

FORMATION OF SLOW NEGATIVE IONS IN SINGLE COLLISIONS BETWEEN FAST
NEGATIVE HYDROGEN AND OXYGEN IONS AND GAS MOLECULES

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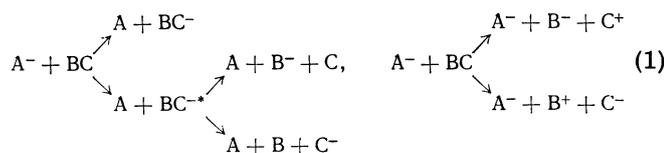
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The total cross sections for the formation of negative ions have been measured for single collisions between H⁻ and O⁻ ions and O₂, CCl₄ and SF₆ molecules in the energy range from 10 to 50 kev. The slow negative and positive ions formed when H⁻ and O⁻ ions pass through these gases have been analyzed by a mass-spectrometer technique. An analysis has also been made of the negative ions formed in collisions between O⁻ ions and H₂O and CO₂ molecules. The experimental data for ion collisions are compared with the corresponding data for electron collisions.

INTRODUCTION

SLOW negative ions can be formed as a result of two processes when fast negative ions move through a rarefied gas:



(BC^{-*} is the excited ion).

Although the analogous reactions that occur when electrons move through a gas have been studied, very little work has been done on the formation of slow negative ions due to the passage of fast negative ions through a rarefied gas. We are acquainted only with reference 1, in which cross sections have been measured for the formation of slow negative ions in collisions between O₂ molecules and Na⁻, K⁻, O⁻, Cl⁻, OH⁻, and O₂⁻ with energies of 720 ev. No mass analysis was made of the slow negative ions in this work.

In order to obtain further data on the formation of slow negative ions in the interaction of fast negative ions with gas molecules, we have measured the cross sections for the formation of negative ions in collisions of H⁻ and O⁻ ions with energies from 10 to 15 kev and the molecules O₂, CCl₄, and SF₆. In addition to measuring the total cross sections for the formation of negative ions we have carried out a mass-spectrometer analysis of the negative and positive ions formed in the gas.

APPARATUS AND METHOD OF MEASUREMENT

The experimental apparatus used to investigate the formation of slow negative ions has been described by the authors in detail in earlier papers^{2,3} in which the ionization of gases by negative ions was investigated.

The total cross section for the formation of slow negative ions σ_i^- is measured by the familiar potential technique. In order to distinguish slow negative ions from electrons produced by stripping a fast negative ion and by ionization of the gas molecules, we used a magnetic field parallel to the axis of the primary beam. The same field suppressed the secondary electron emission from the electrodes of the measurement capacitor.

Before measuring σ_i^- , we obtained for each ion-molecule pair the characteristic curves $i_H^-/I_0 = f(H)$ and $i_H^-/I_0 = f(V)$, where i_H^- is the negative current to the measurement electrode with the magnetic field on, and I_0 is the primary beam current. Using these characteristic curves we determined the magnetic field strength necessary for complete separation of the slow negative ions from the electrons, and the potential difference V between the electrodes of the measurement capacitor required to obtain saturation current. To find the conditions which must be satisfied to obtain single collisions, we studied the dependence of i_H^-/I_0 for the investigated gas on the pressure in the collision chamber. For all gases studied (except SF₆) and for all beam energies, the curve $i_H^-/I_0 = f(p)$ is linear up to 1.5×10^{-4} mm Hg, indicating that we are dealing with single collisions. In the single-collisions region the cross section

σ_i^- was computed from the formula

$$\sigma_i^- = i_H^- / I_0 n L, \quad (2)$$

where n is the number of gas molecules per cubic centimeter and L is the length of the measurement electrode.

In SF_6 , the $i_H^- / I_0^- = f(p)$ curve is found to be parabolic, starting at low gas pressures. In this case σ_i^- was determined from the pressure dependence of the quantity $(i_H^- / I_0^-) / p$ by a method which has been described earlier.⁴ The error in the measurement of σ_i^- , as estimated from the spread in the measured results, is $\pm 10\%$. The error in the energy measurement is $\pm 3\%$.

The slow negative and positive ions were analyzed in a magnetic mass spectrometer with a beam turning angle of 60° and a mean trajectory radius of 16.4 cm. The relative intensity of a mass spectrometer line was computed from the formula

$$\alpha_n = h_n / \sum_i h_i, \quad (3)$$

where h_n is the height of the line corresponding to the n -th ion while $\sum_i h_i$ is the sum of the heights for all the spectral lines.

The cross section for the formation of a given negative ion σ_n^- was computed from the intensity of the mass-spectrometer line and from the total cross section for the formation of slow negative ions, by means of the formula

$$\sigma_n^- = \alpha_n \sigma_i^-. \quad (4)$$

Fedorenko and Afrosimov⁵ have shown that α_n gives the true composition of the slow ions in the zone of interaction between the primary beam and the gas only when it is independent of the mass spectrometer exit slit width, the extraction potential V_e , the acceleration voltage V_a , and the focusing voltage V_f (cf. Fig. 1. in reference 1). For each ion-molecule pair and for each primary-ion energy we determined the dependence of α_n on the parameters given above. The operating values of V_e , V_a , V_f and the slit width were then chosen to correspond to points on the plateaus of the appropriate curves.

In order to find the gas pressure in the collision chamber necessary to ensure single collisions, we obtained the curve $I_n^- / I_0^- = f(p)$, where I_n^- is the current at the peak of a given mass-spectrometer line. Most of the measurements of α_n were carried out at a gas pressure of $1 - 1.5 \times 10^{-4}$ mm Hg. The error in the measurement of σ_n^- is made up of the errors in σ_i^- and α_n and is $\pm 10\%$ for high intensity peaks and $\pm 35\%$ for low intensity peaks.

RESULTS OF THE MEASUREMENTS

The total cross sections for the formation of slow negative ions in oxygen are shown in Fig. 1 as a function of the velocities of the H^- , D^- and O^- ions. The cross section for $H^- - O_2$ is $(1 - 3) \times 10^{-17}$ cm²; for $O^- - O_2$ these cross sections are an order of magnitude larger. In, Afrosimov,

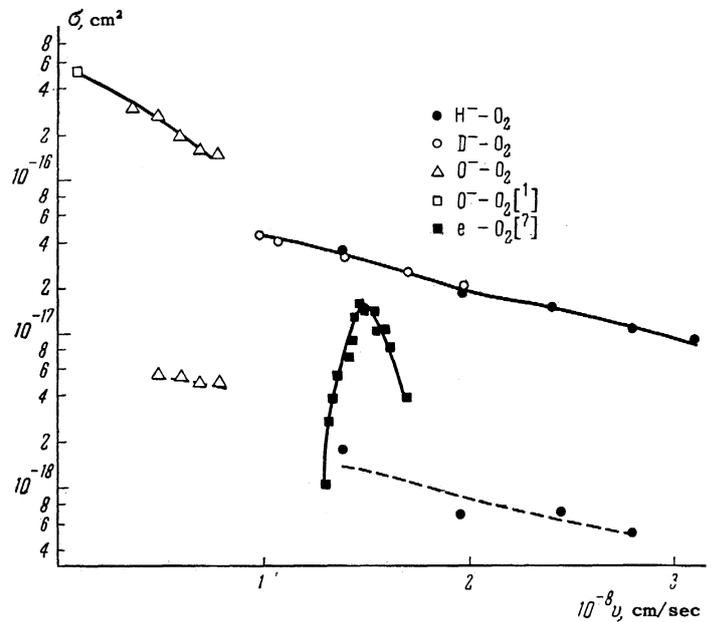


FIG. 1. The cross sections for the formation of slow negative ions σ_i^- in oxygen as a function of velocity (solid curve); the dashed curve is the function $\sigma_o^-(v)$.

and Fedorenko⁶ have estimated the cross sections for the dissociation of O_2 molecules into positive and negative ions by collisions with protons with energies of 10 to 30 keV. These cross sections are of the order of 10^{-19} cm². Since it is not very likely that the cross sections for the dissociation of the O_2 molecules by impact with H^- ions are much larger than the corresponding cross sections for the H^+ ion, it is reasonable to assume that σ_i^- for $H^- - O_2$ and $O^- - O_2$ represents the cross section for charge exchange of H^- and O^- ions in oxygen. The following conclusions follow from an analysis of the curves in Fig. 1.

1. The cross section σ_i^- is independent of ion mass, since the experimental points for H^- and D^- ions lie on the same curve.

2. The reduction in σ_i^- with increasing ion velocity is fairly well described by the formula $\sigma_i^- = \sigma_0 e^{-kv}$. The constant k in this formula is different for hydrogen and oxygen ions. It should be noted that the experimental point for $O^- - O_2$ at 720 ev^1 also lies on the curve $\sigma_i^- \sim e^{-kv}$.

The mass spectrum for the slow negative ions from $H^- - O_2$ and $O^- - O_2$ contains the O_2^- ion and, in very small quantities, the O^- ion. This result indicates that when H^- or O^- ions pass through O_2 the most important reaction is $A^- + O_2 \rightarrow A + O_2^-$; the reactions $A^- + O_2 \rightarrow O_2^{*-} \rightarrow O$ and $A^- + O_2 \rightarrow A^- + O^- + O^+$ are characterized by low probabilities.

The formation of negative ions in collisions between electrons and molecules exhibits entirely different characteristics. In this case the dependence of the negative ion formation cross section on the electron velocity is characterized by a resonance effect. In Fig. 1 we show this dependence in O_2 , using the data reported by Buchel'nikova.⁷ When the electron "sticks" to the O_2 molecule, the reaction $O_2 + e \rightarrow O_2^{*-} \rightarrow O^- + O$ occurs, that is to say, the O^- ion is formed only as a result of the dissociation of the excited O_2^- ion.⁸ As has been noted above, charge exchange of H^- and O^- with O_2 molecules results primarily in the formation of O_2^- ions. This difference in charge exchange of negative ions and attachment of electrons to molecules is completely reasonable. Since the radiation process $O_2 + e \rightarrow O_2^- + h\nu$ is characterized by a small probability, the attachment of the electron to the O_2 molecule leads to the formation of the excited O_2^- ion. Because of the low gas pressure this ion cannot be stabilized by transfer of excitation energy to another particle so that it must dissociate. In the case of charge exchange, say for $O^- - O_2$, the resonance defect ΔE is equal to the difference in the electron affinity for O_2 and O , more precisely, to $0.15 - 1.48 = -1.33$ ev, so that ΔE is negative;* therefore, energy is absorbed rather than released. A stable O_2^- ion can be formed in charge exchange because of this effect.

In charge exchange of negative ions, as in electron capture by singly-charged positive ions and neutral atoms, the maximum cross section as a function of velocity is determined by the well-known Massey adiabatic criterion;^{11,12} assuming that the quantity a which appears in the adiabatic criterion is the same for this process as for one-electron charge exchange in singly-charged positive ions, i.e. $8A$, we find the peak for $O^- + O_2 \rightarrow O + O_2^-$ at an energy of 5.5 kev. However, it is not very likely that the maximum value of $\sigma_i^- (v)$ for this process lies at 5.5 kev; the value of σ_i^- in the energy range 10 – 50 kev, obtained in the present work, and the value at 0.7 kev, obtained by Dukel'skiĭ and Zandberg,¹ correspond to a smooth curve which increases monotonically between 0.7

*The electron-affinity values are taken from references 9 and 10.

and 50 kev. It is more probable that the maximum value of $\sigma_i^- (v)$ for $O^- - O_2$ lies at an energy lower than 0.7 kev. If this is the case, then the condition for applying the Massey adiabatic criterion to charge exchange of negative ions means that the value of a for $O^- + O_2 \rightarrow O + O_2^-$ is considerably smaller than $8A$. The resonance defect for $H^- + O_2 \rightarrow H + O_2^-$ is -0.58 ev, which is still smaller than for $O^- + O_2 \rightarrow O + O_2^-$; therefore the maximum cross section for the first process is also expected to be at a low energy.

In Fig. 2 we show the $\sigma_i^- (v)$ curves for $H^- - CCl_4$ and $O^- - CCl_4$. The cross section σ_i^- for $H^- - CCl_4$ remains essentially constant over the velocity range studied; for $O^- - CCl_4$ this cross section diminishes as the velocity increases, in accordance with the empirical relationship established for $H^- - O_2$ and $O^- - O_2$.

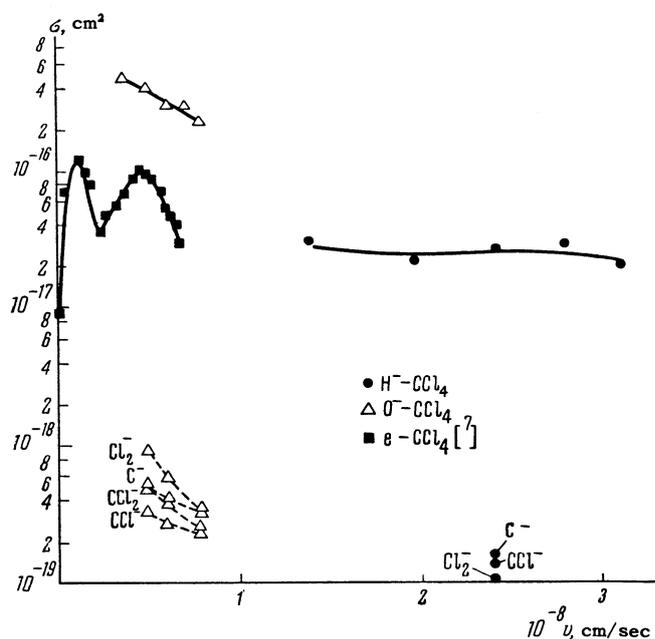


FIG. 2. The cross sections for the formation of slow negative ions in CCl_4 gas as a function of velocity (solid curve). The dashed curves show the corresponding curves for the individual ions. For the ions C^- , CCl^- and Cl_2^- , the cross sections for bombardment by H^- have been measured only at 30 kev.

The relative intensities of the mass-spectrometer lines, for negative and positive ions produced when H^- and O^- ions with energies of 30 kev bombard CCl_4 , are shown in the table. For purposes of comparison we also show in this table the corresponding data for electrons with energies of 75 ev.¹³ The data in the table indicate that in the negative-ion spectra characteristic of collisions of negative ions and electrons with the CCl_4 molecule, the greatest relative intensity is to be assigned to the Cl^- ion so that $\sigma_i^- \approx \sigma_{Cl^-}$. This result

Secondary ion	CCl ₄			SF ₆			CCl ₂ F ₂			
	Particle in the primary beam			Secondary ion	Particle in the primary beam		Secondary ion	Particle in the primary beam		
	O ⁻	H ⁻	e		O ⁻	e		O ⁻	H ⁻	e
Cl ⁺⁺	2	0.34	—	F ⁺	16.2	1.93	C ⁺⁺	0.17	—	—
Cl ⁺	38.3	28	14.1	S ⁺	21	3.4	F ⁺⁺	0.02	—	—
CCl ₂ ⁺⁺	—	—	0.4	SF ⁺	13.4	5.24	C ⁺	6.9	4.05	4.9
CCl ₂ ⁺	9.2	12.5	12	SF ₃ ⁺	7.1	3.47	F ⁺	7.5	4.18	0.65
CCl ₁ ⁺	18.8	15	14.2	SF ₃ ⁺	8.5	16.8	CCl ⁺⁺	0.6	0.7	—
CCl ₃ ⁺⁺	—	—	0.8	SF ₄ ⁺	2.5	5.43	CF ⁺	14.3	17.2	10.8
Cl ₂ ⁺	1.0	1.26	0.18	SF ₅ ⁺	31.2	60.2	Cl ⁺	20	18.35	10
CCl ₃ ⁺	23.5	38	51.3	SF ₅ ⁺⁺	—	0.82	CCl ₂ F ₂ ⁺⁺	—	—	0.48
CCl ₄ ⁺	0.05	0.09	0.01	SF ₅ ⁺⁺	—	0.22	CCl ⁺ +CF ₂ ⁺	39.3	40.5	—
C ⁺	7.1	3.8	7.4	SF ₄ ⁺⁺	—	2.46	CCl ⁺	—	—	3.5
C ⁻	0.13	0.28	0.01	SF ₆ ⁻	63	96.1	CF ₂ ⁺	—	—	8.1
Cl ⁻	99.4	99.3	99.9	SF ₅ ⁻	3.5	3.9	CCl ₃ F ⁺⁺	—	—	0.4
CCl ⁻	0.09	0.18	0.005	F ⁻	33.5	0.04	CClF ⁺	8.4	12.3	2.3
Cl ₂ ⁻	0.2	0.24	0.1				CCl ₂ F ⁺	—	—	4.3
CCl ₂ ⁻	0.12	—	—				CClF ₂ ⁺	2.5	2.8	54
							F ₂ ⁺¹	—	—	0.21
							Cl ₂ ⁺	—	—	0.16
							CCl ₂ F ₂ ⁺	0.1	—	0.16
							C ⁻	4	4.1	0.22
							F ⁻	73.5	74.6	30.4
							Cl ⁻	22.6	21.3	69.4

Note: For O⁻ the velocity is 6×10^7 cm/sec; for H⁻ $v = 2.4 \times 10^8$ cm/sec; for the electrons $v = 5.18 \times 10^8$ cm/sec.

has been verified by other authors.^{14,15} On the other hand, the CCl₄⁻ ion has not been observed in any of this work. Thus, charge exchange (negative ions) and electron attachment in CCl₄ lead to dissociation of the CCl₄⁻ ion which is formed. Inasmuch as a stable negative molecular ion can be formed in charge exchange (cf. above), the absence of such ions in the present case can be explained by the fact that the electron affinity of the CCl₄ molecule is negative. Judging from the relative intensity of the mass lines in the negative-ion spectrum, at least for O⁻ - CCl₄, we can say that this ion decays chiefly via the reaction CCl₄^{-*} → Cl⁻ + CCl₃. In the case of H⁻ ions and electrons with higher velocities than the O⁻ ion, a contribution to the formation of the Cl⁻ ion arises from the well-known dissociation process CCl₄ → Cl⁻ + CCl₃⁺. To some extent this interpretation is verified by the presence of a large number of CCl₃⁺ ions in the positive-ion spectrum. It should be kept in mind, however, that these ions can be formed as a result of ionization and subsequent dissociation of the excited CCl₄ ion. It is interesting to note that the number of CCl₄⁺ ions is very small. It is found that in CCl₄ both attachment and detachment of an electron lead to the formation of unstable molecular ions. The absence of the CCl₃⁻ ion in the negative ion spectrum* indicates the small probability of the decay of the CCl₄⁻ ion via the reaction CCl₄^{-*} → CCl₃⁻ + Cl as com-

*The CCl₃⁻ ion has been observed in work reported by Dibeler and Mohler, but the relative content was very small (approximately 0.1%).¹⁶

pared with the decay reaction CCl₄^{-*} → Cl⁻ + CCl₃. The situation which has been pointed out is understandable because in the decay of the CCl₄⁻ ion the excess electron will be attached to the shell with the higher electron affinity, that is to say, to the Cl atom rather than the CCl₃ radical. On the other hand, the absence of the CCl₃⁻ ion indicates the small probability for the dissociation process CCl₄ → CCl₃⁻ + Cl⁺ whereas in electron impact the process CCl₄ → Cl⁻ + CCl₃⁺ has a rather high probability.¹⁴

Thus, in their general features, the spectra of the negative and positive ions are the same for H⁻ and O⁻ and for electrons. However, there is a big difference in the cross section for the formation of negative ions as a function of velocity of the primary particles, as is apparent from Fig. 2; in this figure, we show the $\sigma_i^-(v)$ curves obtained in the present work and the $\sigma(v)$ curve for the electron attachment process in CCl₄ taken from the work of Buchel'nikova.⁷

The cross sections for the formation of negative ions in SF₆ bombarded by H⁻ and O⁻ ions are weak functions of ion velocity in the velocity region which has been studied (Fig. 3). σ_i^- for SF₆ is considerably smaller than for O₂ and CCl₄, as is apparent from Fig. 4, in which we compare the $\sigma_i^-(v)$ curves for these three gases. Just as in O₂ and CCl₄, the $\sigma_i^-(v)$ curve for electron attachment in SF₆ is very different from the curve for charge exchange between O⁻ ions and the SF₆ molecule (cf. Fig. 3).⁷

In the table we give the results of a mass-spec-

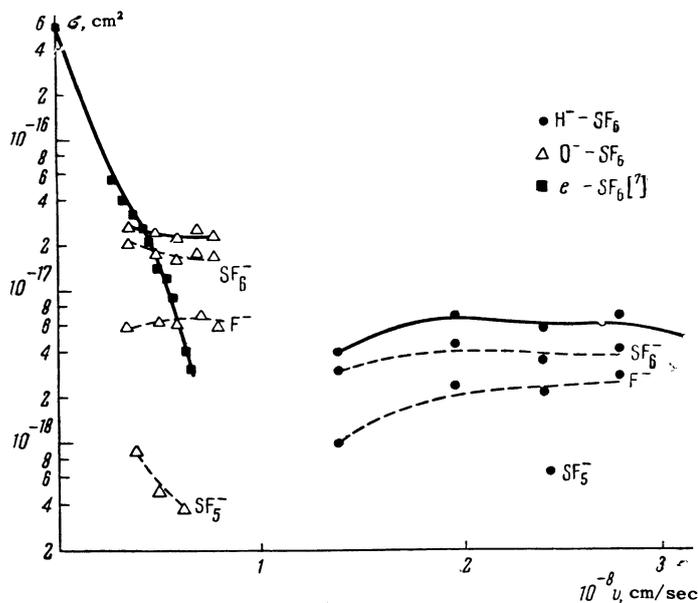


FIG. 3. The cross sections for the formation of slow negative ions in the gas SF_6 as a function of velocity (solid curve). The dashes indicate the corresponding curves for the individual ions. For the ion SF_5^- the cross section for bombardment by H^- has been measured at only 30 kev.

trometer analysis of the negative and positive ions formed by passing 30-kev O^- ions through SF_6 . For purposes of comparison, in this same table we give data on the composition of the positive ions formed in SF_6 by electrons with energies of 50 ev.¹⁶ The data on negative ions given in the table refer to electron energies close to zero, since it is at this energy that there is a maximum cross section for the formation of the ions SF_6^- , SF_5^- , and F^- .¹⁷ It is apparent that there is a considerable difference in the relative intensities for the SF_6^- and F^- ions when they are formed by O^- ions and by electrons. In electron collisions, excited SF_6^* ions are formed in the overwhelming majority of cases;

these excited ions have lifetimes which exceed the time-of-flight in the mass spectrometer. In charge exchange of O^- ions with SF_6 molecules, however, a large portion of the SF_6^- ions which are formed decay with the formation of F^- ions ($\text{SF}_6^- \rightarrow \text{SF}_5 + \text{F}^-$) while a considerably smaller part of these ions decay via the process $\text{SF}_6^* \rightarrow \text{SF}_5 + \text{F}$. In this case, just as in decay of CCl_4^- ion, the more probable decay process is the one in which the electron becomes attached to the shell with the higher electron affinity. Attention is merited by the fact that the positive ion spectrum does not contain the SF_6^+ ion whereas SF_6^- exhibits the highest intensity in the negative ion spectrum. This means that the detachment of the electron from the SF_6^+ molecule always results in dissociation of the SF_6^+ ion formed. Attachment of the electron to the SF_6 molecule is much more likely, especially the attachment of a free low-energy electron, which results in the formation of an excited SF_6^* ion with an appreciable lifetime.

The investigation of the spectrum of the negative ions formed in collisions of H^- and O^- with the freon molecule CCl_2F_2 shows, that in addition to the ions F^- , Cl^- and C^- , this spectrum contains a large number of H^- ions (approximately 50%). Inasmuch as the water vapor is carefully removed from the freon in the collision chamber, we may assume that the H^- ion appears as a consequence of impurities (in the freon) containing molecules in which one or more halogen atoms are replaced by hydrogen atoms. It is well known that it is difficult to remove these impurities from freon. For this reason, a systematic investigation of $\sigma_1^-(v)$ was not carried out for CCl_2F_2 . However, we have estimated $\sigma_1^-(v)$ for $\text{H}^- - \text{CCl}_2\text{F}_2$ for H^- energies of 30 kev. This estimate yields a value of $2.5 \times 10^{-18} \text{ cm}^2$, which is 25 times smaller than

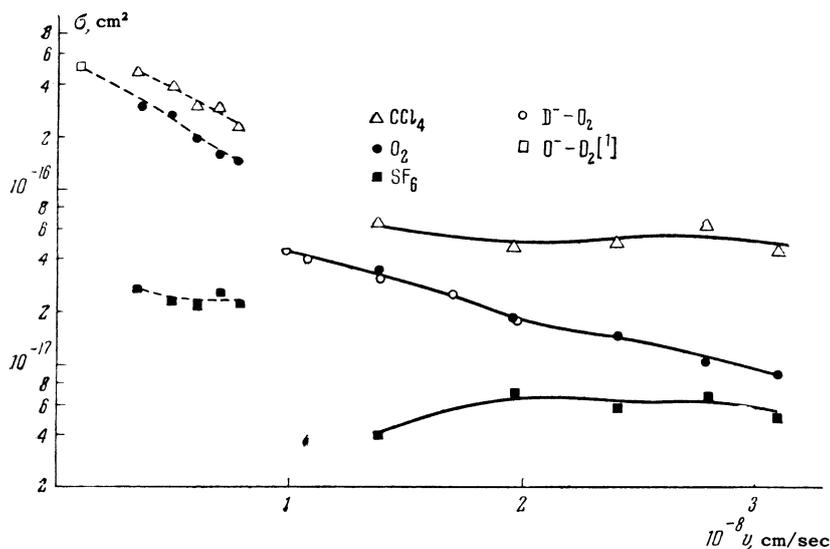


FIG. 4. The solid curves show the function $\sigma_1^-(v)$ for H^- while the dashed curves apply for O^- .

for $H^- - CCl_4$ at the same ion energy. From this result we may conclude that replacement of Cl atoms by F atoms in CCl_4 causes a marked reduction in σ_i^- .

The relative numbers of different negative and positive ions which appear in collisions of H^- and O^- ions with CCl_2F_2 molecules is given in the table together with the data on electron impact.¹³ It is apparent from these data that in charge exchange with H^- and O^- and in electron attachment, the CCl_2F_2 molecule does not form the ion $CCl_2F_2^-$; on the other hand, in ionization by these particles only a very small number of $CCl_2F_2^+$ ions are formed. In this respect, CCl_2F_2 is similar to CCl_4 (cf. above). We may note that electron impact results in the formation of more Cl^- ions than F^- . On the other hand, in ion impact, more F^- is formed than Cl^- .

In addition to the investigation of O_2 , CCl_4 , SF_6 and CCl_2F_2 , attempts were made to measure σ_i^- in bombardment of CO , CO_2 , H_2O , NO and NH_3 by H^- and O^- . In all these molecules σ_i^- was found to be much smaller than in O_2 , CCl_4 , and SF_6 . Furthermore, the characteristic curves for $i_{\bar{H}}/I_0 = f(V)$ obtained in the bombardment of these gases by O^- show that $i_{\bar{H}}/I_0$ increases continuously with increasing potential difference V ; this effect is apparently caused by scattered ions from the primary beam, which strike the measurement electrode, or by the high initial velocities of the negative ions formed. In any case, because the $i_{\bar{H}}/I_0 = f(V)$ characteristic does not have a plateau, it is impossible to obtain reliable values for σ_i^- in CO , CO_2 , H_2O , CH_4 , NO and NH_3 . When H^- ions pass through these gases, the $i_{\bar{H}}/I_0 = f(V)$ characteristic does exhibit a plateau, but the value of $i_{\bar{H}}/I_0$ at the plateau cannot be measured reliably because of the low sensitivity of the device used to measure the current $i_{\bar{H}}$. In any case σ_i^- in these gases is smaller than $2 - 3 \times 10^{-18} \text{ cm}^2$.

For the same reason (small current at the mass-spectrometer collector) negative ion spectra could be analyzed only for the molecules H_2O and CO_2 . In $O^- - H_2O$ the spectrum exhibits H^- ions (58%) and O^- ions (42%). Judging from the relative intensity of the H^- and O^- peaks, the decay processes $H_2O^- \rightarrow H^- + OH$ and $H_2O^- \rightarrow O^- + H_2$ have approximately the same probability. Similar results have been obtained in investigations of the negative ion spectra for collisions of electrons with the H_2O molecule.^{18,19} In the negative ion spectrum for $O^- - CO_2$ we observe O^- (85%) and O_2^- ions (15%). Thus, the probability for the decay process $CO_2^- \rightarrow CO + O^-$ is appreciably

greater than for the process $CO_2^- \rightarrow C + O_2^-$. In the negative ion spectrum characteristic of electron attachment to the CO_2 molecule, only the O^- ions are observed.²⁰ The maximum electron attachment cross section is $5 \times 10^{-19} \text{ cm}^2$.

The experimental data reported in the present paper indicate that there is an important difference in the cross sections σ_i^- and the shapes of the $\sigma_i^-(v)$ curves for the attachment of free electrons in molecules and for charge exchange of negative ions with the same molecules. This difference arises because in the first case the negative ion is formed as a consequence of attachment of a free electron to the molecule. In this case the transition from molecule into a negative ion proceeds in accordance with the Franck-Condon principle and the $\sigma_i^-(v)$ curve must exhibit a resonance.²¹ In the second case the negative ion is formed by electron transitions between discrete states of the fast negative ion and the gas molecule, so that the general features of the $\sigma_i^-(v)$ curve are similar to these curves in other charge exchange processes.

The data presented on the formation of negative ions in atomic collisions, point to the desirability of further investigations at low velocities, where the maxima of the $\sigma_i^-(v)$ curves are located. The locations of these maxima (v_{max}) and the behavior of the $\sigma_i^-(v)$ curves for $v < v_{\text{max}}$ will allow us to examine the applicability of the adiabatic hypothesis to charge exchange of negative ions.

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