COMPOSITION OF SLOW IONS FORMED ON PASSAGE OF FAST HYDROGEN ATOMS THROUGH MOLECULAR GASES

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Submitted to JETP editor July 18, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) 48, 404-415 (February, 1965)

The composition of slow negative and positive ions produced by fast hydrogen atoms passing through gaseous O_2 , N_2 , NO, and CO has been investigated with a mass spectrometer. The variation of the intensity of individual mass spectrum lines with hydrogen atom energy has been determined. These curves are compared with those for the energy dependence of the cross sections for electron loss and capture by hydrogen atoms.

INTRODUCTION

I N our work^[1,2] on the study of electron capture and loss by fast hydrogen atoms passing through diatomic gases, we established that for some atom-molecule pairs a structure is observed in the energy dependence of the corresponding cross sections $\sigma_{0-1}(\epsilon)$ and $\sigma_{01}(\epsilon)$. In the case of both the electron loss and electron capture processes the structure is explained on the basis of Massey's adiabatic criterion. The explanation is based on the assumption that the individual peaks in the structure correspond to the following:

a) Processes in which slow positive (for electron loss) and negative (for electron capture) molecular ions are formed in different states.

b) Processes of decay of these positive and negative molecular ions to atomic ions and neutral atoms in different excited states.

c) Processes of decay of the negative molecular ions into neutral atoms (in different excited states) and an electron.

The hypothesis assumed for the origin of the structure in the $\sigma_{0-1}(\epsilon)$ and $\sigma_{01}(\epsilon)$ curves is confirmed by the fact that the energy interval in which the structure of these curves is observed agrees rather well with the energy interval in which the peaks are expected in processes a, b, and c on the basis of Massey's adiabatic criterion.

Additional proof of the validity of this hypothesis can be obtained from study of the mass spectra of the slow positive and negative ions and in particular from study of the intensity of individual mass spectrum lines as a function of the energy of the fast atoms. In the work reported below we have carried out these studies for hydrogen atoms which have passed through the gases N_2 , O_2 , NO, and CO.

APPARATUS AND EXPERIMENTAL TECHNIQUE

In order to carry out experiments on the mass spectra of the slow ions formed in a gas on passage of fast hydrogen atoms, the apparatus in which our previous studies were carried $out^{[3]}$ was largely rebuilt.

A schematic drawing of the redesigned apparatus is shown in Fig. 1. A hydrogen ion beam of a specified energy was produced by the ion gun 1.^[3] The electrostatic deflecting plates 2 allowed us to correct the ion beam trajectory. The magnetic mass selector 3 then selected a beam of monoenergetic protons which was focused by the electrostatic quadrupole lens 4 into a chamber containing a mercury vapor target 5 where the proton beam was neutralized in an ultrasonic jet of mercury vapor.¹⁾ The hydrogen atom beam emerging from the mercury target chamber was cleared of positive and negative ion impurities by the two plane electrostatic deflecting electrodes 7 and 8 and entered the collision chamber 10. Collimation of the beam of atoms was accomplished by two diaphragms 6 and 9 whose diameters were respectively 3 and 2 mm. The effective length of the collision chamber was 400 mm. The chamber contained a measuring electrode 11 consisting of 5 pairs of plane parallel plates allowing measurement of absolute cross sections by the potential method. Analysis of the slow ions extracted from

¹⁾The apparatus for obtaining the ultrasonic jet has been described by Fogel' et al.^[4]



the gas filling the collision chamber by a transverse electric field was accomplished by a mass spectrometer 12 connected to the side of the chamber.

FIG. 1. Drawing of the apparatus.

The ion current at the exit of the mass spectrometer was measured by an electron multiplier 13 connected to an ÉMU-3 vacuum tube electrometer. An accurate evaluation of the sensitivity of this current-measuring device was not made; an indirect estimate gives a value of the order of 10^{-16} A/div. The equivalent current in the hydrogen atom beam entering the collision chamber was between 5×10^{-9} and 3×10^{-8} A. The beam intensity increased with increasing energy of the hydrogen atoms as the result of better focusing of the proton beam at higher energies.

The plane electrostatic deflector 14 separated the beam of fast particles emerging from the collision chamber into neutral, positive, and negative components. The charged components were measured by the Faraday cups 15 and 16, and the neutral component by the vacuum thermopile $17.^{5}$ The collision chamber was connected with the source of fast particles by a bellows 19 and along with the mass spectrometer was mounted on a moveable frame not shown in the figure. This gave the possibility of rotating the axis of the collision chamber with respect to the axis of the fastparticle source by an angle of the order of 10° . With such a rotation it was possible by means of the electric field of the plane deflecting electrode 7 to direct into the chamber pure beams of positive or negative ions and to study their interactions with gases.

Differential pumping of the collision chamber was accomplished by an M-2500 oil diffusion pump, and additional pumping of the mass spectrometer chamber by an MM-40 pump. The pressure of the gas admitted to the collision chamber was measured by a Knudsen gauge calibrated by a McLeod gauge. The residual gas pressure in the collision chamber was 10^{-5} mm Hg.

Thus, the redesigned apparatus is capable of measuring absolute cross sections for inelastic interaction processes of charged and neutral particles with gases by the potential and mass-spectrometer methods and of analyzing the slow ions. The measurements necessary in analysis of slow ions have been described in detail pre-viously^[6,7] and we will therefore mention them only very briefly.

For each combination of fast atom and gas molecule and for different primary beam energies we obtained the relative intensity of the spectral lines of a given slow ion J^k/J^0 (J^k is the slow ion current, J^0 is the primary beam current) as a function of the voltages V_e , V_a , and V_f (V_e is the extraction voltage between the plates of the deflector 11, V_a and V_f are the accelerating and focusing voltages applied to the slow ion charge analyzer). The working values of V_e , V_a , and V_f were chosen on the plateaus of the respective curves.

For each primary beam energy we measured the variation of the ratio J^{k}/J^{0} with gas pressure in the collision chamber. All of the experimental data reported in the present paper refer to a pressure of 10^{-4} mm Hg, which satisfies the condition for single occurrence of the processes studied. We made a study of the slow ion mass spectra of all the gases investigated with different widths of the mass-spectrometer exit slit 18. It



FIG. 2. Mass spectrum of slow positive and negative ions formed in NO.

turned out that with a slit width of 2 mm it was possible to separate the mass lines of ions differing in mass by one unit. Figure 2 shows the mass spectrum of the slow positive and negative ions formed in the NO gas.

The ions N_2^* , O_2^* , O_2^- , H_2O^+ , and OH^+ , and partially N^+ and O^+ appear in the mass spectrum as the result of interaction of H atoms with residual gas molecules. The ions H^+ and H_2^+ appear as the result of penetration of the hydrogen admitted to the ion source into the collision chamber.

Study of the intensity of individual mass spectrum lines at different primary beam energies as a function of the primary beam current showed a linear dependence over the range of currents admitted to the collision chamber. From these tests we concluded that the gain of the electron multiplier did not depend on the intensity of the incident particle beam.

Measurement of the relative intensities of the spectrum lines was carried out over a small range of primary beam energies (1-2 kV). For each energy the value of J^k/J^0 was obtained as the average of three or four measurements, and the statistical error of the measurements did not exceed 2-3%.

EXPERIMENTAL RESULTS AND DISCUSSION

<u>A. Mass spectrum of slow negative ions</u>. As the result of the mass-spectrometric analysis of



FIG. 3. The process $H^0 \rightarrow H^+$ in O_2 : $1 - H^0 + O_2 \rightarrow H^+ + O_2^-$; $2 - H^0 + O_2 \rightarrow H^+ + O_2^- [{}^{1}\Delta_g]$; $3 - H^0 + O_2 \rightarrow H^+ + O_2^- [{}^{1}\Sigma_g^+]$; $4 - H^0 + O_2 \rightarrow H^+ + O_2^- [{}^{3}\Sigma_u^-]$; $5 - H^0 + O_2 \rightarrow H^+ + O_2^- [{}^{3}\Sigma_u]$; $6 - H^0 + O_2 \rightarrow H^+ + (O_2^-)^* \rightarrow H^+ + O^- + O^*$ (the O atom is found both in the ground state and in all the excited states up to the ionization level).

the composition of the slow negative ions arising in collisions of H atoms with O_2 molecules, we established that O_2^- ions are the main product and that O^- ions are formed only in small quantity (of the order of a few percent). Consequently the charge-exchange process

$$H + O_2 \rightarrow H^+ + O_2^-$$
 (1)

with formation of a negative molecular oxygen ion has a considerably greater probability than the process

$$H + O_2 \rightarrow H^+ + (O_2^-)^* \rightarrow H^+ + O^- + O,$$
 (2)

in which the unstable O_2^- ion dissociates into an O atom and an O⁻ ion. The processes of forming negative atomic oxygen ions in the charge exchange of neutral alkali metal atoms in oxygen^[8] and negative hydrogen ions in oxygen^[9] also have a low probability.

Figure 3 shows the curve obtained for the relative intensity of the O_2^- ion beam as a function of primary beam energy. Because of the insufficient sensitivity of our apparatus we were unable to obtain a curve of $J^-/J^0 = f(\epsilon)$ for O^- ions. A calculation based on Massey's adiabatic criterion² shows that the peak in process (1) with formation of an O_2^- ion in the ground state should occur at an energy of 3.5 keV and consequently the number of O_2^- ions at energies above 3.5 keV should increase with decreasing energy of the neutral hydrogen atom beam. As we can see from Fig. 3, the behavior of the $J^-/J^0 = f(\epsilon)$ curve agrees with these

²⁾The calculation of the location of the peaks was carried out both here and in the other cases on the basis of the assumption that the value a = 2.4 Å determined for the combination H-CO[¹] is valid also for other combinations.

conclusions. The existence of the plateau in this curve in the energy region 8-16 keV can be explained if we assume that in addition to process (1) electron capture by the O_2 molecule occurs with simultaneous excitation of this molecule to different electronic states.³) The positions of the peaks associated with these processes are shown by the arrows in Fig. 3.

Comparison of the curve $J^{-}/J^{0} = f(\epsilon)$ for O_{2}^{-} ions with the curve $\sigma_{01}(\epsilon)$ for the pair $H - O_{2}^{[1]}$ permits us to conclude that these curves correspond in the sense that structure is absent in both curves. Process (2), in view of its low probability, also cannot produce structure in the curve $\sigma_{01}(\epsilon)$ in the energy region (designated by the arrows 6 in Fig. 3) where the peaks due to this process should be located.

In the spectrum of negative ions formed in collisions of H atoms with NO molecules (Fig. 2) we observed NO⁻ ions (about 95%) and O⁻ ions (about 5%). There are contradictory data on the existence of the NO⁻ ion. In a number of studies ^[11-15] of the formation of negative ions in collisions of slow electrons with molecules of NO, N₂O, and NO_2 , the NO^- ion was not observed. Only in one investigation (see [16]) have NO⁻ ions been observed, but the quantity was very small in comparison with O⁻ ions. Kalmykov^[17] observed NO⁻ ions in the two-electron charge exchange of NO^+ ions. The cross section for this process for an NO⁺ ion energy of 22 keV was 1.4×10^{-19} cm² and was of the same order as for the ions OHand CH⁻.

This result shows that the probability of formation of NO⁻ ions in heavy-particle collisions is appreciable. The present work leads to the same conclusions. It is quite possible that in processes involving heavy particles the probability of forming NO⁻ ions is considerably greater than in collisions of electrons with NO molecules.

The curves $J^{-}/J^{0} = f(\epsilon)$ for NO⁻ and O⁻ ions are shown in Fig. 4. As we can see from this figure, some structure is observed in the J^{-}/J^{0} = $f(\epsilon)$ curve for NO⁻ ions for hydrogen atom energies of 6–10 keV. If the formation of NO⁻ ions took place as the result of the process

$$H + NO \rightarrow H^+ + NO^-$$
(3)

with a resonance defect $\Delta E = S(NO) - V_i(H)$ (S(NO) is the electron affinity of the NO molecule, V_i(H) is the ionization potential of the hydrogen atom), the curve $J^-/J^0 = f(\epsilon)$ for NO⁻



FIG. 4. The process $H^0 \rightarrow H^+$ in NO: $1 - H^0 + NO \rightarrow H^+ + NO^-$; $2 - H^0 + NO \rightarrow H^+ + NO^ [A^2\Sigma^+]$; $3 - H^0 + NO \rightarrow H^+ + NO^ [D^2\Sigma^+]$; $4 - H^0 + NO \rightarrow H^+ + NO^ [F^2\Delta]$; $5 - H^0 + NO \rightarrow H^+ + (NO^-)^* \rightarrow H^+ + O^- + N^*$ (the N atom is found in the ground state and in all excited states up to the ionization level).

ions would have one peak. If we assume that $S(NO) \approx 0$, then according to a calculation based on Massey's adiabatic criterion this peak should be at an energy of the order of 3 keV⁴ (arrow 1 in Fig. 4). Examination of Fig. 4 shows that the peak in the 3 keV region is missing, while instead there is structure in the region 6–10 keV.

We can explain the structure in the curve $J^{-}/J^{0} = f(\epsilon)$ for NO⁻ ions if we assume that as the result of process (3) metastable excited NO⁻ ions are formed in which the excess electron is bound to an NO molecule which is in one of the electronic states $A^2\Sigma^+$, $D^2\Sigma^+$, and $F^2\Delta$. The peaks in process (3) with formation of metastable NO⁻ ions, according to a calculation based on Massey's adiabatic criterion, ⁵) should be located at the energies indicated by the arrows 2, 3, and 4 in Fig. 4. We can see from Fig. 4 that the structural features in the $J^{-}/J^{0} = f(\epsilon)$ curve for NO⁻ ions lie in exactly the energy region where we should expect the peaks for process (3) with formation of metastable NO⁻ ions. The absence of a peak in the 3 keV region corresponding to process (3) (with transfer of an electron to an NO molecule in the ground state) can result from the fact that the NO molecule cannot be combined with an electron in the ground state.

Let us dwell for a moment on the discussion of the $J^-/J^0 = f(\epsilon)$ curve for O⁻ ions. The O⁻ ion is formed as the result of the charge-exchange

³⁾The electronic states of the O_2 molecule were taken from the work of Gaydon.^[10]

⁴)The ionization and excitation energies of the atoms and positive atomic ions both here and in the remaining cases are taken from the work of Moore:[¹⁸]

 $^{^{5)}}The$ energies of the electronic states $A^{2}\Sigma^{+}$, $D^{2}\Sigma^{+}$, and $F^{2}\Delta$ are taken from the work of Huber.[^{19}]

process

$$H + NO \rightarrow H^+ + (NO^-)^* \rightarrow H^+ + N^* + O^-,$$
 (4)

which involves dissociation of the NO⁻ ion to an O⁻ ion and an N atom. In this process the N atom can be formed both in the ground state and in various excited states. The locations of the peaks calculated for process (4) are shown by the arrows 5 in Fig. 4. The main peak in the J^-/J^0 = f(ϵ) curve for O⁻ ions is located in the energy region corresponding to process (4) with formation of nitrogen atoms in the ground state and in low excited states. The peak in the 15 keV region is apparently associated with process (4) with formation of nitrogen atoms in highly excited states.

We can raise the question, in what degree is the structure observed by us in the curve σ_{01} = $f(\epsilon)$ for the pair H-NO^[2] associated with processes (3) and (4). As we can see from Fig. 4, in which along with the curves $J^{-}/J^{0} = f(\epsilon)$ for NO⁻ and O⁻ ions we have plotted the curve σ_{01} = $f(\epsilon)$ taken from our earlier work, ^[2] some correspondence of the structural features of these curves is observed. However, the quantitative evaluations presented below show that the structure in the $\sigma_{01} = f(\epsilon)$ curve is not associated with processes (3) and (4). In fact, the fluctuations in the $\sigma_{01} = f(\epsilon)$ curve can be produced by processes with cross sections of the order of 10^{-17} cm². By means of the potential method we have measured the total cross section σ^- for formation of slow negative ions for the pair H-NO in the energy range 6–30 keV. The value of σ^- in this energy range varies from $3-5 \times 10^{-18}$ cm². It is clear from this that process (3) and all the more process (4) have cross sections too small to explain the structure in the $\sigma_{01} = f(\epsilon)$ curve. In view of this, there remains only one possibility of explaining the structure in the $\sigma_{01} = f(\epsilon)$ curve for the pair H-NO. Apparently this structure is due to processes in which the NO⁻ ion formed breaks up into atoms of nitrogen and oxygen and an electron. The peaks corresponding to processes of this type are located in the energy range 6-40 keV (see Fig. 1 in our earlier paper^[2]), i.e., they overlap the energy region in which fluctuations are observed in the $\sigma_{01} = f(\epsilon)$ curve.

In spite of the data of Donahue and Hushfar,^[20] a careful study of the mass spectrum of negative ions arising in the passage of hydrogen atoms through CO, carried out for different primary beam energies, showed that no CO⁻ ions were present. This result agrees with experiments on the two-electron charge exchange of CO⁺ ions.^[17] In the mass spectrum of slow negative ions formed in passage of hydrogen atoms through CO, there are 93% O⁻ ions and 7% C⁻ ions. Consequently the probability of charge exchange with dissociation of the CO⁻ ion into a C⁻ ion and an O atom is considerably less than the probability for the process with dissociation of CO⁻ into an O⁻ ion and a C atom.

We obtained a $J^-/J^0 = f(\epsilon)$ curve (Fig. 5) for O⁻ ions formed as the result of the chargeexchange process

$$H + CO \rightarrow H^+ + (CO^-)^* \rightarrow H^+ + C^* + O^-,$$
 (5)

which involves the dissociation of the unstable CO^- ion into a C atom and an O^- ion.

According to a calculation based on Massey's adiabatic criterion, the peak in process (5) with formation of the C atom in the ground state should occur at an energy of 8 keV. The remaining peaks for process (5), with formation of C atoms in excited states, should be located in the interval 8-19 keV. We can see from Fig. 5 that the curve $J^{-}/J^{0} = f(\epsilon)$ for O⁻ ions for the region 8-12.5 keV contains structure with a main peak at 8 keV. We measured the total cross section σ^{-} for formation of slow negative ions for the pair H–CO in the energy range 11–15 keV. The value of the O⁻ cross section in this range varies from 3.4×10^{-19} to 2.7×10^{-19} cm².

From comparison of the curves of J^-/J^0 = f(ϵ) for O⁻ ions and $\sigma_{01} = f(\epsilon)$ for the pair H—CO,^[1] and also from the smallness of the cross section for formation of slow negative ions, we can conclude that the structure in the σ_{01} = f(ϵ) curve cannot be associated with process (5). As in the case of the H—NO pair, the structure in the $\sigma_{01} = f(\epsilon)$ curve for the H—CO pair is apparently due to the process

$$H + CO \rightarrow H^+ + (CO^-)^* \rightarrow H^+ + C^* + O^* + e.$$
 (6)

The peaks for process (6) are located in the energy region from 10-40 keV.



FIG. 5. The process $H^0 \rightarrow H^+$ in CO: $1 - H + CO \rightarrow H^+ + (CO^-)^* \rightarrow H^+ + O^- + C^*$ (the C atom is found both in the ground state and in all excited states up to the ionization level).

We were unable to measure the relation $J^{-}/J^{0} = f(\epsilon)$ for the H-H₂ pair because of the low intensity of the H⁻ ion beam.

The general conclusion which follows from the studies described above is that the structure in the $\sigma_{01} = f(\epsilon)$ curves for interaction of hydrogen ions with NO and CO molecules is not associated with formation of molecular or atomic negative ions in the charge exchange of hydrogen atoms with these molecules. Apparently this structure is due to processes such as (6).

B. Mass spectrum of slow positive ions. A mass spectrum analysis was also carried out for slow positive ions arising in passage of fast hydrogen atoms through the gases N₂, O₂, NO, and CO. Figures 6 to 9 show the results of a study of intensities of individual mass spectrum lines as a function of primary beam energy. The same figures show the energy dependence of the cross sections σ_{0-1} for electron capture by hydrogen atoms for the corresponding molecular gases, taken from our previous papers.^[1,2] The arrows indicate the locations of the peaks for the processes $H^0 \rightarrow H^-$, calculated with Massey's adiabatic criterion for a = 3 Å.⁶

It must be noted that slow positive ions are found not only in processes of electron capture by fast atoms, but also in processes of gas molecule ionization. Therefore the curves $J^+/J^0 = f(\epsilon)$ given in Figs. 6 to 9 refer to the total number of slow positive ions formed as the result of these two processes. Since the curves of the ionization cross section as a function of primary beam energy usually have only one peak, the structure which appears in the $J^+/J^0 = f(\epsilon)$ curves can be due only to electron capture processes. The presence or absence of structure in the J^+/J^0 $= f(\epsilon)$ curves depends on the relative probability of the electron capture and ionization processes. The structure can be absent or appear weakly if the probability of electron capture is small in comparison with the probability of ionization. These circumstances occur for the pairs H-N₂ and $H - O_2$.

In the $J^+/J^0 = f(\epsilon)$ curve for the ion N_2^+ , a break is observed near 11 keV which may be associated with the process $H^0 \rightarrow H^-$, accompanied by excitation of the N_2^+ ion.⁷

The absence of a falloff in the low-energy



FIG. 6. The process $H^0 \rightarrow H^-$ in N_2 : $1 - H^0 + N_2 \rightarrow H^- + N_2^+$; $2 - H^0 + N_2 \rightarrow H^- + N_2^+ [^2\Sigma_u^+]$; $3 - H^0 + N_2 \rightarrow H^- + (N_2^+)^* \rightarrow H^- + N^* + N^+$ (the N atom is found both in the ground state and in excited states).

region of the curve $J^+/J^0 = f(\epsilon)$ for the O_2^+ ion is apparently due to processes $H^0 \rightarrow H^-$ in which the O_2^+ ion is formed both in the ground state and in excited states. The flat peaks in these curves in the vicinity of 16 and 14 keV for the pairs $H-N_2$ and $H-O_2$, respectively, are probably related to ionization processes. For the case of $H-N_2$ this is confirmed by the data of Solov'ev et al.^[23]

Structure is absent in the $J^+/J^0 = f(\epsilon)$ curve for the N⁺ ion. It is clear that the processes $H^0 \rightarrow H^-$ accompanied by dissociation of the N⁺₂ ion into an N⁺ ion and an N atom have a low probability and therefore do not show up in the J^+/J^0 = $f(\epsilon)$ curve for N⁺ ions. The peaks corresponding to these processes also do not appear in the $\sigma_{0-1}(\epsilon)$ curve.

In the $J^+/J^0 = f(\epsilon)$ curve for the O⁺ ion a break is observed in the vicinity of 10 keV, corresponding to dissociation of the O⁺₂ ion.

We can see from Fig. 8 that in the case of the pair H—NO structure is observed in the J^+/J^0 = f(ϵ) curves for the ions N⁺, O⁺, and NO⁺. It follows from a theoretical calculation that this



FIG. 7. The process $H^0 \rightarrow H^-$ in O_2 : $1 - H^0 + O_2 \rightarrow H^- + O_2^+$; $2 - H^0 + O_2 \rightarrow H^- + O_2^+ [^2\Pi_u]$; $3 - H^0 + O_2 \rightarrow H^- + (O_2^+)^* \rightarrow H^- + O^+ + O^*$ (the O atom is found in the ground state and excited states).

⁶⁾The value $a = 3 \stackrel{\circ}{A}$ characterizes the processes $A^{\circ} \rightarrow A^{-}$.

⁷⁾The excitation energies of the ions CO⁺, N_2^+ , and O_2^+ were taken from the work of Mulliken,[²²] and the dissociation energies from Gaydon's book.[¹⁰]



FIG. 8. The process $H^{\circ} \rightarrow H^{-}$ in NO: $1 - H^{\circ} + NO \rightarrow H^{-} + NO^{+}$; $2 - H^{\circ} + NO \rightarrow H^{-} + NO^{+}$ $[a^{3}\Sigma^{+}]$; $3 - H^{\circ} + NO \rightarrow H^{-} + NO^{+}$ [x]; $4 - H^{\circ} + NO \rightarrow H^{-} + NO^{+}$ $[A^{1}\Pi]$; $5 - H^{\circ} + NO \rightarrow H^{-} + (NO^{+})^{*} \rightarrow H^{-} + N^{*} + O^{+}$; $6 - H^{\circ} + NO \rightarrow H^{-} + (NO^{+})^{*} \rightarrow H^{-} + N^{+} + O^{*}$ (in processes 5 and 6 the N and O atoms can be left both in the ground states and in all excited states up to the ionization level).

structure is associated with $H^0 \rightarrow H^-$ processes accompanied by excitation of the NO⁺ ion and its dissociation into excited fragments. The flat peak in the $J^+/J^0 = f(\epsilon)$ curve for the NO⁺ ion near 13 keV is apparently due to an ionization process. There are more positive nitrogen ions in the spectrum of the NO molecule than there are positive oxygen ions. It follows from this that dissociation of the NO⁺ ion into an N⁺ ion and an O atom is more probable.

In the case of the H—CO pair (Fig. 9) structure is also observed in the $J^+/J^0 = f(\epsilon)$ curves for the ions CO⁺, O⁺, and C⁺. The flat peak in the $J^+/J^0 = f(\epsilon)$ curve for the ion CO⁺ in the 17—22 keV region is apparently due to an ionization process.

Examination of Figs. 8 and 9 shows agreement of the energy ranges in which structure is observed in the σ_{0-1} curves and the $J^+/J^0 = f(\epsilon)$ curves for slow positive ions. However, the correspondence of individual peaks in the two structures is very difficult to establish, in view of the multiplicity and close spacing of the peaks.

We express our gratitude to V. A. Gusev, student and thesis candidate at Khar'kov State University, who took part in the measurements. We consider it a pleasure to thank Professor A. K. Val'ter for his constant interest and attention.



FIG. 9. The process $H^0 \rightarrow H^-$ in CO: $1 - H^0 + CO \rightarrow H^- + CO^+$; $2 - H^0 + CO \rightarrow H^- + CO^+$ [A²II]; $3 - H^0 + CO \rightarrow H^- + CO^+$ [B² Σ^+]; $4 - H^0 + CO \rightarrow H^- + (CO^+)^* \rightarrow H^- + C^+ + O^*$; $5 - H^0 + CO \rightarrow H^- + (CO^+)^* \rightarrow H^- + C^* + O^+$ (in processes 4 and 5 the C and O atoms can be left both in the ground states and in all excited states up to the ionization level).

³ Fogel', Ankudinov, Pilipenko, and Topolya, JETP **34**, 579 (1958), Soviet Phys. JETP **7**, 400 (1958).

⁴ Fogel', Krupnik, and Ankudinov, ZhTF **26**, 1208 (1956), Soviet Phys. Technical Phys. **1**, 1181 (1957).

⁵ Fogel', Krupnik, Koval', and Slabospitskii,
ZhTF 27, 988 (1957), Soviet Phys. Technical Phys.
2, 902 (1958).

⁶ N. V. Fedorenko and V. V. Afrosimov, ZhTF **26**, 1941 (1956), Soviet Phys. Technical Phys. **1**, 1872 (1957).

⁷ Fogel', Koval', Levchenko, and Khodyachikh, JETP **39**, 548 (1960), Soviet Phys. JETP **12**, 384 (1961).

⁸ Bukhteev, Bydin, and Dukel'skii, ZhTF **31**, 688 (1961), Soviet Phys. Technical Phys. **6**, 496 (1961).

⁹ Fogel', Koval', and Levchenko, JETP **40**, 13 (1961), Soviet Phys. JETP **13**, 8 (1961).

¹⁰ A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, Chapman and Hall, Ltd, London, 1947 (Russ. Transl., IIL, 1949).

¹¹ B. E. Knox and B. P. Burtt, J. Chem. Phys. **28**, 1256 (1958).

¹²G. G. Cloutier and H. I. Schiff, J. Chem. Phys. **31**, 793 (1959).

¹³ R. E. Fox, J. Chem. Phys. **32**, 285 (1960).

¹⁴ R. K. Curran and R. E. Fox, J. Chem. Phys. **34**, 1590 (1961).

¹⁵G. J. Schulz, J. Chem. Phys. **34**, 1778 (1961).
¹⁶ Rudolph, Melton, and Begun, J. Chem. Phys. **30**, 588 (1959).

¹⁷ A. A. Kalmykov, thesis, Khar'kov State University, 1958.

¹D. V. Pilipenko and Ya. M. Fogel', JETP **42**, 936 (1962), Soviet Phys. JETP **15**, 646 (1962).

² D. V. Pilipenko and Ya. M. Fogel', JETP **44**, 1818 (1963), Soviet Phys. JETP **17**, 1222 (1963).

¹⁸ C. E. Moore, Atomic Energy Levels, Circular No. 467, Vol. 2, National Bureau of Standards, Washington, 1952.

¹⁹ K. P. Huber, Helv. Phys. Acta 34, 929 (1961).
 ²⁰ T. M. Donahue and F. Hushfar, Nature 186, 1038 (1960).

²¹Ya. M. Fogel', UFN **71**, 243 (1960), Soviet

Phys. Uspekhi 3, 390 (1960).

²² R. Mulliken, Rev. Mod. Phys. 4, 1 (1932).
 ²³ Solov'ev, Il'in, Oparin, and Fedorenko, JETP

42, 659 (1962), Soviet Phys. JETP 15, 459 (1962).

Translated by C. S. Robinson 55