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FORMATION OF HIGHLY EXCITED ATOMS IN ELECTRON COLLISIONS WITH CO, O_2, AND N_2

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It is shown that highly excited C*, O*, and N* atoms result from the excitation of high-lying Rydberg states, in CO, O_2, and N_2 molecules, which converge to the respective limits for singly and doubly charged ions of the initial molecules. The molecular ions CO^+ and O_2^+ are produced in collisions between highly excited oxygen atoms and CO or O_2 molecules. The formation of long-lived highly excited states of CO, O_2, and N_2 has not been observed. The cross sections for the scattering of highly excited O* and C* colliding with CO molecules are ~2 × and 1.5×10^{-13} cm^2, respectively.

LONG-lived highly-excited states have recently been observed in inert-gas atoms,[1] hydrogen molecules,[2] and deuterium.[3] It has been shown[2] that when electrons collide with molecules that include hydrogen, carbon, oxygen, or nitrogen atoms among their constituents, these atoms become highly excited. However, the processes responsible for the formation of such states have not been investigated.

The ionization potentials of many molecules, such as those of water and the hydrocarbons, are lower than the excitation energies of the hydrogen atoms that are produced in the disintegration of the molecules. Therefore the highly excited hydrogen atoms react with unexcited initial molecules. These processes have been investigated in ethylene,[4] water,[5] and methane.[6]

It has been our purpose in the present work to study the processes involved in the production of long-lived highly excited states in nitrogen, oxygen, and carbon atoms, and also the different ionization processes involved in collisions between the excited atoms and unexcited molecules. These processes occur in the ionosphere and in the plasma of gas discharges.

1. EXPERIMENTAL CONDITIONS AND RESULTS

The experimental equipment and technique have been described in[2,7]. Pure gases or their binary mixtures were introduced into a two-chamber source. The mass spectra of the ions formed in the second chamber were investigated as functions of the gas pressure, as well as of the energy and current of the electrons that excited the gas in the first chamber. The ion source was operated under conditions that prevented the passage of ions and electrons from the first chamber into the second.[1)]

The gas pressure in the ion source was regulated within the broad interval 3×10^{-7}–3×10^{-4} Torr according to the readings of an LM-2 vacuum-tube ion gauge; the pressure was usually $\sim 1.5 \times 10^{-4}$ Torr. The electron energy was varied in the range 5–100 eV, and the total electron current I_e was varied from 0.1 to 1.5 mA. The electron current in the beam was $\sim(0.1-0.3)\,I_e$.

We registered the highly-excited states of atoms entering the second chamber from the first by measuring the ion current produced in one of the following processes:

1) Ionization of a molecule M in a collision with a highly excited atom A*:

$$M + A^* \rightarrow M^+ + A + e; \qquad (1)$$

2) ionization of an atom A* near the surface of the metal (Me) during its passage through the copper grid:

$$A^* + Me \rightarrow A^+ + Me; \qquad (2)$$

3) ionization of an atom A* in an electric field U after traversing the second chamber:

$$A^* + U \rightarrow A^+ + U + e. \qquad (3)$$

Process (1) resembles the familiar Penning ionization that occurs when metastable atoms collide with molecules, if the excitation energy E_A^* of the atom A* exceeds or is of the same order as the ionization potential E_M^* of the molecule M. This happens frequently since the excitation energy of A* is quite high:

$$E_{A^*} \approx E_{A^+} - 13.6 n^{-2}, \qquad (4)$$

where E_A^+ is the ionization potential of unexcited atoms A in electron volts, and n is the principal quantum number.

In some instances, when A possesses considerable electron affinity φ_A reaction (1) can yield negative ions A^-:

$$M + A^* \rightarrow M^+ + A^-. \qquad (5)$$

This becomes energetically possible when

$$E_{A^*} + \varphi_A \gtrsim E_{M^+}, \qquad (6)$$

and therefore $E_A^* < E_M^+$.

Process (2) was first observed in[8] in the case of highly excited positive ions, and was used in[2,9] to register highly excited states of atoms and molecules. Experimental proofs of this effect are given in[10] and a theoretical discussion in[11].

[1)] Between the chambers there was an ion-retarding potential V_r = 22 V and another potential V_d = 38 V that deflected ions and electrons. In addition, the first chamber was immersed in a magnetic field H ~ 250 Oe.

We have neglected the manner in which (1), (2), and (5) might be influenced by the kinetic energy of the particles, which is only ~0.02 eV for molecules and Ar* atoms, but can reach ~2 eV or higher for the "fragment" atoms. In cases (1) and (5), if E_M^+ is large and (6) is not fulfilled, the kinetic energy is important and can overcome the endothermicity of these reactions. Process (2) occurs without the participation of kinetic energy, which the A* atom requires so that the positive ion A^+ formed near the metal surface can overcome the mirror image force between the ion and the induced negative charge in the metal.

Process (3) is used extensively in investigations of highly excited fast hydrogen atoms.[12] It also occurs in the cases of highly excited multi-electron atoms and ions.[10]

Figures 1 and 2 show typical dependences of ion yields on the electron current and gas pressure; Figs. 3 and 4 show dependences on the electron energy.

2. DISCUSSION OF RESULTS

Excited atoms and molecules were produced in the first chamber of the ion source through the following collision reactions:

$$CO + e \to C^* + [O] + e, \qquad (7)$$

$$CO + e \to O^* + [C] + e, \qquad (8)$$

$$CO + e \to CO^* + e, \qquad (9)$$

$$O_2 + e \to O^* + [O] + e, \qquad (10)$$

$$O_2 + e \to O_2^* + e, \qquad (11)$$

$$N_2 + e \to N^* + [N] + e, \qquad (12)$$

$$N_2 + e \to N_2^* + e. \qquad (13)$$

The second chamber, located ~0.7 cm.from the excitation region in the first chamber, was reached by excited particles having sufficiently long lifetimes τ with respect to spontaneous photon emission:[17] $\tau \gtrsim 10^{-6}$ sec for "fragment" atoms and $\gtrsim 3 \times 10^{-5}$ sec for molecules. Metastable states of the atoms and molecules were not investigated, because their excitation energies are small and therefore they did not appear in processes (1)—(3), (5).

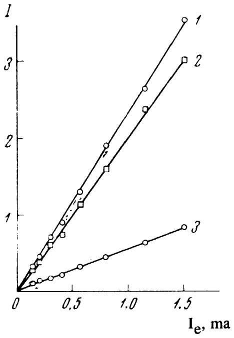

FIG. 1. Influence of the electron current I_e on ion intensities I in the mass spectrum of CO (in arbitrary units): 1–O^+, 2–C^+, 3–CO^+. The electron energy is 80 eV.

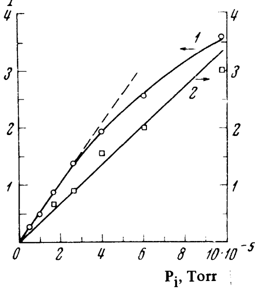

FIG. 2. Influence of CO pressure on ion intensity I: 1–O^+, 2–CO^+/O^+ current ratio. I and I′ are given in arbitrary units; the electron energy is 80 eV and the current is 1.5 mA.

A. Highly Excited Atoms Produced in Molecular Disintegration

Figures 1 and 2 indicate that highly excited C* and O* atoms result from single collisions between electrons and CO molecules; N* is obtained analogously from nitrogen and O* from oxygen. Figures 3 and 4 show that the corresponding thresholds are close to the thresholds for the production of ion fragments in

$$CO + e \to C^+ + O + 2e, \qquad (14)$$

$$CO + e \to O^+ + C + 2e, \qquad (15)$$

$$O_2 + e \to O^+ + O + 2e, \qquad (16)$$

$$N_2 + e \to N^+ + N + 2e. \qquad (17)$$

The dependences of excited atom yields on electron energy exhibit a structure that reflects the excitation of different electronic states in the molecules. A comparison of curves 2 and 3 in Fig. 3 shows that their shapes are essentially independent of the mechanism for transforming an excited atom into a singly-charged ion. Figures 3 and 4 show that structure appears at electron energies that are near the thresholds for

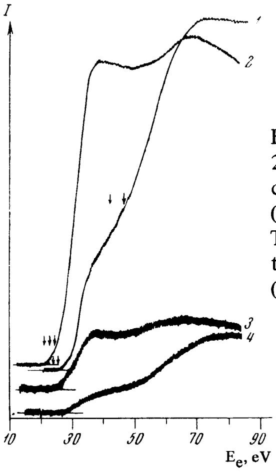

FIG. 3. Influence of electron energy E_e on intensities I of ions from CO: 1–O^+, 2–C^+ [Obtained from O* and C* in process (2)]; 3–C* [obtained from process (3)]; 4–CO^+ obtained from process (5). The arrows indicate the C^+, O^+, and CO^{2+} thresholds in processes (14), (15), and (18), taken from [13,14].

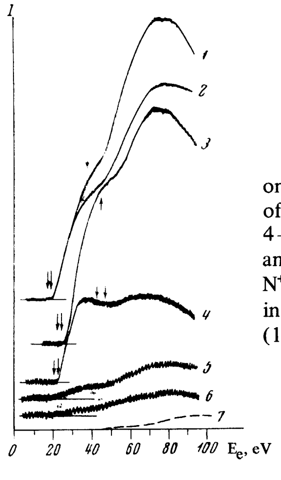

FIG. 4. Influence of electron energy E_e on ion intensities I: 1–O^+ in a 1:2 mixture of CO and O_2, 2–O^+ in O_2, 3–N^+ in N_2, 4–C^+, 5–O_2^+, 6–CO^+ in the mixture of CO and O, 7–N_2^+. The arrows indicate the O^+, N^+, C^+, O_2^{2+}, N_2^{2+}, and CO^{2+} thresholds in processes (16), (17), (14), (19), (20), and (18), taken from [15,16].

doubly-charged ion production in the processes

$$CO + e \rightarrow CO^{2+} + 3e, \tag{18}$$

$$O_2 + e \rightarrow O_2^{2+} + 3e, \tag{19}$$

$$N_2 + e \rightarrow N_2^{2+} + 3e. \tag{20}$$

Structure in the dependences of the highly-excited C*, O*, and N* yields on electron energy indicates that these atoms are produced in various processes. First, in processes (7), (8), (10), and (12) the electrons excite high-lying Rydberg molecular states converging to the corresponding singly-charged ionic states. The molecules then break up into ions according to (14)—(17). In this case the threshold for highly excited atoms should be close to those for the corresponding ions; this is confirmed by observations (Figs. 3 and 4). Secondly, there are processes exciting higher-lying states that converge to the corresponding states of doubly-charged ions. This group comprises mainly the highly-excited states of the singly-charged ions $CO^{+}*$, $O_2^{+}*$, and $N_2^{+}*$, and can include excitations that are sufficiently long-lived to be observed, as has occurred for $O_2^{+}*$.[18] In other instances disintegration yields a positive ion and a highly-excited atom. Consequently, the highly-excited atoms in this group are produced in the processes

$$CO + e \rightarrow C^{*} + O^{+} + 2e, \tag{21}$$

$$CO + e \rightarrow C^{+} + O^{*} + 2e, \tag{22}$$

$$O_2 + e \rightarrow O^{*} + O^{+} + 2e, \tag{23}$$

$$N_2 + e \rightarrow N^{*} + N^{+} + 2e. \tag{24}$$

The existence of many molecular Rydberg series converging to different highly-excited ion states must lead to a more highly developed fine structure[2)] for each group of highly-excited atoms. Monoenergetic electron beams are required to resolve these structures.

We know[19] from the mass spectra of N_2, O_2, and CO that approximately equal fractions of the atomic ions N^{+} and O^{+} as well as of the sum of C^{+} and O^{+} are produced (5.2, 5.1, and 6.4%). Since the total ionization cross sections of these molecules are also nearly identical (2.74, 2.70, and 2.99×10^{-16} cm^{2}),[20] we can therefore assume approximately identical cross sections for the production of N^{+}, O^{+}, and $C^{+} + O^{+}$.

We compared the relative cross sections for N*, O*, and C* + O* formation from N_2, O_2, and CO. At $E_e = 70$ eV, corresponding to maxima in Figs. 3 and 4, $\sigma(N^{*}) \approx \sigma(O^{*}) \approx 1.5\,\sigma(C^{*} + O^{*})$. These relations are obtained by direct measurements of ion currents formed from highly excited atoms in process (2). However, this procedure is not always correct, since we do not know the kinetic energy distribution of the atoms, which can affect the ion yields in (2); this may be the cause of the deviation for CO. When we compare the production cross sections for highly-excited atoms at the lowest electron energy (~40 eV), the differences become further smoothed out and we obtain

$$\sigma(N^{*}) \approx \sigma(O^{*}) \approx \sigma(C^{*} + O^{*}).$$

The relation between the production cross sections for C* and O* in CO at the same electron energy is about the same as that between the cross sections for C^{+} and O^{+} in the CO mass spectrum.

B. Production of Highly-excited Molecules

Transitions to highly-excited states of CO, N_2, and O_2 are observed[21-23] in Rydberg series when the short-wave regions of the photoabsorption spectra are investigated. It is known that electronic transitions to excited states lead to vibrational excitations of many molecules. Since the highly-excited states lie close to the continuum, vibrationally excited molecules in such states lie in the continuous spectrum and are able to autoionize. Since unforbidden autoionization for highly-excited molecules occurs within a time $\sim n^{3} \times 10^{-14}$ sec,[24] practically all the molecules in these states will be autoionized within a time $<10^{-5}$ sec, and cannot therefore be registered with out apparatus. However, a fraction of highly-excited molecules that are in the zeroth vibrational state cannot autoionize because of insufficient excitation energy. This fraction can be determined from the Franck-Condon overlap integrals for molecular ions in the electronic ground state, and is approximately equal to the fraction of ions in the zeroth vibrational state. The latter quantity is given as ~96% for CO^{+} and ~23% for O_2^{+} in[25], and as ~90% for N_2^{+} in[26]. It has already been mentioned that highly-excited H_2 and D_2 molecules have been observed,[2,3] although the ionization of H_2 yields only ~9% H_2^{+} in the vibrational ground state.[27] When pure CO, O_2, N_2, or their binary mixtures were admitted to the ion source, molecular ions of the initial gases were not observed if the electron energy exceeded the appearance potentials of the molecular ions in the processes

$$CO + e \rightarrow CO^{+} + 2e, \tag{25}$$

$$O_2 + e \rightarrow O_2^{+} + 2e, \tag{26}$$

$$N_2 + e \rightarrow N_2^{+} + 2e, \tag{27}$$

i.e., above the threshold for highly-excited molecular states but below the appearance thresholds for fragment ions in (14)—(17), as is shown in Figs. 3 and 4. Control experiments performed with H_2 and Ar showed that under these conditions H_2^{+} and Ar^{+} are formed from highly-excited H_2^{*} and Ar* in process (2). The thresholds for these excited states are close to the ionization potentials of H_2 and Ar, as can be expected for highly-excited states.[1,2]

These results indicate, first, that the mass spectrum does not include molecular ions formed in the first chamber of the source via processes (25)—(27), and secondly, that processes (9), (11), and (13) do not produce a significant number of long-lived highly-excited CO*, O_2^{*}, and N_2^{*} molecules. We therefore conclude that the great bulk of highly-excited CO*, O_2^{*}, and N_2^{*}, even in the zeroth vibrational state, have lifetimes under 3×10^{-5} sec. However, the existence of shorter-lived N_2^{*} was indicated in[28], whose authors concluded that some N_4^{2} ions result from collisions between excited and unexcited N_2 molecules.

Highly-excited molecules can lose their electronic excitation spontaneously through the emission of a photon or electron (auto-ionization), and also by predissociation. The experimentally demonstrated ab-

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[2)] In Fig. 3 some structure is observed on curves 1 and 2 near the thresholds of O* and C* production.

sence of appreciable numbers of long-lived highly-excited CO^*, O_2^*, and N_2^* can be interpreted as proving that these molecules predissociate in the zeroth vibrational state.

Consequently, in addition to the spontaneous decay channel of highly-excited atoms via photon emission, and autoionization for certain states,[3] highly-excited molecules possess autoionization and predissociation as additional channels. For identical values of n, the decay rates via the last two channels can greatly exceed the decay rate via the first channel.

C. Ion Formation in Collisions Between Excited Atoms and Unexcited Molecules

Figures 3 and 4 show that for high electron energies the mass spectra of CO, O_2, and N_2 contain the molecular ions CO^+, O_2^+, and N_2^+. The appearance thresholds for CO^+ and O_2^+ agree to within ~1 eV with the thresholds for highly-excited O^* in (8) and (10). The yields also exhibit similar dependences on electron energy. The CO^+ and O_2^+ ion currents depend linearly on the electron current, as is shown for atomic ions in Fig. 1. However, these currents exhibit a varying influence of the gas pressure. Figure 2 indicates that the intensity I of O^+ ions is proportional to the CO pressure in the region of small pressures. At high pressures the increase is slower, because highly-excited O^* atoms are scattered by the gas. The O^+ intensity satisfies the formula

$$I = \alpha N \exp(-\sigma N l), \tag{28}$$

where N is the CO concentration, σ is the cross-section for the scattering of highly-excited O^*, l is the scattering mean free path, and α is a constant.

When the dependence of I on gas pressure is investigated at high pressures σ can be determined from the condition for the maximum, $\sigma = (Nl)^{-1}$. Such measurements were obtained for the scattering of highly-excited O^* and C^* in CO. The respective cross sections, $\sim 2 \times 10^{-13}$ cm^2 and $\sim 1.5 \times 10^{-13}$ cm^2, can be compared with the scattering cross sections of highly-excited atoms that are given in the literature: $\gtrsim 0.4 \times 10^{-13}$ cm^2 for Ar^* scattered on H_2[29]; $\sim 2.9 \times 10^{-13}$ cm^2, $\sim 7.8 \times 10^{-13}$ cm^2, and $\sim 12 \times 10^{-13}$ cm^2 for He^*, Ne^*, and Ar^* scattered on H_2O[30]; $\sim 2.7 \times 10^{-13}$ cm^2, and $\sim 4.0 \times 10^{-13}$ cm^2 for the same three ions scattered on SO_2. All these cross sections are seen to be very large, exceeding the gas-kinetic cross sections by about three orders of magnitude.

The CO^+ intensity is proportional to the product of the O^+ intensity and the CO pressure. The intensity of O_2^+ ions in oxygen behaves similarly.

An analysis of all these results shows that the molecular ions CO^+ and O_2^+ are formed in collisions between highly-excited O^* and the original molecules:

$$O^* + CO \rightarrow [O + e] + CO^+, \tag{29}$$

$$O^* + O_2 \rightarrow [O + e] + O_2^+. \tag{30}$$

The reaction (28) for slow O^* ions can take place only according to the scheme

$$O^* + CO \rightarrow O^- + CO^+, \tag{31}$$

so that positive and negative ions are formed simultaneously.[4] This follows from the fact that the excitation energy of the O^* atoms is very much lower than the CO ionization potential. The energy deficiency is compensated in this case by the large electron affinity of the O atom (~1.47 eV according to[31]). The excess energy of reaction (31) is distributed among the kinetic energies of the reaction products and the internal excitation of CO^+ ions. In the case of relatively fast O^* atoms a free electron may appear in reaction (29), so that the endothermicity of the reaction is overcome by the kinetic energy of the excited O^* atoms.

In (30) the excitation energy of the O^* atoms is high enough for direct ionization of O_2 (without electron capture). Therefore this process can occur with slow oxygen atoms.

In addition to using pure gases we investigated the formation of the different ions in binary mixtures of CO and O_2 with three different proportions: 1) equal concentrations of CO and O_2, (2) a higher O_2 concentration, and 3) a lower O_2 concentration. In all cases the molecular ion current of one component in the mixture was proportional to the pressure of the other component. The appearance thresholds of the molecular ions and their dependences on electron energy agreed with the appearance threshold of highly-excited oxygen atoms formed from the molecules having the larger concentration in the mixture; one of these dependences is shown in Fig. 4. All these experiments indicate that highly-excited O^* atoms play the principal role in the formation of the molecular ions CO^+ and O_2^+. Fast highly-excited C^* atoms could induce the reaction

$$C^* + CO \rightarrow [C + e] + CO^+, \tag{32}$$

which we were unable to detect. At a high pressure N_2^+ ions appear in the ion source, with an appreciable intensity only for high electron energy, as can be seen in Fig. 4. The mechanism for the formation of these ions was not investigated because of the low intensity.

The NO^+ ions that appear in an oxygen-nitrogen mixture can be formed in reactions between highly-excited N^* and O^* and the appropriate molecules. At high pressures the CO mass spectrum contains very small amounts of CO_2^+ and C_2O^+, which are apparently formed through autoionization of the CO_2^* and C_2O^* complexes that result from collisions of metastable highly-excited O^* and C^* atoms with the original molecules.

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[3] Multielectron atoms possess two low ionization limits to which the high-lying atomic states converge. For example, these limits for Ne and heavier inert-gas atoms are ${}^2P^0_{3/2}$ and ${}^2P^0_{1/2}$. Excited states lying between these limits lead to autoionization.

[4] The electron affinities of atoms and molecules can evidently be determined through similar processes involving different pairs of colliding particles.

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