

Interaction of protons and hydrogen atoms with CO molecules

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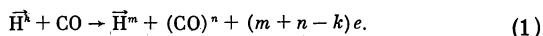
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The cross sections for the elementary processes of change of charge states of particles in collisions between \bar{H}^+ , \bar{H}^0 , and CO molecules are measured in the 5-50 keV range for the impinging particles. A charge and mass analysis was performed for both the fast hydrogen particles and slow ions produced from the target molecules. The particles which are partners of a single-collision act were measured by the coincidence technique.^[1] The retarding potential method was employed for studying the energy spectrum of the C^+ and O^+ ions produced as a result of dissociation of CO molecules. It is shown that the main role in slow ion formation is played by elementary processes involving the formation of fast \bar{H}^0 atoms after the collision (ionization processes for \bar{H}^0 -CO and capture processes for \bar{H}^+ -CO). The contribution of processes involving the formation of fast protons (stripping for \bar{H}^0 -CO and ionization for \bar{H}^+ -CO) increases with growth of the energy and at $T_0 = 50$ keV reaches 50%. The least significant role is played by processes involving the formation of fast negative \bar{H}^- ions (capture for \bar{H}^0 -CO and double capture for \bar{H}^+ -CO). The great majority of O^+ ions possess energies $\epsilon > 1.5$ eV and are formed as a result of dissociation of the $(CO)^+$ and $(CO)^{+2}$ systems from the repulsive states. However, along with the component $\epsilon > 1.5$ eV in the C^+ ion distribution there is a component with lower energies whose role sharply grows with decrease of energy of the incident particles T_0 . It is suggested that this might be due to predissociation of the vibrationally excited bound states of $(C+O^+)$ followed by transition to the repulsive state of (C^++O) and also by dissociation of the vibrationally excited states of (C^++O) due to the direct transfer of kinetic energy of the incident particles to nuclei of the target molecules.

The elementary processes of charge-state changes in $\bar{H}^k + CO$ collisions (with k equal to 0 or +1) can be represented by



Here slow atomic ions can be formed in dissociation processes, $(CO)^n \rightarrow C^p + O^q$, $n = p + q$.

I. EXPERIMENTAL PROCEDURE

In cross section measurements with registration of all the interacting particles following collisions we employed a coincidence technique similar to that described in^[1]. To measure cross sections for \bar{H}^0 -CO interactions we used a beam of 1s atoms produced as described in^[2]. Absolute cross sections for the elementary processes were measured as follows. A charge-state analysis of the slow ions^[3] formed from the target molecules was the basis for determining the absolute total cross sections for the production of slow ions with given ratios (ne/M) of charge n and mass M ; these cross sections are conventionally designated by σ_M^n . From coincidences we then determined the relative values of elementary-process cross sections σ_M^{nkm} , which are components of the total cross sections σ_M^n and correspond to fixed charge states (m) of the fast hydrogen particles after collisions. For this purpose we measured the relative numbers of coincidences of slow ions with given ne/M and the differently charged fast particles \bar{H}^+ , \bar{H}^0 , \bar{H}^- .

The foregoing procedure enabled us to determine the absolute components σ_M^{nkm} of the total cross sections σ_M^n . However, even the cross sections σ_M^{nkm} do not always correspond in each case to a single definite elementary process. In the dissociation of the molecular ions the atomic ions C^+ and O^+ can result both from the dissociation of $(CO)^+$ into an ion and an atom (C^+

+ 0 or $C + O^+$) and from the dissociation of $(CO)^{2+}$ into two ions ($C^+ + O^+$). Consequently, the immediate result of the described experiment utilizing the coincidence technique is that we determine the combined cross sections

$$\sigma_{C^+}^{km} = \sigma_{C^+,0}^{km} + \sigma_{C^+,O^+}^{km}, \quad \sigma_{O^+}^{km} = \sigma_{C^+,O^+}^{km} + \sigma_{C^+,O^+}^{km}. \quad (2)$$

To distinguish the process wherein a pair of slow atomic ions results from a single collision (σ_{C^+,O^+}^{km}) we utilized the difference between the respective times of flight of the C^+ and O^+ ions from their point of origin to the detector. For this purpose all the slow ions were extracted from the collision chamber by an electric field and reached the detector directly without analysis in a magnetic field. The ne/M separation of the ions was based on their times of flight. When registering coincidences between fast (\bar{H}^m) and slow ions (in this case C^+ and O^+), adjustment of the delay time permitted separate measurements of the numbers of $\bar{H}^m - C^+$ and $\bar{H}^m - O^+$ coincidences. When the delay time in the coincidence scheme corresponded to the C^+ time of flight, coincidence pulses were registered for both $C^+ + 0$ and $C^+ + O^+$ dissociations. When the delay time corresponded to the O^+ time of flight, coincidence pulses were registered only if the CO^+ molecular system dissociated into C and O^+ . The cause lies in the fact that when an ion pair $C^+ + O^+$ was formed the O^+ ion reached the detector only 0.2 μ sec later than the C^+ ion. The "dead time" of the electronics was ~ 0.4 μ sec, so that the O^+ ion could not be registered.

The ratio of the numbers of coincidences, of fast \bar{H}^m with C^+ and of fast \bar{H}^m with O^+ , can therefore be represented by

$$\frac{N_{12}(\bar{H}^m, C^+)}{N_{12}(\bar{H}^m, O^+)} = \frac{\sigma_{C^+,0}^{km} + \sigma_{C^+,O^+}^{km}}{\sigma_{C^+,O^+}^{km}} \quad (3)$$

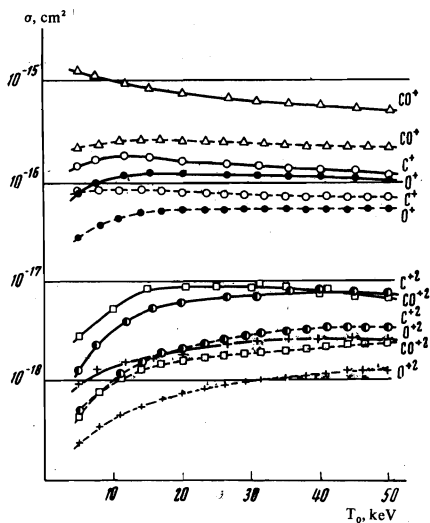


FIG. 1. Total cross sections for the production of slow ions in \bar{H}^+ - CO collisions (solid curves) and \bar{H}^0 - CO collisions (dashed curves). Slow ions: Δ - CO^+ , \circ - C^+ , \bullet - O^+ , \square - CO^{2+} , \ominus - C^{2+} , $+$ - O^{2+} .

The absolute cross sections $\sigma_{C^+O^+}^{km}$, $\sigma_{C^+O^+}^{km}$, and $\sigma_{C^+O^+}^{km}$, were determined from (2) and (3).

To determine the instrumental corrections for the efficiency of registering and collecting slow ions we counted the coincidences of fast negative ions \bar{H}^- with slow atomic ions from interactions of protons with CO molecules. These events were chosen because the production of atomic ions through the capture of two electrons by a proton involves the process $\bar{H}^+ + CO \rightarrow \bar{H}^- + C^+ + O^+$, which clearly leads to the production of an ion pair. In the ideal case of the complete collection and registration of slow ions only $\bar{H}^- - C^+$ coincidences could be observed, while $\bar{H}^- - O^+$ coincidences should be absent. The actually measured ratio of $\bar{H}^- - O^+$ to $\bar{H}^- - C^+$ coincidences permitted an experimental determination of the collection and registration efficiency of slow ions.

The described procedure was employed to investigate the elementary processes wherein, following collisions, fast hydrogen particles existed as \bar{H}^+ , \bar{H}^0 , or \bar{H}^- and the ions CO^+ , C^+ , C^{2+} , O^{2+} , and CO^{2+} appeared in the gas. An investigation of processes that produce more highly charged slow ions ($n > 2$) does not increase the number of qualitatively different charge-changing processes; therefore we did not study such processes. We had previously^[4] investigated the production of the slow negative ions O^- and C^- in collisions of protons and hydrogen atoms with CO molecules.

II. CROSS SECTIONS FOR PROCESSES OF CHARGE-STATE CHANGES

1. Total cross sections for the production of slow ions.

Figure 1 shows data on the total cross sections for the production of molecular and atomic ions from CO molecules. It is seen that the cross section for the production of any slow ion in a \bar{H}^+ - CO collision is more than twice as great as in a \bar{H}^0 - CO collision. The cross sections for CO^+ production are largest in both collisions. At $T_0 = 5$ keV, σ_{CO^+} for \bar{H}^+ - CO is $1.2 \times 10^{-15} \text{ cm}^2$ and increases further as the proton energy is reduced below 5 keV; the maximum of σ_{CO^+} for

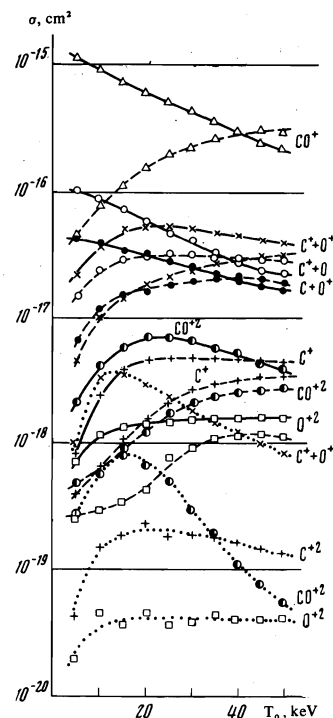


FIG. 2. Cross sections for elementary processes changing the charge states of particles in \bar{H}^+ - CO collisions. Solid curves—capture, and capture with ionization ($\bar{H}^+ \rightarrow \bar{H}^0$); dashed curves—ionization (without changing the charge of the fast particle \bar{H}^+); dotted curves—double capture ($\bar{H}^+ \rightarrow \bar{H}^-$). The curves are labeled with the corresponding slow ions.

\bar{H}^0 - CO is $2.7 \times 10^{-16} \text{ cm}^2$ at ~ 20 keV. Next in size are the cross sections for the production of the atomic ions C^+ and O^+ ; at $T_0 > 25$ keV these cross sections are close in size for collisions of both \bar{H}^+ and \bar{H}^0 with CO and diminish as T_0 increases. Below 10 keV we observe an important difference between the dependences of σ_{C^+} and σ_{O^+} on the energy of the fast particles. As T_0 decreases, σ_{C^+} decreases considerably more slowly than σ_{O^+} ; at $T_0 = 5$ keV the former is about twice as large as σ_{O^+} in \bar{H}^+ - CO collisions and four times larger in \bar{H}^0 - CO collisions.

The cross sections for the production of doubly-charged ions are smallest. It is important to note the high probability that dissociation does not accompany the capture of two electrons ($\sigma_{CO^{2+}}$). The total cross sections for production of slow ions in the present work agree quite well with those obtained by Browning and Bilbody in^[5].

2. Cross sections for elementary processes. The cross sections for the elementary processes involving changes of charge states i.e., the components of the total cross sections σ_M^n , were measured for the first time in the present work and are shown in Fig. 2 (for \bar{H}^+ - collisions) and in Fig. 3 (for \bar{H}^0 - CO collisions). In almost the entire investigated range of T_0 the greatest contribution to slow-ion production is seen to come from collision processes yielding fast hydrogen atoms \bar{H}_0 (capture of a single electron for \bar{H}^+ - CO and ionization for \bar{H}^0 - CO). Increase of T_0 enhances the cross sections for processes yielding fast protons, \bar{H}^+ (ionization for \bar{H}^+ - CO and stripping with ionization for \bar{H}^0 - CO). The cross sections for these elementary processes reach their maximum sizes at $T_0 \geq 50$ keV. Processes involving the production of fast negative

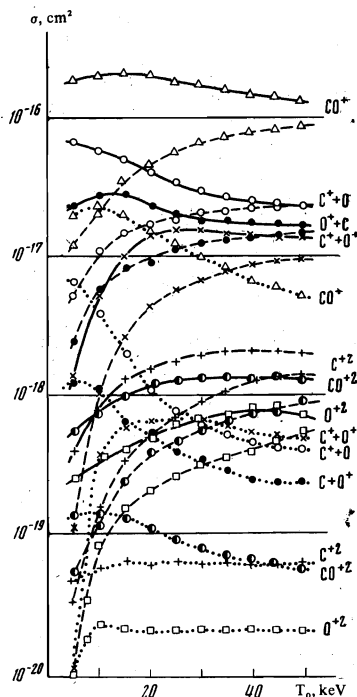


FIG. 3. Cross sections for the elementary processes in $\bar{H}^0 - CO$ collisions. Solid curves—ionization (without changing the charge of the fast particle \bar{H}^0); dashed curves—stripping with ionization ($\bar{H}^0 \rightarrow \bar{H}^+$); dotted curves—capture, and capture with ionization ($\bar{H}^0 \rightarrow \bar{H}^-$). The curves are labeled with the corresponding slow ions.

\bar{H}^- ions are important only at 5–20 keV, where their peaks are observed.

For both $\bar{H}^+ - CO$ and $\bar{H}^0 - CO$ collisions it should be noted that a large contribution to the production of the atomic ions C^+ and O^+ comes from elementary processes yielding the ion pair $C^+ + O^+$. An electronic transition from the ground state of the CO molecule to a state of $(CO)^{2+}$ requires a greater expenditure of energy ($\Delta E \geq 43$ eV) than a transition to a state of $(CO)^+$ ($\Delta E \geq 14.6$ eV)^[6] and is less likely to occur. However, in the great majority of cases (>90%) the $(CO)^{2+}$ system dissociates, while the $(CO)^+$ system remains in a bound state. Consequently, at $T_0 \sim 30\text{--}50$ keV the cross sections for the formation of atomic ions through transitions to states of $(CO)^+$ and $(CO)^{2+}$ are of comparable size.

Another characteristic of the elementary processes is that with decreasing energy T_0 the probability that $(CO)^+$ will dissociate into $C^+ + O$ increases over the probability of dissociation into $O^+ + C$. This is observed when all elementary processes occur which yield singly-charged atomic ions and is clearly evident for ionization with dissociation (in $\bar{H}^0 - CO$ collisions) and for capture with dissociation (in $\bar{H}^+ - CO$ collisions). These are the processes that determine the different behaviors, total noted in the preceding section, of the cross sections for C^+ and O^+ production as functions of the incident energy T_0 (Fig. 1).

3. Capture and loss of electrons by fast \bar{H}^0 atoms.

In the case of $\bar{H}^0 - CO$ collisions the total cross sections for electron loss σ^{01} ^[7,8] and capture of a single electron σ^{0-1} ^[8] have been measured heretofore. These cross sections were measured by determining the total number of fast ions (H^+ and H^- , respectively) following $\bar{H}^0 - CO$ collisions. The observed dependences of σ^{0-1} and

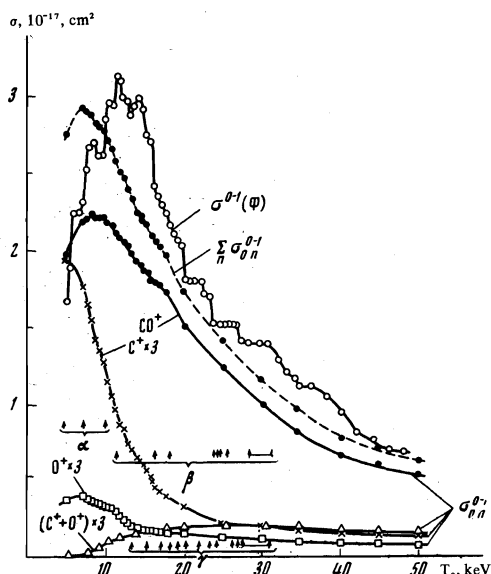
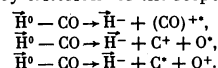


FIG. 4. Cross sections for capture of electrons in CO by fast hydrogen atoms. The curves are labeled with the corresponding slow ions. $\sigma^{0-1}(\Phi)$ —total capture cross sections in [8]; $\Sigma \sigma_{Mn}^{0-1}$ —total capture cross section in present work. α, β, γ —regions where the maxima of [8] should be located on the basis of the Massey criterion for the respective processes



The arrows designate expected positions of the maxima for specific excited states of the particles.

σ^{01} on the incident energy T_0 revealed structure that was explained by Pilipenko and Fogel^[8] on the basis of Massey's criterion. They believe that the peaks on the curve of the capture cross section $\sigma^{0-1}(T_0)$ correspond in the incident energy range 5–10 keV to the formation of CO^+ ions in different excited states, and in the range 10–30 keV to dissociation of the molecular ion into $C^+ + O$ and $C + O^+$ (Fig. 4). The peaks on the curve of the electron loss cross section $\sigma^{01}(T)$ were attributed to molecular capture of an electron followed by dissociation of CO^- into an atom and ion in different channels.

It was reasonable to expect that measurements of the elementary processes, fixing the change of charge of the fast particle and also the charges and masses of the slow ions, would reveal more clearly any structure in the curves of the cross sections as functions of T_0 . For example, for the elementary processes providing the components of the total cross section σ^{0-1} that involve formation of CO^+ , $C^+ + O$, and $C + O^+$ it is possible to indicate the energy region where the curves of σ_{Mn}^{0-1} should exhibit structure (Fig. 4).

The measurements of cross sections for elementary processes involving electron loss or capture by fast hydrogen atoms did not confirm the existence of structure in the $\sigma^{01}(T_0)$ and $\sigma^{0-1}(T_0)$ curves. It should be remembered, of course, that in the case of electron loss by a fast particle any structure in the $\sigma^{01}(T_0)$ curve might possibly not be associated with the formation of slow ions, but only with the excitation of a target molecule. This situation does not arise in connection with capture. The formation of a fast \bar{H}^- ion always leads to the formation of a slow positive ion, and the coincidence

technique enables measurements of the cross sections for all the elementary processes providing components of the total capture cross section σ^{0-1} . Figure 4 shows that all the elementary processes of charge-state changes are represented by smooth $\sigma_{Mn}^{0-1}(T_0)$ curves. Naturally, then, the dependence on T_0 of the total capture cross section $\sum_n \sigma_{Mn}^{0-1}$ based on our data is smooth. At the same time, the absolute value of $\sum_n \sigma_{Mn}^{0-1}$ agrees

quite well with the results obtained by Pilipenko and Fogel.^[8] We must only note the difference in the position of the peak on the σ^{0-1} curve (~ 12 keV according to^[8] and ~ 7 keV according to our present data).

4. Dissociation of the molecular system $(CO)^+$.

Electronic transitions to a repulsive state of $(CO)^+$, leading to the formation of singly-charged ions (dissociation into $C^+ + O$ or $C + O^+$), require a larger expenditure of energy than transitions to a bound state of CO^+ . Therefore, in transitions that obey the Franck-Condon principle we will expect that the relative probability of $(CO)^+$ dissociation will diminish as T_0 decreases. The cross section measurements of the elementary processes show that, except in the case of the charge exchange $\bar{H}^+ + CO \rightarrow \bar{H}^0 + (CO)^+$, the relative probability of $(CO)^+$ dissociation is always enhanced with the decrease of T_0 . This result indicates the presence of another mechanism of $(CO)^+$ dissociation, which is different from the mechanism of electronic transitions, obeying the Franck-Condon principle; to repulsive states of $(CO)^+$.

Figure 5 illustrates the increasing probability of dissociation following $CO - (CO)^+$ transitions as T_0 decreases in $\bar{H}^0 - CO$ collisions, and the contributions of the two decay channels, $C^+ + O$ and $C + O^+$. We had previously observed the increasing probability of molecular ion dissociation with the decrease of incident energy, in collisions of protons and hydrogen atoms with hydrogen molecules.^[9] This effect was associated with dissociation of the molecular ion resulting from direct transfer of kinetic energy of the incoming particle to nuclei of the target molecule. When the transferred energy exceeds the binding energy of the particles in the molecular system, dissociation of $(CO)^+$ is possible. The probability of the formation of the atomic ions C^+ and O^+ then increases. As the incident kinetic energy T_0 decreases, more energy is transferred to the nuclei of the target molecule. Thus, in the Coulomb interaction between the particles the cross section for transfer of kinetic energy exceeding a certain value D is proportional to $1/DT_0$.^[10]

It is interesting that in $\bar{H}^+ - CO$ and $\bar{H}^0 - CO$ collisions an increasing probability of dissociation is observed only for processes leading to the formation of $C^+ - O$ pairs. The relative probability of $(CO)^+$ dissociation into $O^+ + C$ remains constant within the entire range of energies. The relative probability of dissociation into $C^+ + O$ increases sharply for $T_0 < 20$ keV. The picture is similar for capture and stripping with ionization in $\bar{H}^0 - CO$ collisions, and also for ionization in $\bar{H}^+ - CO$ collisions. To account for these experimental results we must know how the potential energy $U(R)$ of the interaction depends on the internuclear distance for different states of the $(CO)^+$ system.

At the present time we unfortunately lack such data, but we can utilize the $U(R)$ curves shown in Fig. 6 for

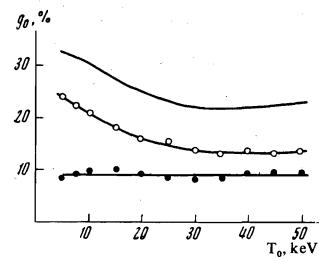


FIG. 5. Relative probability of dissociation of $(CO)^+$. Solid curve—combined relative probability, \circ —to $C^+ + O$, and \bullet —to $C + O^+$, in the ionization process $\bar{H}^0 + CO \rightarrow \bar{H}^0 + (CO)^+ + e$ (T_0 in keV).

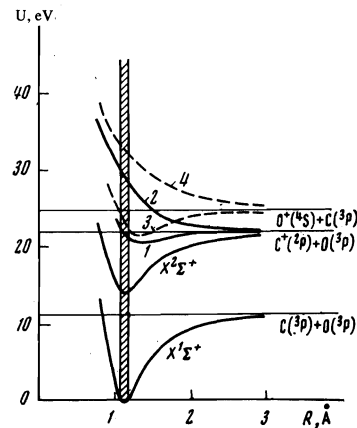


FIG. 6. Potential energy curves of the CO system.

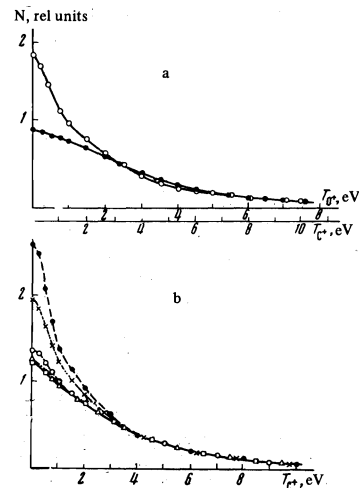


FIG. 7. Integrated kinetic energy spectra of slow ions which are dissociation products of $\bar{H}^0 - CO$ collisions. a— α —for C^+ and O^+ formed at incident particle energy $T_0 = 10$ keV: \circ —for C^+ , \bullet —for O^+ . b— β —for C^+ formed at different incident particle energies: \bullet —5 keV, \times —10 keV, Δ —20 keV, \square —50 keV.

the purpose of a qualitative explanation. Ground-state curves for the molecule, $(CO)X^1\Sigma^+$, and for the ion, $CO^+(C^+ + O)X^2\Sigma^+$, were obtained from^[11,12]. The potential curves of the systems $C^+ + O$ (curves 1, 2) and $C + O^+$ (curves 3, 4) were obtained from data on the ionization potentials of C and O atoms and the appearance potentials of C^+ and O^+ ions from CO in electron impacts.^[6] These data enable us to determine the positions of the potential curves at large internuclear distances ($R \rightarrow \infty$) and in the region of equilibrium distances for the CO molecule. Since the ionization potential of the oxygen atom exceeds that of the carbon atom by 2.3 eV, the discrete vibrational spectrum of $(C + O^+)$ bound

states must overlap the continuous spectrum of ($C^+ + O$). This permits a predissociation process (a transition from curve 3 to curve 2) that leads to the dominance of C^+ production. The kinetic energy of C^+ ions formed by predissociation should not exceed ~ 1.3 eV.

The retarding potential technique was used to analyze the kinetic energies of slow C^+ and O^+ ions formed in $\bar{H}^+ - CO$ and $\bar{H}^0 - CO$ collisions. Figure 7 shows the integrated spectra of C^+ and O^+ in $\bar{H}^0 - CO$ collisions at $T_0 = 10$ keV. The energy scales of the C^+ and O^+ ions are such that a single abscissal point corresponds to all ions possessing identical momentum. Clearly, for dissociation into an ion pair the retardation curves of the C^+ and O^+ ions must coincide for these scales.

Figure 7a shows that the C^+ and O^+ energy spectra differ markedly at low energies. The C^+ ions have a strong component in the 0–1.5 eV region, where O^+ ions are not observed. At $\epsilon \geq 3$ eV for C^+ and $\epsilon \geq 2$ eV for O^+ , which according to^[6] correspond to dissociation from repulsive states of $(CO)^+$ and $(CO)^{2+}$, the retardation curves are close. Consequently, the probabilities of transitions to repulsive states of $C^+ + O$ and $O^+ + C$ do not differ significantly. The presence of a low-energy C^+ component supports the hypothesis that predissociation causes the greater total yield of C^+ ions than of O^+ ions. The probability of predissociation can be strongly dependent upon the population of the vibrational bound states of $(C + O^+)$ (curve 3 of Fig. 6) that lie closest to the intersection point of curves 2 and 3 in Fig. 6. The population of these excited levels must grow with increasing direct transfer of energy from incident particles to nuclei of the molecules. As already mentioned, this transfer increases as T_0 diminishes,—an effect that appears to be reflected in the growing number of slow C^+ ions as T_0 decreases (Fig. 7b).

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