \quad (6)$$

where ΔE_i and ΔE_1 are resonance defects of processes responsible for the i-th and first maxima respectively.

The values of $\Delta E_i/\Delta E_1$ depend on which process is responsible for the first maximum. If the first maximum is due to process I, i.e., if we assume that stable CO^- ions can exist, then the values of $\Delta E_i/\Delta E_1$ are those listed in the fourth column of the adjoining table. Each number in that column represents an average value of $\Delta E_i/\Delta E_1$ for closely spaced maxima. Comparison of the values of $v_{i\,max}/v_{1\,max}$ (third column of the table) with the $\Delta E_i/\Delta E_1$ values shows that Eq. (6) is not satisfied. However, Eq. (6) is obeyed if it is assumed that the first maximum is due to the process II in which C atoms are not excited ($\Delta E = -21.74$ eV). It follows that the structure of the $\sigma_{01}(\epsilon)$ curve for $H^0 \rightarrow H^+$ in CO can be explained by assuming that electron loss by hydrogen atoms (formation of free electrons) is accompanied by electron capture by CO molecules and the resultant unstable CO^- ions dissociate. Maxima on the curve in Fig. 1 occur at velocities which are in agreement with the adiabatic Massey criterion. The average value of the quantity a in the criterion is found to be 2.4 Å for the processes II—IV, i.e., it is close to the value $a \approx 3$ Å for electron capture by fast atoms.[3] The conclusion that stable CO^- ions do not exist agrees with experiments on the $CO^+ \rightarrow CO^-$ proc-

*The quantity a is approximately the same for the processes $A^+ \rightarrow A^-$ and $A^0 \rightarrow A^-$ with particles in either the ground and/or the excited states.[3]

ε_{max}, keV	10^{-8}v, cm/sec	v_{imax}/v_{1max}	$\Delta E_i/\Delta E_1$	$\Delta E_i/\Delta E_1$	Processes
8.5	1.28	1	1	1.03	2; 3
10	1.39	1.09	1.61	1.1	2; 3; 4
12.0	1.52	1.19	1.73	1.2	2; 3
14.5	1.68	1.31	1.8	1.35	2
17.5	1.85	1.44	1.91	1.43	2; 3
19	1.92	1.5	2.16	1.52	2; 3
22	2.06	1.62	2.24	1.67	3; 4
25.5	2.22	1.74	2.27	1.76	4
28.5	2.35	1.84	2.42	1.84	4
31.5	2.47	1.93	2.56	1.93	4
34.0	2.57	2.01	2.63	2.0	4
35.5	2.62	2.05	2.82	2.04	4
37.5	2.70	2.11	2.91	2.12	4
40.0	2.78	2.17	3.5	2.20	4

esses carried out previously in our laboratory.[10] These experiments show that if the process $CO^+ \rightarrow CO^-$ does occur, then its cross section is less than 10^{-22} cm^2. This result contradicts Donahue and Hushfar's report[6] that CO^- ions were found in the spectrum of slow ions formed on passage of hydrogen atoms through CO.

There is further confirmation of our interpretation of the $\sigma_{01}(\epsilon)$ structure. Figure 1 shows that the structure disappears at energies lower than 8.5 keV and higher than 40 keV. This is because the maximum at 8.5 keV corresponds to the process II with the smallest resonance defect and the maximum at 40 keV corresponds to the process IV with the largest resonance defect.

The structure maxima on the $\sigma_{01}(\epsilon)$ curve given by Donahue and Hushfar[4] correspond also to velocities that obey the adiabatic Massey criterion if it is assumed that the first maximum corresponds to the process II. However, since the positions of the maxima reported by Donahue and Hushfar[4] are shifted somewhat toward higher energies as compared with our curve (Fig. 1), the average value of a in the Massey criterion obtained from the data of Donahue and Hushfar is 2.8 Å.

Figure 2 shows the $\sigma_{01}(\epsilon)$ curve for $H^0 \rightarrow H^+$ in H_2. The same figure gives the $\sigma_{01}(\epsilon)$ curve obtained by Curran and Donahue.[5] Our $\sigma_{01}(\epsilon)$ curve does not have the pronounced maximum at 15 keV which was detected by the American workers. Our data show only a small inflection in the 20 keV region. The existence of a maximum at 7 keV could not be confirmed since the accuracy of our measurements at hydrogen atom energies lower than 10 keV was insufficient to reveal the structure of the $\sigma_{01}(\epsilon)$ curve.

The structure of the $\sigma_{01}(\epsilon)$ curve for the $H-H_2$ pair can be explained in the same way as for the H—CO pair. The arrows in Fig. 2 indicate the positions of the maxima that represent capture of electrons by H_2 molecules, followed by dissociation of the H_2^- ions into H^- and H^0 in the ground or an excited state. In calculations of the energies corresponding to the maxima on the $\sigma_{01}(\epsilon)$ curve the quantity a was assumed to be the same as in the process $H^0 \rightarrow H^+$ in CO, i.e., $a \approx 2.4$ Å.

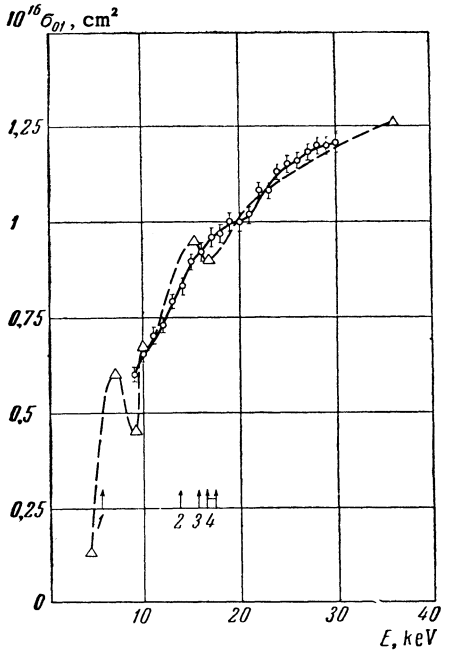

FIG. 2. Cross sections for electron loss in H_2: o—our results; Δ—Curran and Donahue's data.[5] 1) $H + H_2 \rightarrow H^+ + H_2^- \rightarrow H^+ + H + H^-$ −17.32 eV; 2) $H + H_2 \rightarrow H^+ + H_2^- \rightarrow H^+ + H\,[^2P^0] + H^-$ −27.52 eV; 3) $H + H_2 \rightarrow H^+ + H_2^- \rightarrow H^+ + H\,[^3P^0] + H^-$ −29.37 eV; 4) $H + H_2 \rightarrow H^+ + H_2^- \rightarrow H^+ + H^* + H^-$ (all subsequent excited states of H atoms, up to ionization energy).

The $\sigma_{01}(\epsilon)$ curve for the $H^0—O_2$ pair is given in Fig. 3. In the energy range 7—27.5 keV the $\sigma_{01}(\epsilon)$ curve is smooth (to within the experimental error). If it is assumed that electron capture by O_2 molecules is followed by dissociation of the O_2^- ions into O^- ions and O atoms in the ground or excited state, then the quoted energy range should contain a large number of maxima (this is correct only if the quantity a for $H^0 \rightarrow H^+$ in O_2 is the same as for $H^0 \rightarrow H^+$ in CO, i.e., $a \approx 2.4$ Å).

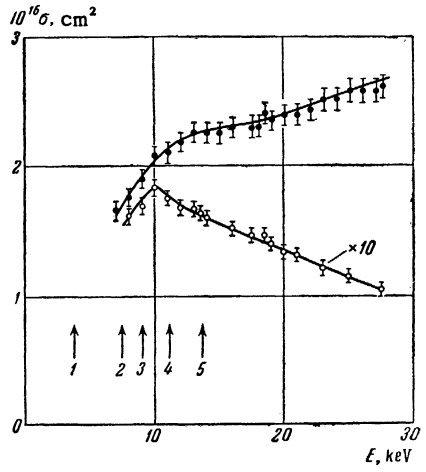

FIG. 3. Cross sections for electron loss and capture in O_2: ●—σ_{01} (ε); ○—σ_{0-1} (ε). 1—$H+O_2 \rightarrow H^- + O_2^+ - 11{,}75$ eV, 2—$H + O_2 \rightarrow H^- + O_2^+ [^2\Pi_u] - 16{,}48$ eV, 3—$H + O_2 \rightarrow H^- + O_2^+ \rightarrow H^- + O + O^+ - 18.23$ eV, 4—$H + O_2 \rightarrow H^- + O_2^+ \rightarrow H + O['D] + O^+ - 20.2$ eV, 5—$H + O_2 \rightarrow H^- + O_2^+ \rightarrow H^- + O['S] + O^+ - 22.42$ eV

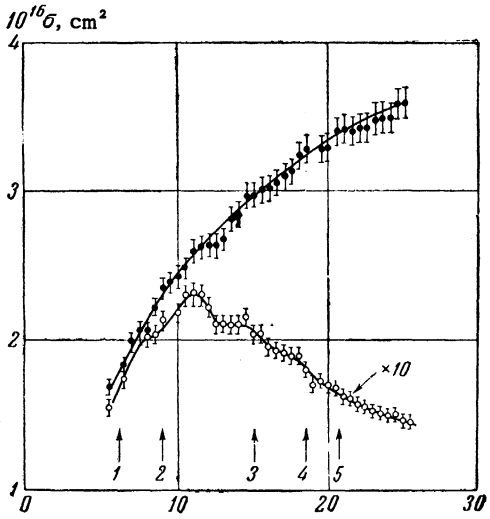

FIG. 4. Cross sections for electron loss and capture in N_2: ● — σ_{01} (ε), ○ — σ_{0-1} (ε). 1 — $H^0 + N_2 \rightarrow H^- + N_2^+ - 15.05$ eV, 2 — $H^0 + N_2 \rightarrow H^- + N_2^+ [^2\Sigma^+ u] - 18{,}2$eV, 3 — $H^0 + N_2 \rightarrow H^- + N_2^+ \rightarrow H^- + N + N^+ - 23.75$ eV, 4 — $H^0 + N_2 \rightarrow H^- + N_2^+ \rightarrow H + N [^2D] + N^+ - 26.13$ eV, 5 — $H^0 + N_2 \rightarrow H^- + N_2^+ \rightarrow H^- + N [^2P^0] + N^+ - 27.32$ eV

The absence of structure indicates that these processes have low probability.

The capture of electrons by O_2 molecules is followed by the formation of stable O_2^- ions. The maximum corresponding to this process lies at 3.5 keV and, therefore, the $\sigma_{01}(\epsilon)$ curve for the H—O_2 pair is particularly interesting at low energies. Unfortunately we could not carry out measurements below 7 keV because of the low intensity of the hydrogen beam at low energies.

The $\sigma_{01}(\epsilon)$ curve for the H^0—N_2 pair also had no structure in the 5.5—25 keV energy range (Fig. 4). For this pair only the process $H^0 + N_2 \rightarrow H^+ + N^* + N + e$ is possible because the stable N_2^- ion does not exist and the probability of formation of N^- is very low.[10] Maxima corresponding to this process should occur in the energy range available to us but in fact no structure was observed. This means that the probability of of the suggested process is also low.

The experimental data given here indicate that structure in the $\sigma_{01}(\epsilon)$ curves is observed when unstable molecular ions are formed which then dissociate into a negative ion and a neutral atom (processes in CO and H_2). If the formation of stable negative molecular ions (processes in O_2) is possible then no structure is observed. In the latter case the $\sigma_{01}(\epsilon)$ curves have only one maximum[7] representing the formation of stable O_2^- ions. Bukhteev et al[7] showed that the number of O^- ions in the slow-ion spectrum is very small and this confirms our suggestion of the low probability of dissociation of O_2^- ions formed from O_2 molecules by capture of electrons from hydrogen atoms.

When neither formation of stable negative molecular ions nor dissociation of the virtual state of such ions (into negative atomic ions and neutral atoms) is possible, the $\sigma_{01}(\epsilon)$ curves again have no structure. To check the general validity of our conclusions it is necessary to continue studies of electron loss by neutral atoms and negative ions during passage through molecular gases. To obtain a more reliable interpretation it is desirable to measure not only the total cross sections for electron loss but also to obtain the mass spectra of slow negative ions formed in the gas.

b) Electron capture. The effective cross sections for electron capture, σ_{0-1}, were measured for hydrogen atoms in CO, O_2, and N_2 gases. Figures 3—5 give the dependences of σ_{0-1} on the energy of the hydrogen atoms. Figure 5 shows structure in the $\sigma_{0-1}(\epsilon)$ curve for the process $H^0 \rightarrow H^-$ in CO. This structure is due to the fact that $H^0 \rightarrow H^-$ can be accompanied by excitation of CO^+ and its dissociation into excited products. The arrows in Fig. 5 indicate maxima calculated for processes accompanied by dissociation and excitation of CO^+, using the adiabatic Massey criterion with a = 3 Å (characteristic of $A^0 \rightarrow A^-$ processes[3]).* With a large number of simulta-

*The energies of the CO^+, N_2^+, and O_2^+ ions were taken from Mulliken's work,[11] and the dissociation energies were taken from Gaydon's book.[12]

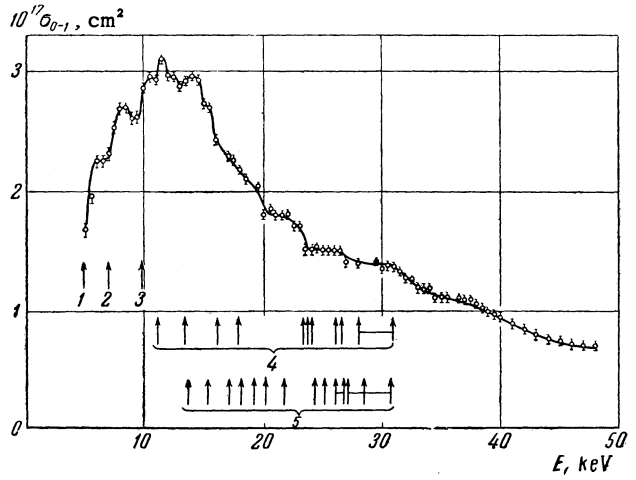

FIG. 5. Cross sections for electron capture in CO. *1* — $H^0 + CO \rightarrow H^- + CO^+ - 13.35$ eV, *2* — $H^0 + CO \rightarrow H^- + CO^+[A^2\Pi] - 15.87$eV, *3* — $H^0 + CO \rightarrow H^- + CO^+[B^2\Sigma^+] - 18.98$ eV, *4* — $H^0 + CO \rightarrow H^- + CO^+ \rightarrow H^- + C^+ + O$ where C^+ and O are in various excited states; *5* — $H^0 + CO - H^- + CO^+ \rightarrow H^- + C + O^+$ where C and O^+ are in excited states.

neous processes it is difficult to ascribe a particular maximum to a particular process but in general the structure in the $\sigma_{0-1}(\epsilon)$ curve occurs in the region where the arrows are located.

For hydrogen atoms with energies greater than 35 keV the cross section was found to decrease monotonically with increasing energy.

The $\sigma_{0-1}(\epsilon)$ curve for the H—O_2 pair (Fig. 3) has no structure although the energy range investigated should contain a large number of maxima due to $H^0 \rightarrow H^-$ processes accompanied by excitation and dissociation of O_2^+ ions. The positions of some of these postulated maxima are shown by arrows in Fig. 3. The absence of structure indicates the low probability of $H^0 \rightarrow H^-$ processes in O_2 compared with the process responsible for the main maximum, which is electron capture by hydrogen atoms accompanied by dissociation of O_2^+ ions into excited products.

Structure in the $\sigma_{0-1}(\epsilon)$ curve for the H^0—N_2 pair (Fig. 4) is due to the simultaneous occurrence of the process $H^0 + N_2 \rightarrow H^- + N_2^+$ and other electron capture processes accompanied by the excitation and dissociation of the N_2^+ ions. As in the case of electron capture by CO molecules, capture is more likely to be followed by the formation of excited ions than by the formation of ions in the ground state. The structure of the $\sigma_{0-1}(\epsilon)$ curve for the H—H_2 pair[5] can be accounted for in the same way as for the pairs H—CO and H—N_2.

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154