# *ELECTRON CAPTURE AND LOSS ON PASSAGE OF FAST ATOMS THROUGH MOLECULAR GASES*

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The cross sections were measured for electron loss ($\sigma_{01}$) and capture ($\sigma_{0-1}$) by hydrogen atoms in NO and by carbon atoms in CO. The structure of the energy dependence curves $\sigma_{01}(\epsilon)$ and $\sigma_{0-1}(\epsilon)$ for the H–NO pair is explained by means of the Massey adiabatic criterion.

## INTRODUCTION

STRUCTURE was detected in the $\sigma_{01}(\epsilon)$ curves by several workers[1-4] who measured the effective cross sections $\sigma_{01}$ for electron loss by hydrogen atoms in collisions with molecules of various molecular gases; here $\epsilon$ is the energy of the hydrogen atoms. In their earlier paper[4] the present authors gave an explanation of this structure based on the fact that on passage of fast atoms through a gas two processes of electron loss by the fast atom are possible: 1) electron loss followed by transition into a state with a continuous spectrum, and 2) transfer of an electron from the atom to a molecule with formation of a slow stable or unstable negative molecular ion.[1)] If the effective cross sections of these two processes are denoted by $\sigma'_{01}$ and $\sigma''_{01}$ respectively, then the measured cross section is $\sigma_{01} = \sigma'_{01} + \sigma''_{01}$. Experimental studies of electron loss by fast atoms in inert gases,[1,6,7] i.e., in cases when the second process is impossible, have shown that the $\sigma'_{01}(\epsilon)$ curve is smooth. Thus structure may appear in the $\sigma_{01}(\epsilon)$ curve only in the case when there is structure in the $\sigma''_{01}(\epsilon)$ curve and the value of $\sigma''_{01}(\epsilon)$ is not too small compared with $\sigma_{01}(\epsilon)$. The structure of the $\sigma''_{01}(\epsilon)$ curve was explained[4] on the assumption that the negative ions formed on capture of electrons by the gas molecules dissociate into negative atomic ions and neutral atoms in various excited states. Consequently the curve $\sigma''_{01}(\epsilon)$ is itself the result of superposition of several curves representing various dissociation processes of the negative molecular ion. Since each of these dissociation processes has its own value of the resonance defect, then, according to the Massey adiabatic criterion, the dependences of the effective cross sections of these processes on the energy of the fast atom have maxima at different energies and consequently the result of their superposition gives a $\sigma''_{01}(\epsilon)$ curve with structure.

The experimental material given in [4] allowed us to draw a preliminary conclusion that structure in the $\sigma_{01}(\epsilon)$ curve is observed in those cases (CO, $H_2$ gases) when the probability of formation of a stable negative molecular ion as a result of electron capture by a gas molecule is very low, but when this ion can dissociate into a negative ion and a neutral atom. In those cases where a stable negative molecular ion can be formed ($O_2$ gas) there is no structure in the $\sigma_{01}(\epsilon)$ curve. There is likewise no structure in the case of $N_2$, where the formation of $N_2^-$ ions and their dissociation into $N^-$ ions are both very unlikely.[8]

The data given here, from measurements of the cross sections $\sigma_{01}$ for the pairs H–NO and C–CO, were obtained for the purpose of providing additional confirmation of the suggested causes of the structure in the $\sigma_{01}(\epsilon)$ curves, and of finding in which molecular gases this structure appears. For the pairs H–NO and C–CO, apart from the cross-sections $\sigma_{01}$, the cross sections for electron capture $\sigma_{0-1}$ by hydrogen atoms were also determined. The apparatus and experimental method have been described in detail in our previous papers.[6,7]

## RESULTS OF MEASUREMENTS AND DISCUSSION

a) Electron loss processes. Figure 1 shows the $\sigma_{01}(\epsilon)$ curve obtained in the present work for the process $H^0 \rightarrow H^+$ in NO. Each experimental point represents the average result of five measure-

[1)] The possibility of the second process was first pointed out by Bukhteev, Bydin, and Dukel'skiĭ.[5]

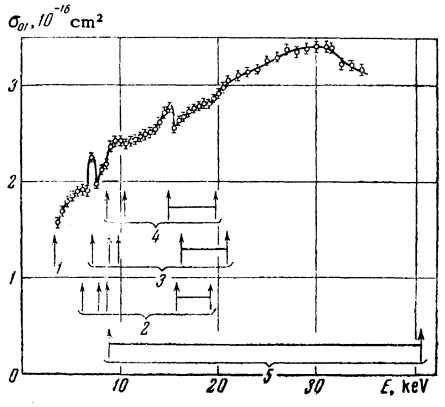


FIG. 1. Cross section for electron loss by H atoms in NO. Arrows indicate the calculated positions of the maxima of the $\sigma''_{01}(\epsilon)$ curves for the following processes:

$1 - H^0 + NO \rightarrow H^+ + NO^- - 13.59eV$,
$2 - H^0 + NO \rightarrow H^+ + (NO^-)^* \rightarrow H^+ + N^* + O^-$, $3 - H^0 + NO \rightarrow H^+ + (NO^-)^* \rightarrow H^+ + N^* + O + e$, $4 - H^0 + NO \rightarrow H^+ + (NO^-)^* \rightarrow H^+ + N + O^* + e$,
$5 - H^0 + NO \rightarrow H^+ + (NO^-)^* \rightarrow H^+ + N^* + O^* + e$

(in the processes 2–5 the N and O atoms may be in the ground state or in any excited state up to ionization).

ments. The accidental error in our measurements varied within the limits 1—3% (depending on the intensity of the primary beam, residual gas pressure in the collision chamber, and the value of the cross section). Figure 1 shows that the $\sigma_{01}(\epsilon)$ curve for the process $H^0 \rightarrow H^+$ in NO has structure. An explanation of this structure is given below on the basis of the considerations advanced at the beginning of this paper.

Some electrons are lost by H atoms as a result of the following processes of electron capture by the NO molecule, either with the formation of stable $NO^-$ ions or with the formation of unstable $NO^{-*}$ ions followed by their dissociation:

$$H + NO \rightarrow H^+ + NO^-, \quad (I)$$

$$H + NO \rightarrow H^+ + NO^{-*} \rightarrow H^+ + N^* + O^-, \quad (II)$$

$$H + NO \rightarrow H^+ + NO^{-*} \rightarrow H^+ + N^* + O^* + e. \quad (III)$$

In processes II and III the N and O atoms may be formed both in the ground and excited states. The resonance defects of the processes I—III may be calculated from the formulas:

$$\Delta E_1 = S(NO) - V_I(H), \quad (1)$$

$$\Delta E_2 = -[V_I(H) + D(NO) - S(O) + E(N)], \quad (2)$$

$$\Delta E_3 = S(NO) - [V_I(H) + D(NO) + E(N) + E(0)], \quad (3)$$

where S(NO) and S(O) are the electron affinities of the NO molecule and the O atom, $V_I(H)$ is the ionization potential of the hydrogen atom, D(NO) is the dissociation energy of the NO molecule, and E(N) and E(O) are the excitation energies of the N and O atoms.[2)]

The probability of process I is obviously very small. This conclusion is based on the fact that in almost all the work[11-16] dealing with the formation of negative ions in collisions of slow electrons with NO, $N_2O$ and $NO_2$ molecules the stable $NO^-$ ion was not observed. Only Rudolph et al,[12] who used a very sensitive mass spectrometer, found that $NO^-$ ions were formed on collisions of electrons with NO and $N_2O$ molecules. The number of these ions was very small ($10^{-3}$ compared with the $O^-$ ions in the case of $N_2O$, and $3 \times 10^{-4}$ in the case of NO). From these results it follows that the probability of the formation of $NO^-$ ions in electron-molecule collisions is very small and there are no reasons for assuming that it may be considerably greater in charge-exchange processes. Thus, NO gas conforms to the rule established in [4] that structure of the $\sigma_{01}(\epsilon)$ curves is observed for molecules which form mainly unstable negative molecular ions which dissociate into neutral and negative atomic components.

Having calculated the resonance defects of processes I—III, using formulas (1)—(3), we can then calculate, employing the Massey adiabatic criterion, the positions of the maxima of the $\sigma''_{01}(\epsilon)$ curves which determine the structure of the $\sigma_{01}(\epsilon)$ curve. We carried out these calculations taking the quantity a in the adiabatic criterion to be the same as in the case of $H \rightarrow H^+$ processes in CO and $H_2$ gases, i.e., equal to 2.4 Å. The calculated positions of the maxima for the processes I—III are indicated in Fig. 1 by arrows. This figure shows that the structure features of the $\sigma_{01}(\epsilon)$ curve lie in the regions where the maxima of the $\sigma_{01}(\epsilon)$ curves occur, i.e., in the case of NO the structure of the $\sigma_{01}(\epsilon)$ curve has the same cause as in the cases of CO and $H_2$ gases.

Further confirmation of the correctness of our

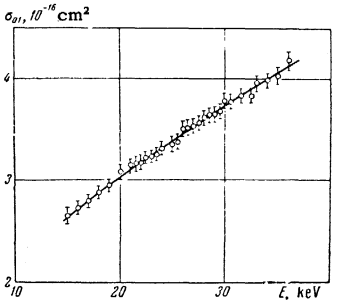


FIG. 2. Cross sections for electron loss by C atoms in CO.

[2)]The dissociation energy of the NO molecule was taken from Gaydon's book,[9] and the excitation energies of the N and O atoms were taken from [10].

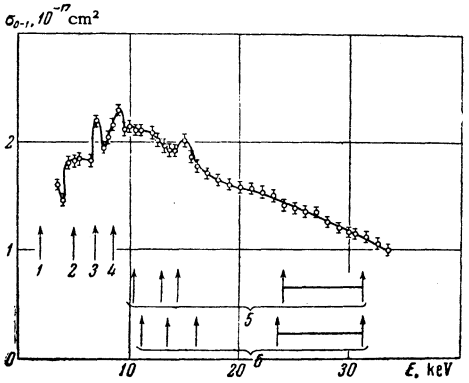


FIG. 3. Cross sections for electron capture by H atoms in NO. Arrows indicate the calculated positions of the maxima of the $\sigma''_{0-1}(\epsilon)$ curves for the following processes:

*1* — $H^0 + NO \rightarrow H^- + NO^+ - 8.51$ eV, *2* — $H^0 + NO \rightarrow H^- + NO^+ [a^3\Sigma^+] - 13.47$ eV, *3* — $H^0 + NO \rightarrow H^- + NO^+ [X] - 15.74$ eV, *4* — $H_0 + NO \rightarrow H^- + NO^+ [A'\Pi] - 17.53$eV, *5* — $H^0 + NO \rightarrow H^- + (NO^+)^* \rightarrow H^- + N^* + O^+$, *6* — $H^0 + NO \rightarrow H^- + (NO^+)^* \rightarrow H^+ + N^+ + O^*$

(in the processes 5 and 6 the N and O atoms may be in the ground state or in any excited state up to ionization).

interpretation of the structure of the $\sigma_{01}(\epsilon)$ curves is provided by the results of measuring the cross sections for the process $C \rightarrow C^+$ in CO. In this case, if a = 2.4 Å, the maximum related to process I should be observed in the region of 26 keV and the structure related to processes II and III should be observed at energies greater than 80 keV. As shown in Fig. 2, the curve $\sigma_{01}(\epsilon)$ for the process $C \rightarrow C^+$ in CO, obtained by us in the range 15—36 keV, is completely smooth. The absence of a maximum corresponding to process I is fully understandable, since we have shown[4] that the formation of the stable $CO^-$ ion by charge exchange is unlikely. As for the structure corresponding to the processes II and III, it was outside the range of energies which we investigated.

b) Electron capture processes. Effective cross sections for electron capture, $\sigma_{0-1}$, were measured for H atoms in NO and C atoms in CO. Figures 3 and 4 give the $\sigma_{0-1}(\epsilon)$ curves for these processes. Examination of Fig. 3 shows that there is structure in the $\sigma_{0-1}(\epsilon)$ curve for the process $H \rightarrow H^-$ in NO. This structure, as in the case of the H–CO and H–$N_2$ pairs, can be explained by the fact that the process of electron capture by a fast atom may be accompanied by the excitation of a positive molecular ion, as well as by its dissociation with the formation of excited components. The arrows in Fig. 3 show the positions of the maxima calculated by means of the Massey adiabatic criterion with a = 3 Å[3)] for the processes accompanied by excitation and dissociation of the $NO^+$ ion.[4)] Figure 3 shows that the structure of the $\sigma_{0-1}(\epsilon)$ curve is observed in the same region of energies as the arrows corresponding to the electronic excitation of the NO molecule (Fig. 4) and to the dissociation processes of the $NO^+$ ion with the formation of components in lower excited states.

[3)]The value a = 3 Å represents the processes $A^0 \rightarrow A^-$.[17]

[4)]The excitation energies of the $NO^+$ ion were taken from [18].

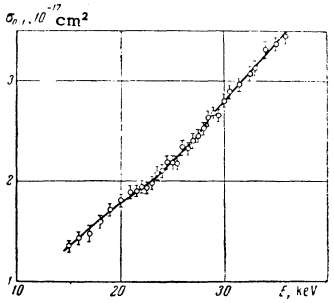


FIG. 4. Cross sections for electron capture by C atoms in CO.

The $\sigma_{0-1}(\epsilon)$ curve for the $C^0 \rightarrow C^-$ process in CO has no structure. Calculation shows that the structure related to the formation of the excited $CO^+$ ion and its dissociation should be observed at energies considerably greater than the maximum energy used in our study.

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287