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Dissociation of Diatomic Molecules into Ions by Impact of Fast Ions and Atoms

V. A. Gusev, A. A. Oksyuk, and Ya. M. Fogel'
Physico-technical Institute, Ukrainian Academy of Sciences

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The mass-spectrometer technique is employed for measuring the relative effective cross sections for formation of slow atomic negative ions produced in collisions between fast ions of hydrogen, helium, neon, argon and krypton atoms (3–50 keV energy) and O_2, CO and NO molecules. The difference between the functions $\sigma^{+}_{B^-}$ (v) and $\sigma^{0}_{B^-}$(v) is ascribed to the contribution to the measured cross section of processes involving dissociative electron capture by the target molecules. Some considerations regarding the mechanism of diatomic molecule dissociation into positive and negative ions are presented.

INTRODUCTION

THE processes of dissociation of diatomic molecules by impact with heavy particles have been the subject of many investigations. In the overwhelming majority of cases, either the processes of dissociation of fast diatomic molecular ions colliding with atoms or molecules of gases, or else dissociative ionization or charge exchange in collisions of fast ions or atoms with diatomic molecules have been studied. In both cases, the features of the dissociation process were deduced from the formation of positive ions, fast in the former case and slow in the latter.

Another possible process, in addition to the indicated ones, is

$$A^{0(+)} + B_2 \rightarrow A^{0(+)} + B^+ + B^- \qquad (1)$$

representing the dissociation of the molecule B_2 into positive and negative ions by impact with a fast atom A^0 or ion A^+. The distinguishing features of the process (1) can be deduced by studying the formation of the ions B^-. It must be emphasized that the negative ions produced in collisions between fast ions and diatomic molecules can result only from the dissociative process (1).[1)] The situation is different when fast atoms collide with diatomic molecules. In this case the ions B^{-1} can result not only from the process (1). Another possible process is

$$A^0 + B_2 \rightarrow A^+ + B_2^{-*} \rightarrow A^+ + B^- + B^* \qquad (2)$$

representing the dissociative charge exchange of the atom A^0 with the molecule B_2, leading to formation of the ion B^-. This circumstance must be taken into account when interpreting the results of an investigation of the process (1) with participation of fast atoms.

In distinction from other processes of dissociation in collisions of heavy particles, process (1) has not been sufficiently well investigated.[2)] In our preceding article[1] we presented the results of an investigation of the process (1) in collisions of fast protons and hydrogen atoms with oxygen molecules. The apparatus and procedure used to investigate the process (1) are described in that article. The present paper is aimed at obtaining a much larger volume of information concerning the process (1). To this end we investigated, using the same apparatus and procedure as in [1], the process (1) for a large number of incident particle—diatomic molecule pairs.

EXPERIMENTAL RESULTS AND DISCUSSION

We measured, in relative units, the effective cross sections $\sigma^{+}_{B^-}$ and $\sigma^{0}_{B^-}$ ($\sigma^{+}_{B^-}$ is the effective cross section of the process (1) with participation of fast positive ions, and $\sigma^{0}_{B^-}$ is the effective cross section for the production of B^- ions in collision of fast atoms with molecules,

$$\sigma_{B^{-0}} = \sigma^{\text{diss}}_{B^-} + \sigma^{\text{ce}}_{B^-} ,$$

where $\sigma^{\text{diss}}_{B^-}$ is the effective cross section of process (1) with participation of fast atoms, and $\sigma^{\text{ce}}_{B^-}$ is the effective cross section of the process (2)). In our experiments, the incident particles were the ions H^+, He^+, Ne^+, Ar^+, Kr^+, and Kr^{++} with energies 3–50 keV (the Kr^+ ions had energies 3–20 keV, and Kr^{++} energies 10–80 keV), and the atoms H, He, Ne, Ar, and Kr with energy 5–50 keV (the Kr atoms had energies 5–20 keV). The target particles were the molecules O_2, CO, and NO. The measurement results are shown in Figs. 1–3 in the form of plots of $\sigma^{+}_{B^-}$(v) and $\sigma^{0}_{B^-}$(v) (v is the velocity of the incident particles).

A characteristic feature of a number of the obtained $\sigma^{+}_{B^-}$(v) curves is the presence of a maximum in the velocity range $(2-5) \times 10^7$ cm/sec. As is well known, the velocity $v_{\max}$ at which the main maximum[3)] of the σ(v) curve is located is determined by the Massey-Hasted adiabatic maximum rule:[2]

$$v_{\max} = a|\Delta E|_\infty / h, \qquad (4)$$

where a is the radius of the forces of interaction between the colliding particles, ΔE_∞ is the resonance defect of the process or the distance between the potential surfaces of the initial and final states of the system of colliding particles at an infinitely large distance between them, and h is Planck's constant.

[1)] This statement is quite correct when the incident ion has no electron shell (H^+, He^{++}, etc.), and in the opposite case, in principle, the process

$$A^+ + B_2 \rightarrow A^{++} + B_2^{-*} \rightarrow A^{++} + B^- + B^* \ldots$$

is also possible. Owing to the large resonance defect of this process, however, its effective cross section will be small.

[2)] A list of papers reporting observation of the process (1) is given in[1].

[3)] The σ(v) curve quite frequently has, besides the main maximum, also one or several additional maxima located at velocities lower than $v_{\max}$ (see, for example[3]). These maxima are attributed to the intersection of the potential surfaces of the final and initial states of the system of colliding particles.

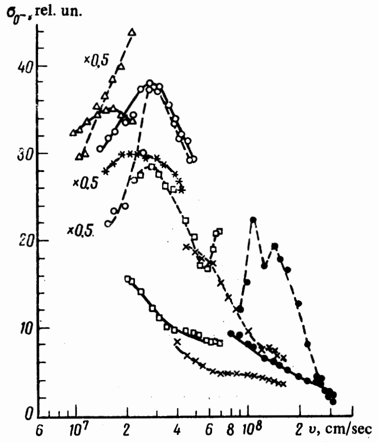

FIG. 1. Plot of $\sigma^{+}_{O^-}(v)$ and $\sigma^{0}_{O^-}(v)$ for O_2. The solid and dashed lines are for ions and atoms, respectively; ●—H^+ and H^0 (from the data of [1]), ×—He^+ and He^0, □—Ne^+ and Ne^0, ○—Ar^+ and Ar^0, Δ—Kr^+ and Kr^0, *—Kr^{++}.

Assuming that the maxima of the $\sigma^{+}_{B^-}(v)$ curves in the velocity region $(2-5)\times 10^7$ cm/sec are the principal ones, we can calculate with the aid of (4) the value of the quantity a in this formula. To this end it is necessary to substitute in (4) the experimentally obtained values of v_{max} and the values of the resonance defect ΔE_∞ of the process (1). The latter quantity is calculated from the formula

$$\Delta E_\infty = S_B - (I_B + E_{\text{diss}}), \tag{5}$$

where S_B and I_B are the electron-affinity energy and the ionization potential of the atom B, and E_{diss} is the dissociation energy of the molecule B_2. The values of a calculated in this manner are listed in the table.

The comparison of the $\sigma^{+}_{B^-}(v)$ and $\sigma^{0}_{B^-}(v)$ curves in Figs. 1–3 leads to the following conclusions: 1) the $\sigma^{0}_{B^-}(v)$ curves have in a number of cases maxima in the same velocity region $(2-5)\times 10^7$ cm/sec as the $\sigma^{+}_{B^-}(v)$ curves; 2) if the incident particles have equal velocities, then we have the inequality $\sigma^{0}_{B^-} > \sigma^{+}_{B^-}$; 3) the $\sigma^{0}_{B^-}(v)$ curves have in the velocity region $v > 5\times 10^7$ cm/sec maxima that are missing from the $\sigma^{+}_{B^-}(v)$ curves (see the $\sigma^{0}_{B^-}(v)$ and $\sigma^{+}_{B^-}(v)$ curves for the pairs $H^{0(+)}-O_2$, $H^{0(+)}$—CO and $H^{0(+)}$—NO).

The indicated differences between the $\sigma^{0}_{B^-}(v)$ and $\sigma^{+}_{B^-}(v)$ curves is attributed to the fact that negative ions can be produced in collisions between fast atoms and molecules not only as a result of process (1) but also a result of process (2). If it is assumed that the effective cross section of the process (1) depends little on the charge state of the incoming particle (see below), and the effective cross section of the process (2) is not small compared with the cross section for process (1), then we should have the inequality $\sigma^{0}_{B^-} > \sigma^{+}_{B^-}$, which is indeed observed in experiment.

On the other hand, if the $\sigma^{0}_{B^-}(v)$ curve is the resultant of both processes (1) and (2), then this curve can have several maxima connected either with process (1) or process (2). Unfortunately, the velocity interval investigated in the present study is not wide enough to be able to observe maxima from both processes on the $\sigma^{0}_{B^-}(v)$ curves for different pairs of colliding particles we can verify that both processes in question do indeed contribute to the effective cross section $\sigma^{0}_{B^-}$, and it is necessary for this purpose to examine the maxima of the $\sigma^{0}_{B^-}(v)$ curves both in the velocity range $(2-5)\times 10^7$ cm/sec and at velocities $v > 5\times 10^7$ cm/sec.

The values of a calculated from formula (4) for the maxima of the $\sigma^{0}_{B^-}(v)$ curves in the velocity region $(2-5)\times 10^7$ cm/sec are listed in the table. As seen from the table, these values are, on the average, the same for the maxima of the $\sigma^{+}_{B^-}(v)$ curves in the same velocity region. A probable conclusion of this comparison is that the maxima of the $\sigma^{0}_{B^-}(v)$ curves in the velocity region $(2-5)\times 10^7$ cm/sec are connected with the dissociation of the molecule into positive and negative ions by impact with the fast atom.

We can attempt to interpret the cause of the maxima on the $\sigma^{0}_{B^-}(v)$ curves for the pairs H^0—CO, H^0—O_2, and H^0—NO, located in the velocity region $v > 5\times 10^7$ cm/sec, on the basis of the fact that they are connected with one of the following three processes: 1) the process (1), 2) the process (1) with excitation of the incident atom, and 3) the process (2).

The value of a calculated from these maxima on the basis of the first assumption is several times larger than the value obtained in the calculation for maxima located in the velocity region $(2-5)\times 10^7$ cm/sec. Numerous experiments[2,4] have established that the value of a in (4) is characteristic of a definite atomic-collision process and depends little on the nature of the partners in the colliding particle pair. Thus, the interpretation of the maxima on the basis of the first assumption has low probability.

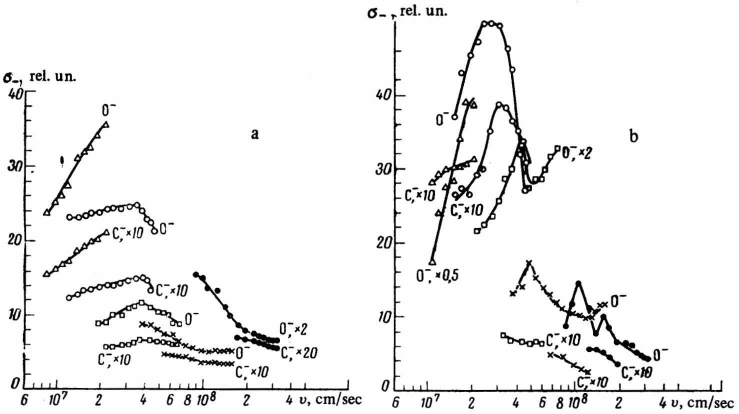

FIG. 2. a—plots of $\sigma^{+}_{O^-}(v)$ and $\sigma^{+}_{C^-}(v)$ for CO, b—plots of $\sigma^{0}_{O^-}(v)$ and $\sigma^{0}_{C^-}(v)$ CO, ●—H^+ and H^0, ×—He^+ and He^0, □—Ne^+ and Ne^0, ○—Ar^+ and Ar^0, and Δ—Kr^+ and Kr^0.

O_2			CO			NO		
Incident particle	Process	a, Å	Incident particle	Process	a, Å	Incident particle	Process	a, Å
Ar^+	$Ar^+ + O_2 \rightarrow Ar^+ + O^+ + O^-$	0.6	Ne^+	$Ne^+ + CO \rightarrow Ne^+ + C^+ + O^-$	0.7	Ne^+	$Ne^+ + NO \rightarrow Ne^+ + N^+ + O^-$	0.8
Kr^+	$Kr^+ + O_2 \rightarrow Kr^+ + O^+ + O^-$	0.4	Ne^+	$Ne^+ + CO \rightarrow Ne^+ + C^- + O^+$	0.8	Ar^+	$Ar^+ + NO \rightarrow Ar^+ + N^+ + O^-$	0.7
Kr^{++}	$Kr^{++} + O_2 \rightarrow Kr^{++} + O^+ + O^-$	0.6	Ar^+	$Ar^+ + CO \rightarrow Ar^+ + C^+ + O^-$	0.7	Kr^{++}	$Kr^{++} + NO \rightarrow Kr^{++} + N^+ + O^-$	0.8
Ar^0	$Ar^0 + O_2 \rightarrow Ar^0 + O^+ + O^-$	0.6	Ar^+	$Ar^+ + CO \rightarrow Ar^+ + C^- + O^+$	0.7	Ne^0	$Ne^0 + NO \rightarrow Ne^0 + N^+ + O^-$	0.7
			He^0	$He^0 + CO \rightarrow He^0 + C^+ + O^-$	1.0	Ar^0	$Ar^0 + NO \rightarrow Ar^0 + N^+ + O^-$	0.5
			Ne^0	$Ne^0 + CO \rightarrow Ne^0 + C^+ + O^-$	0.8			
			Ar^0	$Ar^0 + CO \rightarrow Ar^0 + C^+ + O^-$	0.5			
			Ar^0	$Ar^0 + CO \rightarrow Ar^0 + C^- + O^+$	0.6			

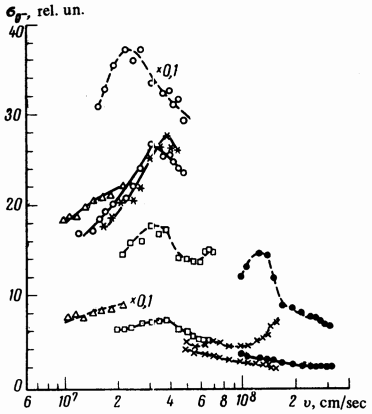

FIG. 3. Plots of $\sigma^+_{\text{O}^-}$(v) and $\sigma^0_{\text{O}^-}$(v) for NO. The solid and dashed lines represent ions and atoms, respectively, ●–H^+ and H^0, X–He^+ and He^0, □–Ne^+ and Ne^0, O–Ar^+ and Ar^0, Δ–Kr^+ and Kr^0.

If it is assumed that the maxima in question are connected with the dissociation of the molecule into positive and negative ions with simultaneous excitation of the incident atom, then the value of a calculated under this assumption turns out to be approximately twice as large as the average 0.7 Å obtained from the maxima of the curves in the velocity region $(2-5) \times 10^7$ cm/sec. In addition, the resonance defect of the process (1) with excitation of the incident atom is much larger than the defect for the process (1), in which the incident particle is not excited. Thus, if we adhere to the point of view that the effective cross section of the process (1) depends little on the charge state of the incident particle, it follows that the effective cross section $\sigma^0_{\text{B}^-}$ for process (1) with excitation of the incident atom will be smaller than the effective cross section $\sigma^+_{\text{B}^-}$ of the process (1) with participation of a charged particle of the same nature. Actually, as follows from the examination of Figs. 1–3, the opposite inequality is obtained.

Finally, if we calculate the value of a on the basis of the third assumption, then its value, averaged for the three considered atom-molecule pairs, turns out to be 2.4 Å. This value of a is close to the value $a \approx 3$ Å characteristic of electron capture by fast atoms,[4] which is related in nature to the process (2). Thus, the foregoing reasoning leads to the conclusion that the most probable cause of the appearance of maxima on the $\sigma^0_{\text{B}^-}$(v) curves in the velocity region $v > 5 \times 10^7$ cm/sec is that in collisions between atoms and diatomic molecules the process (2) is effected with noticeable probability. A certain confirmation of this conclusion can be found in the presence of branches of the $\sigma^0_{\text{B}^-}$(v) curves that increase towards larger velocities for the pairs Ne–O_2, Ne–CO, and Ne–NO. This is apparently due to the fact that in accordance with (4) the maxima due to the process (2) in collisions of the indicated pairs are located at the velocities 1.4, 1.8, and 1.5×10^8 cm/sec, respectively.

In the discussion of the possible mechanism of the process (1), attention should be called to the fact that the quantity a in (4), which determines the position of the principal maxima on the σ(v) curve for this process, has the smallest value in comparison with other atomic-collision processes.[2,4,5] On the other hand, this quantity is somewhat smaller than the equilibrium internuclear distance in the investigated molecules. The indicated circumstances suggest that collisions with deep crossing of the electron shells of the colliding particles (the so-called "hard collisions"[6]) can play a role in the dissociation of molecules into positive and negative ions. In this case the molecule dissociates as a result of direct transfer of momentum from the incident particle to one or both nuclei of the molecule. The momentum transfer from the nucleus of the incoming particle to the nucleus of the molecule is effected in this process by the Coulomb interaction force, but with allowance for the screening by the electron charge located between the colliding particles.

The proposed model for the dissociation of molecules into positive and negative ions agrees to some degree with certain facts observed in the present study. These facts include the weak dependence of the effective cross section $\sigma^+_{\text{B}^-}$ on the charge of the incident ion (see the $\sigma^+_{\text{O}^-}$(v) curves on Figs. 1 and 3 for the ions Kr^+ and Kr^{++}), the monotonic increase of this cross section with increasing charge of the nucleus of the incoming noble-gas ion,[4] and, finally, the weak dependence of the effective cross section $\sigma^+_{\text{B}^-}$ on the type of molecules having close values of nuclear charge (see, for example, the $\sigma^+_{\text{O}^-}$(v) curves in Fig. 4 for the pairs Ar^+–O_2, Ar^+–CO, and Ar^+–NO). As an additional argument favoring the assumption that the diatomic molecule dissociates into a pair of ions as a result of "hard collisions" we can refer to the fact that, according to the data of [1,7] the effective cross section for the dissociation of an H_2 molecule into a pair of ions is much smaller than the cross section for the corresponding dissociations of the molecules O_2, CO, and NO. It should be borne in mind, however, that the appreciable decrease of the cross section $\sigma^+_{\text{B}^-}$ in the case of H_2 molecules can be attributed to another cause, namely the small value of the electron-affinity energy of the hydrogen atom. The large influence of the electron-affinity energy of

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[4] It should be noted, however, that this relation is valid for the pairs Kr^+—O_2 and Kr^+—NO.

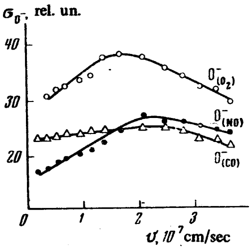

FIG. 4. Plots of $\sigma^+_{O^-}(v)$ for Ar^+–O_2, Ar^+–CO, Ar^+–NO; ○–O_2, ●–NO, △–CO.

the atom contained in the molecule on the effective cross section $\sigma^+_{B^-}$ is confirmed by our results, as can be verified by comparing the $\sigma^+_{O^-}(v)$ and $\sigma^+_{C^-}(v)$ curves on Fig. 2 (S_O = 1.465 eV, S_C = 1.25 eV).

In conclusion it should be indicated that the dissociation of the investigated molecules into positive and negative ions can result not only from the "hard collision" mechanism. The considered dissociation process can also be realized in collisions having another mechanism. Collisions of this kind were extensively investigated in the case of the dissociation of a number of diatomic positive molecular ions (see, for example, [6,8,9]), and it turned out that an appreciable contribution is made to the dissociation of the molecular ions by electron-excitation processes in Franck-Condon transitions to the upper electronic state with a potential curve of the repulsion type. A process of this type, in the case of dissociation of a molecule into a pair of protons, is impossible in view of the absence of upper electronic states of the repulsion type, which tend to the state $B^+ + B^-$ when the internuclear distance becomes infinite. However, the dissociation into a pair of ions as a result of electronic excitation of the molecule by the incident particle is possible in the case when the Franck-Condon transitions cause population of states in the vibrational continuum of the upper electronic state with a potential curve of the stable type, which tends to the state $B^+ + B^-$ at an infinitely large internuclear distance. Such a situation can arise if the minimum of the potential curve of the upper electronic state is shifted relative to the minimum of the potential curve of the ground state of the molecule.

To get an idea of the relative contribution of the two considered mechanisms to the effective cross section for the dissociation of diatomic molecules into a pair of ions, it is necessary to perform experiments to study the energy- and angular distributions of the negative ions produced as a result of the dissociation process. We are planning to perform such experiments in the future.

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[1] V. A. Gusev, A. A. Oksyuk, D. V. Pilipenko, and Ya. M. Fogel', Zh. Eksp. Teor. Fiz. **59**, 1909 (1970) [Sov. Phys.-JETP **32**, 1032 (1971)].

[2] J. B. Hasted, Physics of Atomic Collisions, Butterworth, 1964.

[3] G. N. Polyakova, V. A. Gusev, V. F. Erko, Ya. M. Fogel', and A. V. Zats, Zh. Eksp. Teor. Fiz. **58**, 1186 (1970) [Sov. Phys.-JETP **31**, 637 (1970)].

[4] Ya. M. Fogel', Usp. Fiz. Nauk **71**, 243 (1960) [Sov. Phys.-Usp. **3**, 390 (1960)].

[5] M. C. Poulizac, J. Desesquelles, and M. Dufay, Ann. Astrophys. **30**, 301 (1967).

[6] J. Schopman, J. Los. Physica **48**, 190 (1970).

[7] V. V. Afrosimov, G. A. Leĭko, Yu. A. Mamaev, and M. N. Panov, Zh. Eksp. Teor. Fiz. **56**, 1204 (1969) [Sov. Phys.-JETP **29**, 648 (1969)].

[8] M. Vogler and W. Seibt, Z. Phys. **210**, 337 (1968).

[9] J. Durup, P. Fournier, and Pham Dông, In. J. Mass Spectr. Ion Phys. **2**, 311 (1969).

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