ELECTRON LOSS AND FORMATION OF SLOW NEGATIVE IONS IN COLLISIONS OF H ATOMS AND H IONS WITH GAS MOLECULES

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The paper presents results of measurements of the cross section σ_{-10} for the energy loss by negative hydrogen ions of energies between 3 and 30 keV in collisions with O_2, NO and CO molecules. The cross sections σ_i^- for the formation of slow negative ions in collisions of hydrogen atoms or negative hydrogen ions with the same molecules and in the same energy range have also been measured. The plot of the effective cross section $\sigma_{-10}(\epsilon)$ for the combination H^--CO vs. the energy ϵ of the fast particle shows a structure which can be explained by means of the adiabatic criterion of Massey. The magnitude of the cross section σ_i^- and the shape of the curve for $\sigma_i^-(\epsilon)$ depend on the nature of the target gas and on the binding energy of the electron in the fast particle. The positions of the maxima in the dependence of $\sigma_i^-(\epsilon)$ on the energy of the primary beam agree with the adiabatic criterion of Massey.

INTRODUCTION

THE electron loss in collisions of fast atoms with molecules of several diatomic gases was studied in our previous papers [1-3]. For certain combinations of atom and molecule we established the existence of a structure in the function $\sigma_{01}(\epsilon)$ (σ_{01} is the cross section for the loss of an electron by the fast atom, ϵ is the energy of the latter). We suggested an explanation of this structure on the basis that some contribution to the cross section σ_{01} comes from processes of charge exchange, with the transfer of an electron from the atom to the molecule and the formation of a negative molecular ion and its subsequent disintegration. The positions of the individual maxima in the structure were established by means of Massey's adiabatic criterion. In order to separate the contributions of the various charge exchange processes in the collisions between atoms and gas molecules (processes a, b and c, see [3]) to the structure in the curve for $\sigma_{01}(\epsilon)$ one has to compare the magnitude of the fluctuations in this structure with the magnitude of the total cross section σ_i^- for the formation of slow negative ions. Such a comparison for the gases NO and CO was carried out in [3], where the order of the cross section σ_i^- for these gases was determined. In the present paper we present $\sigma_i^-(\epsilon)$ curves for CO, NO and O_2. It appeared interesting to compare the cross section for electron loss and for the formation of slow negative ions upon passage of hydrogen atoms and negative hydrogen ions of the same energy through the same gases. For this purpose we have measured the cross section σ_{-10} (cross section for the electron loss by a negative hydrogen ion) and the cross section σ_i^- for negative hydrogen ions passing through CO, NO and O_2.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results given below were obtained with the apparatus described in detail in [3]. The cross section σ_i^- was determined from the current of slow negative ions falling on the plate of a capacitor placed in a magnetic field parallel to the plane of the condenser plate. The method of measuring the cross section σ_i^- is described in [4]. The cross section was measured by a mass-spectrographic method described previously [5,6]. The statistical error of the cross section measurements did not exceed 3-4%. The energy variation of the cross section $\sigma_i^-(\epsilon)$ for hydrogen atoms and negative ions in O_2, NO and CO is shown in Figs. 1-3 respectively. Figure 1 shows also the curve for $\sigma_i^-(\epsilon)$ for H^- ions from [4]. Examination of Figs. 1-3 leads to the following conclusions.

1. The cross section σ_i^- for H or H^- at a given energy depends on the nature of the gas. The relative magnitudes of the cross sections

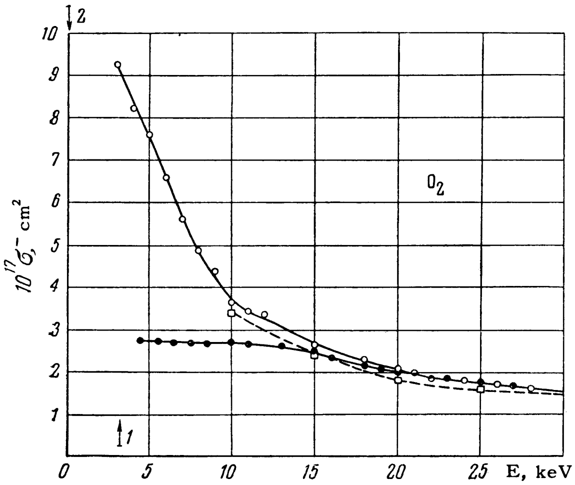

FIG. 1. Cross section σ_i^- in O_2: ● – hydrogen atoms, ○ – negative hydrogen ions, □ – data from reference [4]. The arrows show the maxima of the reactions: 1: $H^0 + O_2 \rightarrow H^+ + O_2^-$, 2: $H^- + O_2 \rightarrow H + O_2^-$.

are as follows: $(\sigma_i^-)_{O_2} > (\sigma_i^-)_{NO} > (\sigma_i^-)_{CO}$.

2. The shape of the curves $\sigma_i^-(\epsilon)$ for H^- ions is the same in all the gases studied. The curves show that the greatest value of σ_i^- is reached at low energies.

3. The curves also show that at the maximum the cross section σ_i^- for H^- ions is much larger than for H atoms. With rising particle energy the magnitudes of the cross section σ_i^- for H^- ions and H atoms approach each other and for O_2 and NO become approximately equal.

Some of these facts can be explained if one starts from the view that in the gases under investigation slow negative ions will be formed as a result of processes which involve the transfer of an electron from the atom or negative ion of hydrogen to the gas molecule,[1)] i.e., as a result of the reactions

$$H^{0-} + O_2 \rightarrow H^{+0} + O_2^-, \quad \text{(I)}$$
$$H^{0-} + NO \rightarrow H^{+0} + NO^-, \quad \text{(II)}$$
$$H^{0-} + CO \rightarrow H^{+0} + CO^-. \quad \text{(III)}$$

A study of the mass spectrum of slow negative ions formed in oxygen by the passage of hydrogen atoms or negative hydrogen ions showed [3,4] that in O_2 the ions formed are predominantly O_2^-. This proves that the reaction (I) is accompanied by the formation of a stable O_2^- ion, and that charge-exchange collisions with subsequent decay $O_2^- \rightarrow O + O^-$ are insignificant. This behavior explains the absence of structure in the $\sigma_i^-(\epsilon)$ curve in Fig. 1. From the same fact we can, on the other hand, deduce that the curves for $\sigma_i^-(\epsilon)$ and $J^-/J^0 = f(\epsilon)$ should have identical form.[2)] A comparison of these curves (see Fig. 1 of the present paper and Fig. 3 of reference [3]) confirms this conclusion.

The resonance defect ΔE^0 for the charge exchange of a hydrogen atom with an oxygen molecule is given by the formula

$$\Delta E^0 = S_{O_2} - V_{iH}, \quad (1)$$

where S_{O_2} is the electron affinity of the O_2 molecule and V_{iH} is the ionization potential of the hydrogen atom. In the case of the charge exchange of H^- with O_2 the resonance defect is given by the formula

$$\Delta E^- = S_{O_2} - S_H, \quad (2)$$

where S_H is the electron affinity of the hydrogen atom. If one inserts in (1) and (2) the values for the quantities V_{iH}, S_{O_2} and S_H, one finds

$$\Delta E^0 = -13.42 \text{ eV}, \quad \Delta E^- = -0.6 \text{ eV}.$$

In other words, ΔE^0 is much larger than ΔE^-. Since the maximum cross section for charge exchange usually decreases with increasing magnitude of the resonance defect, the inequality $|\Delta E^0| \gg |\Delta E^-|$ suggests that in our experiments $(\sigma_i^-)_{max}$ should be much larger for the charge exchange of H^- ions in oxygen than for hydrogen atoms in the same gas. On the other hand according to Massey's adiabatic criterion, it follows from the inequality $|\Delta E^0| \gg |\Delta E^-|$ that the maximum of the $\sigma_i^-(\epsilon)$ curve for charge exchange of H^- with O_2 should be displaced towards lower energies by comparison with the maximum of the same curve for the charge exchange of H and O_2.[3)] It is clear from an inspection of Fig. 1 that such a displacement is indeed present.

A mass-spectroscopic analysis of the slow negative ions formed in collisions of hydrogen atoms with NO molecules showed [3] that the number of NO^- ions in the mass spectrum is much greater than that of O^- ions. Consequently the charge exchange between H and NO (reaction (II)) leads mainly to the formation of NO^- ions. One sees from Fig. 2 that the curve for σ_i^- for

[1)]The possibility of the formation of slow negative ions in gases as a result of similar types of charge transfer processes was first pointed out in [7,8].

[2)]The curve $J^-/J^0 = f(\epsilon)$ gives the dependence of the relative intensity of the beam of O_2^- ions on the energy of the hydrogen atom.

[3)]It is assumed here that the quantity a which enters in the adiabatic criterion of Massey does not differ drastically for these two processes.

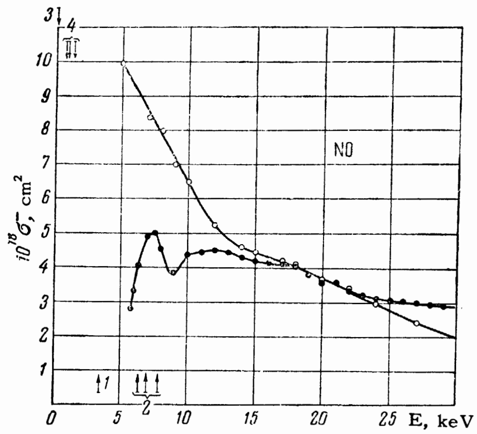

FIG. 2. Cross section σ_i^- in NO: ● – hydrogen atoms, ○ – negative ions. The arrows indicate the maxima of the reactions: 1: $H^0 + NO \rightarrow H^+ + NO^-$, 2: $H^0 + NO \rightarrow H^+ + (NO^-)^*$, 3: $H^- + NO \rightarrow H^0 + NO^-$, 4: $H^- + NO \rightarrow H^0 + (NO^-)^*$.

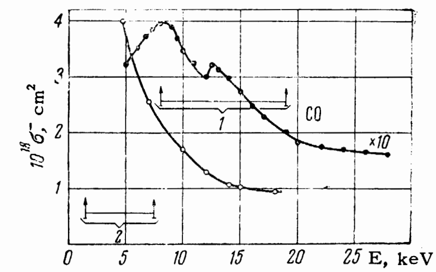

FIG. 3. Cross section σ_i^- in CO: ● – hydrogen atoms, ○ – negative hydrogen ions. The arrows indicate the maxima of the reactions: 1: $H^0 + CO \rightarrow H^+ + (CO^-)^* \rightarrow H^+ + C^* + O^-$, 2: $H^- + CO \rightarrow H^0 + (CO^-)^* \rightarrow H^0 + C^* + O^-$.

the H-NO pair has two maxima, which can be explained by assuming, as was done in [3] that the charge exchange between H and NO results in a metastable NO^- ion, in which the additional electron is combined with an NO molecule in one of its excited electronic states $A^2\Sigma^+$, $D^2\Sigma^+$, or $F^2\Delta$.

The resonance defects for the charge exchange of the combination H-NO with formation of a metastable NO^- ion are given by the formula

$$\Delta E = S_{NO} - V_{iH} - \varepsilon_{ex}, \qquad (3)$$

where ϵ_{ex} is the excitation energy of the relevant state of the NO molecule. If one assumes that the parameter a in the Massey criterion differs little for charge exchange processes of similar type [9] one can calculate the position of the maxima that correspond to the charge exchange collisions between H and NO resulting in NO^- ions either in the ground state or in an excited state. The maximum of $\sigma_i^-(\epsilon)$ for H^- and NO should be shifted towards lower energies by comparison with the maximum of $\sigma_i^-(\epsilon)$ for H and NO, for the same reason as in the case of oxygen. The shape of the curves in Fig. 2 confirms this conclusion. Similar differences in the magnitude of the resonance defect can explain the fact that the maximum of σ_i^- for H^- in NO will evidently be much greater than the corresponding cross section for H in NO.

Figure 3 shows curves for the cross section $\sigma_i^-(\epsilon)$ for the charge exchange reaction of hydrogen atoms and negative hydrogen ions in CO. The curve for H in CO was obtained in the following manner. Measurements of this cross section were carried out only in the energy range from 11 to 15 keV, and then for other energies the cross section was calculated from the data for $\Delta(J^-/J^0)$ for the formation of O^- ions in the CO gas, which had been measured in [3]. The curve for $\Delta(J^-/J^0) = f(\epsilon)$ obtained in this way should not differ appreciably from the correct one, since the mass spectrum of slow negative ions which are formed by the charge exchange between H and CO contains 93% O^- ions and 7% C^- ions[3]. This means also that reaction (III) does not take place, and that all CO^- ions which are formed disintegrate. The positions of the maxima in the reaction $H^{0-} + CO \rightarrow H^{+0} + (CO^-)^* \rightarrow C^* + O^-$ are shown by the arrows in Fig. 3.

The reasons for the lower energy and the greater magnitude of the maximum of $\sigma_i^-(\epsilon)$ for H^- in CO compared to H in CO are the same as in the cases of O_2 and NO.

In concluding the discussion of the results of the measurements of σ_i^- it should be pointed out that the magnitudes of these cross sections for H in NO and H in CO are considerably less than the magnitude of the bumps on the curves for σ_{01} for these cases. This shows that the structure of these curves is not connected with reactions of the type (II) or (III). This was already noted in [3].

Results of measurements of the cross section σ_{-10} for H^- in O_2, H^- in NO and H^- in CO are shown as functions of the energy in Fig. 4.[4)] The values of the cross section σ_{-10} are about one order of magnitude larger than the cross section σ_{01} for H in O_2, NO, or CO. This was to be expected since the binding energy of the last electron in H^- is much less than in H.

Of the three curves shown in Fig. 4 only one, namely the $\sigma_{-10}(\epsilon)$ curve for H^- in CO exhibits a structure. The magnitude of the bumps in this structure are of the order of 10^{-16} cm². Since the

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[4)] The values of σ_{-10} for H^- in O_2 obtained in the present work agree within experimental error with those measured in [10].

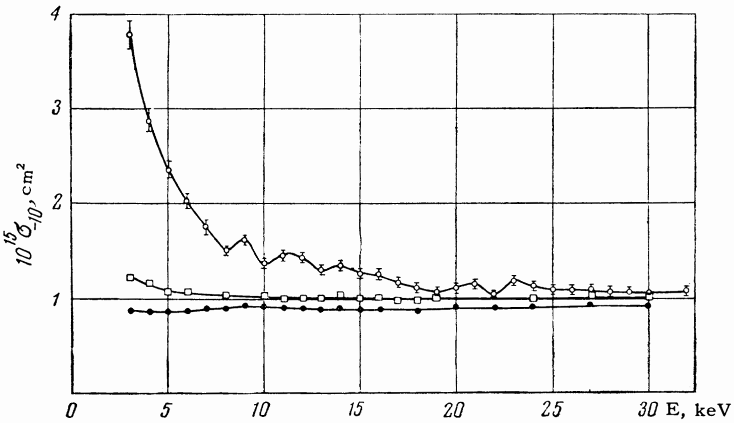

FIG. 4. Electron loss cross section σ_{-10} for negative hydrogen ions in different gases: ○ – CO, □ – NO, ● – O_2.

cross section σ_i^- for this case is of the order of 10^{-18} cm^2 (see Fig. 3), it is impossible to explain the presence of a structure in the $\sigma_{-10}(\epsilon)$ curve by reactions resulting in the formation of slow negative ions in the charge exchange of H^- with CO. There remains only the possibility to account for this structure in terms of the reaction

$$(CO^-)^* \rightarrow C^* + O^* + e \qquad \text{(IV)}$$

in which a CO^- ion breaks up into excited C and O atoms and an electron. If we assume that the maximum of the curve at 23 keV is connected with the reaction (IV) in which the C and O atoms are formed in their lowest excited states, one can compute the parameter a from Massey's adiabatic criterion. This turns out to be 2.5 Å, i.e., close to the value of a for charge-exchange processes of hydrogen atoms with molecules of the same gases (see [1-3]).

From the value a = 2.5 Å we can determine the position of the maximum of the curve which corresponds to the formation in reaction (IV) of C and O atoms in their ground states. This turns out to lie at 2 keV. The absence of structure in the $\sigma_{-10}(\epsilon)$ curve for H^- in CO in the range of 3–8 keV may possibly be connected with the fact that the greatest contribution to the cross section σ_{-10}, which is due to collisions in which an electron is stripped off into the continuum, rises rapidly in this energy range. The absence of a structure in the $\sigma_{-10}(\epsilon)$ curve for H^- in O_2 is explained by the fact that the charge exchange of H^- with O_2 results in a stable O_2^- ion [4].

If one assumes that the parameter a for charge exchange reactions of H^- with NO is also 2.5 Å, then the structure in the curve of $\sigma_{-10}(\epsilon)$ for H^- in NO should lie in the energy region between 1 and 23 keV. In fact no structure is seen between 3 and 23 keV. This would seem to be due to the fact that in this energy range the cross section for reaction (IV) for H^- in NO is small compared to the main part of the cross section σ_{-10}, which is due to the stripping off of an electron into the continuum.

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