Correlations between Survival Probabilities and Ionization Energies of Slow Ions Colliding with Room-Temperature and Heated Surfaces of Carbon, Tungsten, and Beryllium†

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Survival probabilities, S_a (%), of hydrocarbon ions C1, C2, and C3 and several nonhydrocarbon ions (Ar^+, N_2^+, CO_2^+) on room-temperature (hydrocarbon-covered) and heated (600 °C) surfaces of carbon (HOPG), tungsten, and beryllium were experimentally determined using the ion−surface scattering method for several incident energies from a few electronvolts up to about 50 eV and for the incident angle of 30° (with respect to the surface). A simple correlation between S_a and the ionization energy (IE) of the incident ions was found in the semilogarithmic plot of S_a versus IE. The plots of the data at 31 eV were linear for all studied surfaces and could be fitted by an empirical equation $\log S_a = a - b(\mathrm{IE})$. The values of the parameters a and b were determined for all investigated room-temperature and heated surfaces and can be used to estimate unknown survival probabilities of ions on these surfaces from their ionization energies.

Introduction

In the broad range of physical and chemical phenomena occurring in the interaction of slow ions with surfaces, neutralization of the projectile ion is one of the most important processes. This has been documented in numerous studies.[1] The neutralization rate or, vice versa, the percentage of slow ions surviving a collision with the surface (i.e., the survival probability) is one of the basic characteristics of ion−surface interactions.

Ejection of electrons from metals by slow atomic ions and ion neutralization in interaction with metal surfaces was treated in a classical paper by Hagstrum.[2] An extension of this model to molecular ions included dissociation of the molecular species upon neutralization .[3,4] Processes of electron transfer in hydrocarbon collisions with surfaces were treated theoretically by Janev and Krstic.[5] These authors also developed a general analytic expression for the resonant neutralization (RN) transition rate of ions at surfaces, $\omega^{RN}(R)$, in the form $\omega^{RN}(R) = A^{RN}R^{\alpha} \exp(-2\gamma R)$, where A^{RN} and α are constants depending on γ, $\gamma^2/2$ is the electron binding energy, and R is the distance between the surface and the incident particle.

Neutralization of ions at surfaces is of importance in connection with thermonuclear fusion technology. Accurate modeling of divertor and edge plasma regions requires information on processes in collisions of ions with surfaces. In fusion vessels with exposed carbon-based parts, hydrocarbons are released into the plasma, where a variety of hydrocarbon ions is formed. The ions are subsequently neutralized in surface collisions or in the gaseous phase. Information on the survival probability of hydrocarbon and other ions in collisions with surfaces of fusion-related material is therefore of considerable interest.

In this paper, we concentrate on recent experimental data on ion survival probabilities as obtained in our laboratory over several years and on more general conclusions resulting from them that, hopefully, make it possible to estimate ion survival probabilities from ionization energies of projectile ions incident with a specified energy and under a specified angle on a particular surface. As a part of systematic scattering studies of interactions of slow hydrocarbon ions with surfaces relevant to fusion research, we determined the survival probabilities of projectile ions incident with energies from a few electronvolts to about 50 eV on room-temperature and heated (to 600 °C) surfaces of carbon (HOPG),[6−10,13,15] tungsten[14] and beryllium. The ion−surface scattering method used and the procedure used to extract the absolute ion survival probabilities from the scattering data are described in the next sections.

The experiments showed that the surfaces kept at room-temperature were covered by a layer of hydrocarbons from backstreaming pump oil or its hydrocarbon cracked fragments. This universal surface coverage could be sensitively tested by the occurrence of chemical reactions of H-atom transfer between the hydrocarbons on the surface and incident radical cations, for example,[6]

$$CD_4^{\cdot +} + CH_3\text{-}S \rightarrow CD_4H^+ + (^{\cdot}CH_2\text{-}S) \qquad (1)$$

or[8,16]

$$C_2D_4^{\cdot +} + CH_3\text{-}S \rightarrow C_2D_4H^+ + (^{\cdot}CH_2\text{-}S) \qquad (2)$$

Heating the surface to about 600 °C or higher resulted in an effective removal of the hydrocarbon layer, as indicated by the absence of the H-atom transfer reactions.[6,8,9,14] Cooling the surface after heating to room-temperature led to the re-establishment of the hydrocarbon layer on the surfaces within about an hour. Repeated heating and cooling of the surface led, within the experimental error, to the same scattering results (mass spectra of ion products of surface interactions, angular and translational energy of the ion products).

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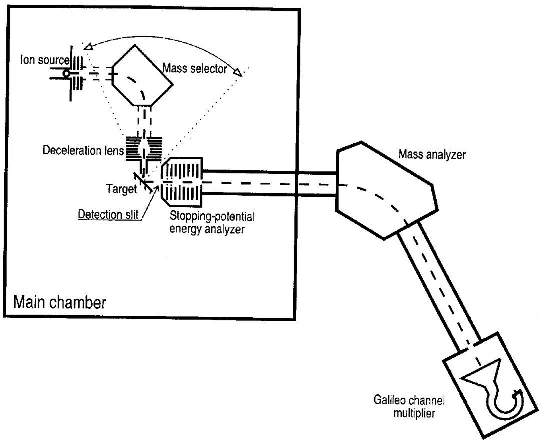

Figure 1. Schematics of the ion-surface scattering apparatus.

Experimental Method

The experiments were carried out with the Prague beam scattering apparatus EVA II modified for ion−surface collision studies (Figure 1).[6−16] Projectile ions were formed by bombardment by 120 eV electrons of hydrocarbons (or their deuterated variants) and of other gases at the ion source pressure of about 3.10^{-5} Torr. The ions were extracted, accelerated to about 150−200 eV, mass analyzed by a 90° permanent magnet, and decelerated to the required energy in a multielement deceleration lens. The resulting beam had an energy spread of 0.2 eV, full width at half-maximum (fwhm), angular spread of about 1.5−2° fwhm, and geometrical dimensions of 0.4×1.0 mm^2. The beam was directed toward the target surface under a preadjusted incident angle Φ_S (with respect to the surface). Ions scattered from the surface passed through a detection slit (0.4×1 mm^2) located 25 mm away from the target into a stopping potential energy analyzer. After energy analysis, the ions were focused and accelerated to 1000 eV into a detection mass spectrometer (a magnetic sector instrument) and detected with a Galileo channel multiplier. The primary beam exit slit, the target, and the detection slit were kept at the same potential during the experiments, and this equi-potential region was carefully shielded by μ-metal sheets. The primary beam-target section could be rotated about the scattering center with respect to the detection slit to obtain angular distributions. The mass spectra of product ions were recorded with the stopping potential of the energy analyzer set at zero.

The energy of the projectile ions was measured by applying to the target a potential exceeding the nominal ion energy by about 10 eV. The target area then served as a crude ion deflector directing the projectile ions into the detection slit. Their energy could be determined with accuracy better than about 0.2 eV. The incident angle of the projectile ions was adjusted by a laser beam reflection with a precision better than 1°. Incident (Φ_S) and scattering (Θ'_S) angles are given with respect to the surface plane.

The carbon surface target was a 5×5 mm sample of highly oriented pyrolytic graphite (HOPG, Union Carbide Coating Service Corp.) from which the surface layer was peeled off immediately before placing it into vacuum. The sample was mounted into a stainless steel holder located 10 mm in front of the exit slit of the projectile ion deceleration system. The carbon target surfaces in the experiments were kept either at room temperature or at an elevated temperature of about 600 °C. For this purpose, the carbon surface could be resistively heated, and its temperature was measured by a thermocouple and by a pyrometer. Practical absence of chemical reactions with surface hydrocarbons indicated that heating the surface to 600 °C or higher decreased the concentration of hydrocarbons on the surface more that 100 times.[6] The temperature of 600 °C was thus regarded as sufficiently high to essentially remove the hydrocarbon layer that covered the HOPG surface at room temperature and the present experiments were carried out at this surface temperature (see also further on). At temperatures above 500 °C, an increased emission of K^+ ions from the sample and/or the sample holder was observed.

The tungsten surface target[14] was a 99.9% tungsten sheet, 0.05 mm thick (Aldridge Chemical Comp.). Before placing it into vacuum, the surface was either mechanically or electrochemically polished. Electrolytic polishing followed the standard procedure of dipping the sample, as anode, for 30 s into a 20% solution of NaOH in water. The sample was mounted into a stainless steel holder located 10 mm in front of the exit slit of the projectile ion deceleration system. Similarly as with the carbon surface, emission of K^+ ions from the sample was observed at the sample temperatures above about 500 °C. Ex situ XPS analysis of the W target after heating showed a sharp increase of tungsten carbides on the surface.

The scattering chamber of the apparatus was pumped by a 1380 L/s turbomolecular pump, and the detector was pumped by a 65 L/s turbomolecular pump; both pumps were backed by rotary vacuum pumps. The background pressure in the apparatus was about 5×10^{-7} Torr; during the experiments, the pressure was about 5×10^{-6} Torr because of the leakage of the source gas into the scattering chamber.

Determination of Survival Probabilities from Experimental Data. The ion survival probability S_a (percentage of ions surviving a surface collision) is defined as a ratio of the sum of intensities of all product ions (P) scattered from the target, ΣI_{PT}, to the intensity of the projectile reactant ions (R) incident on the target, I_{RT}, $S_a = 100\ \Sigma I_{PT}/\ I_{RT}$. The total current of the projectile reactant ions incident on the target, I_{RT}, is the sum of the reactant ion actually measured on the target, I_{RTM}, and the current of ions incident and then scattered from the target into the gaseous phase, ΣI_{PT}; that is, $I_{RT} = I_{RTM} + \Sigma I_{PT}$. In most cases, ΣI_{PT} is negligible in comparison with I_{RTM}, and $I_{RT} \approx I_{RTM}$. Some ions may be trapped on the surface as ions, but they do not influence the value of the survival probability as defined above: either they remain trapped on the surface and then they are lost, or they are trapped and subsequently sputtered into the gas phase as ions and then they contribute to the sum of the scattered ions, ΣI_{PT}. However, we regard contributions of the latter at these low incident energies of the projectile ions as insignificant.

While I_{RTM} was directly measured in the experiments reported here, ΣI_{PT} could not be directly determined and had to be estimated from the sum of intensities of product ion reaching the detector, ΣI_{PD}, taking into account the discrimination of the apparatus (D_A) and the angular discrimination of the scattering differential measurements ($D(\omega)$). The directly measurable quantity was the relative survival probability, $S_{eff} = \Sigma I_{PD}/I_{RT}$, related to S_a (expressed in percents) by $S_a = 100FS_{eff}$, where F summarizes the discrimination effects.

It holds for the intensity of the projectile (reactant) ions registered on the detector (I_{RD}) and incident on the target (I_{RT})

$$I_{RD} = D_A D(\omega)_R I_{RT} \qquad (3)$$

and analogously for the scattered product ions (P)

$$I_{PD} = D_A D(\omega)_P I_{PT} \qquad (4)$$

where $D(\omega)_R$ and $D(\omega)_P$ are angular discriminations of the reactant and product beam, respectively. The derivation of the discrimination factors and the approximations used were in detail described in our previous papers,[6,8,10] and thus it will be only briefly summarized here.

By applying a potential exceeding by about 10 eV the nominal incident energy to the target (see above, Experimental Method), one could deflect the projectile reactant ion beam into the detection slit, measure its intensity entering the slit, I_{RS}, and its angular distribution, and register the ion current reaching the detector, I_{RD}. This procedure did not practically affect the angular distribution of the projectile ion beam as checked by a separate experiment in which the target was removed and the angular distribution of the projectile beam was directly measured. The discrimination of the apparatus was then $D_A = I_{RS} / I_{RD}$.

The angular discrimination factor, $D(\omega)_P/D(\omega)_R$, was derived as $D(\omega)_P/D(\omega)_R = \Theta^2{}_P/\Theta^2{}_R$ where $\Theta^2{}_P$ and $/\Theta^2{}_R$ are squares of the full width at half-maximum (fwhm) of the angular distributions of the projectile ion beam and the product ion beam, respectively. The constant F was then $F = D_A\ [D(\omega)_P/D(\omega)_R]$. The values of D_A and Θ_P were determined for different sets of experiments, and they were given in our previous papers.[6,8−10,13−15] The values of the latter did not differ significantly (1.5−2°). The values of Θ_R were obtained from specific measurements of angular distributions of scattered product ions as reported in the published papers, too.[6,8−10,13−15]

The absolute survival probability of incident ions, S_s, is related to the neutralization rate W_a (%) by $W_a = 1 - S_a$.

Results and Discussion

Survival Probabilities of Hydrocarbon and Other Ions. The absolute survival probabilities of hydrocarbon and several other nonhydrocarbon ions as determined from the above-mentioned experiments are summarized in Tables 1−5 for several incident energies between 15 and 46 eV. The incident angle was 30° (with respect to the surface) for all data in the tables. Table 1 gives the survival probabilities of ions on room-temperature carbon (HOPG) surfaces. Under these conditions, the surfaces were covered by a layer of hydrocarbons, as indicated by the occurrence of chemical reactions (mainly H-atom transfer from the surface hydrocarbons to the open-shell projectile ions) at the surface.[6−10,15,16] Table 2 provides data on absolute survival probabilities of C1 and C2 hydrocarbon ions and $N_2{}^{\bullet+}$ on carbon (HOPG) surfaces heated to 600 °C, where the surface hydrocarbon layer was effectively removed.[6,8] Tables 3 and 4 contain analogous data for room-temperature and heated surfaces of tungsten (W), respectively.[14] Table 5 gives data obtained for room-temperature surfaces of beryllium (Be). References to the data published in our previous papers are given in the tables; data without reference are newly measured data reported here for the first time. The values in the tables are mostly averages of measurements of many spectra, and the error bars give the standard deviation for an average of a series of measured data. The scatter of data of S_a estimates for the same ion reflects the range of experimental inaccuracies resulting from measurement of different sets of experiments, different incident beam intensities, and different detection accuracy (e.g., some of the measurements in Table 2 were made over a span of several years) and/or inaccuracies of the simplified evaluation of the discrimination factors.

The data on survival probabilities of ions in Tables 1−5 confirm that the main process in collisions of the ions with room-temperature and heated surfaces of carbon (HOPG), tungsten, and beryllium is ion neutralization. The data show a clear difference between survival probabilities of radical (odd-electron) ions and even-electron ions. While the survival probabilities of radical cations are about 2−1% or less, the survival probabilities of even-electron ions are in general larger (from several percent to about 10−20%). For most projectile ions, there was no systematic change with incident energy over the investigated incident energy range 15 to 46 eV. However, investigation of survival probabilities of selected radical and even-electron hydrocarbon ions C1 and C2 on room-temperature carbon surfaces at incident energies below 15 eV[10,16] showed a continuous decrease toward zero (Figure 2). This general decrease of S_a may be connected with an increasing importance of trapping of incident ions on the surface.

The survival probabilities of the nonhydrocarbon ions $Ar^{\bullet+}$ and $CO_2{}^{\bullet+}$ were very small, up to 2 orders of magnitude smaller than those for the listed hydrocarbon ions. The S_a value for the carbon dioxide dication $CO_2{}^{2+}$ was more than 10 times larger than for the singly charged radical cation $CO_2{}^{\bullet+}$, in general agreement with earlier findings for hydrocarbon cations and dications.[9]

The data in Tables 1−5 do not show any consistent trend of change of S_a with incident energy of the projectile ions in the measured range with the exception of the general decrease below 15 eV as mentioned above (Figure 2). However, in our previous papers,[11,14] we described a significant dependence of the survival probability on the incident angle of the projectile ions, namely, a substantial increase of the survival probability with decreasing incident angle (with respect to the surface). For ions from ethanol ($C_2H_5OH^{\bullet+}$, $C_2H_7O^+$, $C_2H_5O^+$) impinging on room-temperature (hydrocarbon-covered) stainless steel, the survival probability increased by a factor of about 8 when decreasing the incident angle by 20° between 50° and 10° (with respect to the surface).[11] For collisions of $C_2D_4{}^{\bullet+}$ colliding with room-temperature (hydrocarbon-covered) and heated (600 °C) surfaces of tungsten,[14] the value of S_a increased by a factor of 2 to 5 when decreasing the incident angle by 15° from 45° to 30°.[14]

Information on the survival probabilities of C1, C2, C3, and several other cations on a carbon (HOPG) surface covered at room temperature with hydrocarbons, as summarized in Table 1, provided sufficient data for an attempt to correlate the S_a values observed with a parameter characterizing the incident ions. An obvious characteristic is the recombination energy of these ions with electrons. Unfortunately, little is known about recombination energies of most ions in question. Therefore, we tried to correlate the survival probability values with the ionization energies (IE) of the species, having in mind that the recombination energy may be in some cases somewhat different from the IE, mainly due to conformational changes in the ionization−recombination processes. The values of ionization energies (IE) used are tabulated values,[17] and they are summarized in Table 6 together with the available data on recombination energies (RE) of the ions. The data on recombination energies come mostly from gas phase charge transfer experiments.[18,19] For $CD_5{}^+$, the value used was assumed to be the energy release in the reaction $CD_5{}^+ + e \rightarrow CD_4 + D$ (IE = 7.9 eV).

A simple correlation between S_a and IE was found[15] in a semilogarithmic plot of S_a versus IE, as shown in Figure 3. The data used in Figure 3 were data at the incident energy of 31 eV and incident angle 30° (with respect to the surface) as given in

TABLE 1: Survival Probability, S_a (%), of $\mathrm{C_mH_n^+}$ and $\mathrm{C_mD_n^+}$ (m = 1,2,3,7) Hydrocarbon and Several Non-Hydrocarbon Cations and Dications on Room Temperature Carbon (HOPG) Surfaces (Incident Angle Φ_S = 30°)

projectile ion	E_{inc}= 16 ± 1 eV S_a(%)	E_{inc} = 31 ± 1 eV S_a(%)	E_{inc} = 46 ± 1 eV S_a(%)	ref[a]
$\mathrm{CD_3^+}$	0.12 ± 0.03	0.22 ± 0.04	0.26 ± 0.16	6
$\mathrm{CD_4^{\bullet+}}$	0.37 ± 0.06	0.34 ± 0.2	0.27 ± 0.26	6
$\mathrm{CD_5^+}$	12.5 ± 5	12.0 ± 5	18 ± 7	6
$\mathrm{C_2H_2^{\bullet+}}$	0.1 ± 0.03	0.1 ± 0.03	0.06 ± 0.01	8
$\mathrm{C_2D_2^{\bullet+}}$			0.08 ± 0.02	8
$\mathrm{C_2H_3^+}$	6.4 ± 0.4	4.1 ± 0.7	2.4 ± 0.5	8
$\mathrm{C_2H_4^{\bullet+}}$	2.3 ± 0.6 1.2		0.7 ± 0.1	8
$\mathrm{C_2D_4^{\bullet+}}$		1.0 ± 0.4	0.9 ± 0.2	8
$\mathrm{C_2H_5^+}$	1.1 ± 0.03	1.0 ± 0.1	0.3 ± 0.03	8
$\mathrm{C_3H_2^{\bullet+}}$*(1-propene)*		1.7 ± 0.1	2.5	15
$\mathrm{C_3H_3^+}$*(c-propane)*		3.6 ± 0.3		15
$\mathrm{C_3H_3^+}$*(1-propene)*		7.8 ± 0.5		15
$\mathrm{C_3H_3^+}$*(propane)*	6.3	5.5 ± 0.3	3.9	15
$\mathrm{C_3H_4^{\bullet+}}$*(c-propane)*		2.3 ± 0.7	2.0 ± 0.7	15
$\mathrm{C_3H_4^{\bullet+}}$*(1-propene)*		1.8 ± 0.2		15
$\mathrm{C_3H_5^+}$*(c-propane)*		2.5 ± 0.2	2.0 ± 0.7	15
$\mathrm{C_3D_5^+}$*(D-propane)*		9.9 ± 1.4		15
$\mathrm{C_3H_5^+}$*(propane)*	11.2 ± 0.7	4.6 ± 0.2		15
$\mathrm{C_3H_6^{\bullet+}}$*(c-propane)*		1.8 ± 0.5	2.2 ± 0.1	15
$\mathrm{C_3D_6^{\bullet+}}$*(D-propane)*		4.8 ± 0.9		15
$\mathrm{C_3H_6^{\bullet+}}$*(propane)*	6.6 ± 0.9	7.2 ± 1.2	6.8 ± 2	15
$\mathrm{C_3D_7^+}$*(D-propane)*		20 ± 2.3	16 ± 3	15
$\mathrm{C_3H_7^+}$*(propane)*		11.9 ± 4	17 ± 6	15
$\mathrm{C_3D_8^{\bullet+}}$*(D-propane)*		1.4 ± 0.7		15
$\mathrm{C_3H_8^{\bullet+}}$*(propane)*	0.7 ± 0.3	2.7 ± 0.5	4.2 ± 2	15
$\mathrm{C_7H_7^+}$ *(toluene)*		14.2 ± 4		9
$\mathrm{C_7H_8^{\bullet+}}$ *(toluene)*		11.4 ± 2		9
$\mathrm{Ar^{\bullet+}}$			0.005	15
$\mathrm{CO_2^{\bullet+}}$			0.0035	15
$\mathrm{CO_2^{2+}}$			0.05	15
$\mathrm{C_7H_7^{2+}}$ *(toluene)*		23 ± 4		9
$\mathrm{C_7H_8^{2+}}$ *(toluene)*		20 ± 7		9

[a] References refer to data published by us previously.

TABLE 2: Survival Probability, S_a (%), of C1 and C2 Hydrocarbon Ions on Carbon (HOPG) Surfaces Heated to 600 °C (Incident Angle Φ_S = 30°)

projectile ion	E_{inc} = 16 ± 1 eV S_a(%)	E_{inc} = 31 ± 1 eV S_a(%)	E_{inc} = 46 ± 1 eV S_a(%)	ref[a]
$\mathrm{CD_3^+}$	0.09(±0.03)		0.1(±0.03)	6
$\mathrm{CD_4^{\bullet+}}$	(5)	0.23(±0.1) 0.10 ± 0.025		6
$\mathrm{CD_5^+}$			23(±7) 27.3 ± 8 35.2 ± 8	6
$\mathrm{C_2H_2^{\bullet+}}$	0.1 ± 0.04	0.1 ± 0.04 0.013 ± 0.013	0.36(±0.1)	8
$\mathrm{C_2D_2^{\bullet+}}$		0.07 ± 0.2		8
$\mathrm{C_2H_3^+}$		3.6 ± 0.25 0.81 ± 0.11		8
$\mathrm{C_2H_4^{\bullet+}}$		0.2 ± 0.05 0.06 ± 0.02	0.8 ± 0.2	8
$\mathrm{C_2D_4^{\bullet+}}$		0.4 ± 0.05		8
$\mathrm{C_2H_5^+}$		0.76 ± 0.11		
$\mathrm{N_2^{\bullet+}}$			0.0033 ± 0.0015 0.0006 ± 0.0005	

[a] References refer to data published by us previously; data without references are our new data.

Table 1. The semilog plot of the dependence S_a versus IE indicates a linear decrease over the entire range of ionization energies of the studied incident ion species (7−16 eV). The least-squares fit of the data is described well by the equation log S_a = (3.9 ± 0.5) − (0.39 ± 0.04) (IE). Figure 4 shows an analogous semilogarithmic plot for the data on heated (600 °C) surfaces of carbon (HOPG), as given in Table 2. The straight line showing the least-squares fit of the data (solid line) is steeper than for the room-temperature carbon surfaces (dashed, the straight line from Figure 3 without experimental data). The scatter of points is considerably larger (about 20% for both a and b, see eq 5 later on) than that in Figure 3. The reason for it is in the more difficult monitoring of the intensity of the incident projectile beam during experiments with heated surfaces.

Figure 5 summarizes the data for survival probabilities of ions on room-temperature and heated surfaces of tungsten. Again, the data used in the plot are those of Tables 3 and 4 obtained at the incident energy of 31 eV. The least-squares fit of the plots leads to almost parallel lines, the one for heated surfaces at lower S_a values. This finding seems to be rather

TABLE 3: Survival Probability, S_a (%), of C1, C2, and C3 Hydrocarbon Ions and Several Non-Hydrocarbon Ions on Room Temperature Tungsten (W) Surfaces (Incident Angle $\Phi_S = 30°$)

projectile ion	$E_{inc} = 16 \pm 1$ eV S_a(%)	$E_{inc} = 31 \pm 1$ eV S_a(%)	$E_{inc} = 46 \pm 1$ eV S_a(%)	ref[a]
CD_3^+		0.0185 ± 0.004		
$CD_4^{\bullet+}$	0.03 ± 0.01	0.033 ± 0.01	0.12 ± 0.04	14
CD_5^+	4.7 ± 0.7	0.8 ± 0.1	1.2 ± 0.1	14
$C_2H_4^{\bullet+}$		0.10 ± 0.05		
$C_2D_4^{\bullet+}$	0.17 ± 0.04	0.17 ± 0.04	0.19 ± 0.04	14
$C_2H_5^+$	2.7 ± 0.7	1.6 ± 0.5	0.85 ± 0.3	14
$C_3H_3^+$		1.05 ± 0.24		
$C_3H_5^+$		0.8 ± 0.14		
$C_3H_7^+$		2.16 ± 0.65		
$C_3H_8^{\bullet+}$		0.19 ± 0.05		
$N_2^{\bullet+}$		0.0015 ± 0.0015		
$Ar^{\bullet+}$		0.003 ± 0.002		

[a] References refer to data published by us previously; data without references are our new data.

TABLE 4: Survival Probability, S_a (%), of C1 and C2 Hydrocarbon Ions and N_2^+ on Tungsten (W) Surfaces Heated to 600 °C (Incident Angle $\Phi_S = 30°$)

projectile ion	$E_{inc} = 16 \pm 1$ eV S_a(%)	$E_{inc} = 31 \pm 1$ eV S_a(%)	$E_{inc} = 46 \pm 1$ eV S_a(%)	ref[a]
$CD_4^{\bullet+}$	0.03 ± 0.01	0.02 ± 0.007	0.02 ± 0.007	14
CD_5^+	1.1 ± 0.3	0.5 ± 0.04	0.5 ± 0.04	14
$C_2H_2^{\bullet+}$		0.007 ± 0.005		
$C_2D_4^{\bullet+}$	0.16 ± 0.05	0.1 ± 0.03	0.14 ± 0.04	14
$C_2H_5^+$	0.58 ± 0.1	0.32 ± 0.1	0.24 ± 0.1	14
		0.34 ± 0.04		
$N_2^{\bullet+}$		0.0005 ± 0.0005		

[a] References refer to data published by us previously; data without references are our new data.

TABLE 5: Survival Probability, S_a (%), of C1 and C2 Hydrocarbon Ions on Room Temperature Beryllium (Be) Surfaces (Incident Angle $\Phi_S = 30°$)

projectile ion	$E_{inc} = 16 \pm 1$ eV S_a(%)	$E_{inc} = 31 \pm 1$ eV S_a(%)	$E_{inc} = 46 \pm 1$ eV S_a(%)	ref[a]
$CD_4^{\bullet+}$		0.047 ± 0.015	0.053 ± 0.015	
CD_5^+	2.1 ± 0.5	2.2 ± 0.5	0.8 ± 0.2	
$C_2D_4^{\bullet+}$	0.4 ± 0.1	0.9 ± 0.4		

[a] New data, not published previously.

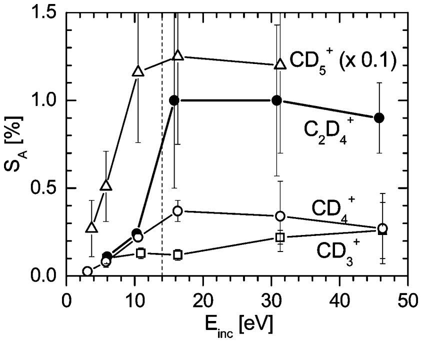

Figure 2. Survival probabilities S_a (%) of hydrocarbon ions on room-temperature carbon (HOPG) surfaces as a function of the incident energy (incident angle 30° with respect to the surface).

TABLE 6: Ionization Energies (IE) of Hydrocarbon and Non-Hydrocarbon Species Used in Correlations S_a−IE and Available Data of Recombination Energies (RE) of the Ions

species	IE (eV)	ref	RE (eV)	ref	species	IE(eV)	ref	RE(eV)	ref
CH_3	9.84	17	~9.8	18	C_3H_3	8.68	17		
CH_4	12.51	17	9.5−12	18	C_3H_4	9.7	17		
CH_5	7.92	17	(7.9)		C_3H_5	8.18	17		
					C_3H_6	9.73	17		
C_2H_2	11.40	17	11.4	18	C_3H_7	7.36	17		
C_2H_3	8.9	17			C_3H_8	10.95	17		
C_2H_4	10.51	17	9−11	18					
C_2H_5	8.13	17			CO_2	13.77	17	13.8	18
					N_2	15.58	17	15.3 (8.0)[a]	18
C_7H_7	7.20	17			Ar	15.75	17	15.7−15.9	18
C_7H_8	8.82	17	8.82	19					

[a] For neutralization of the ground state of the ion to $N_2(B^3\Pi_g)$.[18]

surprising, namely, in comparison with HOPG, where heating the surface led to a different, steeper slope of the plot. A possible explanation may be in the character of changes of the work functions of the room-temperature (hydrocarbon covered) and heated surfaces in question (the work function is one of the parameters of the theoretical treatment of surface neutralization[5]). We know from ex-situ XPS analysis of our heated W surfaces[14] that they were not clean W surfaces, but they contained a considerable amount of tungsten carbide originating in reactions with adsorbed hydrocarbons during the heating procedure. Both hydrocarbon adsorption[20,21] and tungsten carbide coverage[22,23] are known to decrease considerably (by 0.35 eV or more) the work function of tungsten (4.6 eV),[24] and thus they are likely to influence the S_a values in a similar way. On the other hand, in the case of carbon (HOPG) surfaces, the expected decrease of the work function with hydrocarbon coverage should lead, upon heating and hydrocarbon layer removal, to a higher value of the work function of the carbon surface devoid of hydrocarbons (generally accepted value 4.6 eV[25,26]).

Finally, Figure 6 compares the semilogarithmic plots for survival probabilities of ions on different room-temperature (hydrocarbon-covered) surfaces of carbon (HOPG), tungsten, and beryllium. The data for beryllium are available at present

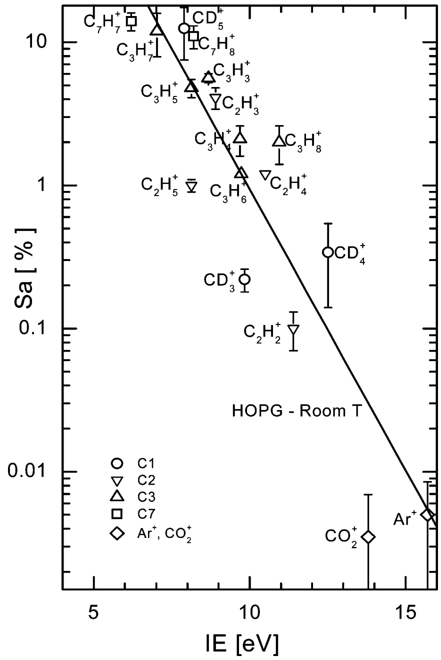

Figure 3. Semilogarithmic dependence of the survival probability S_a of the incident ions on their ionization energy (IE) for a room-temperature carbon (HOPG) surface. Incident energy 31 eV, incident angle 30° (with respect to the surface).

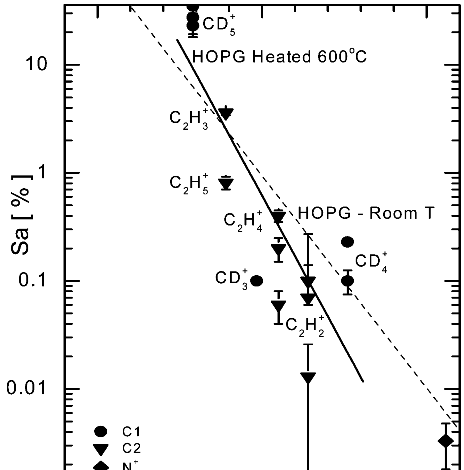

Figure 4. Semilogarithmic plot of the dependence S_a vs IE for a carbon surface heated to 600 °C (points and solid line). Dashed line is the same dependence for a room-temperature carbon (HOPG) surface from Figure 3. Incident energy 31 eV, incident angle 30° (with respect to the surface).

only for the incident ions CD_5^+, $CD_4^{\bullet+}$, and $C_2D_4^{\bullet+}$ (half-closed diamonds in Figure 6). The least-squares fits on data for carbon (HOPG) and tungsten are practically parallel lines mutually shifted in the ordinate scale. The available data for beryllium can be reasonably well-fitted by a straight line parallel with that for carbon (HOPG; see Figure 6).

In general, all semilogaritmic plots of survival probability versus ionization energy of the projectiles in question, log S_a versus IE, can be described by the empirical equation

$$\log S_a = a\text{-}b(\text{IE}) \qquad (5)$$

with different values of parameters a and b for different surfaces and their temperature. The values of parameters a and b for the investigated surfaces, as determined from the described experi-

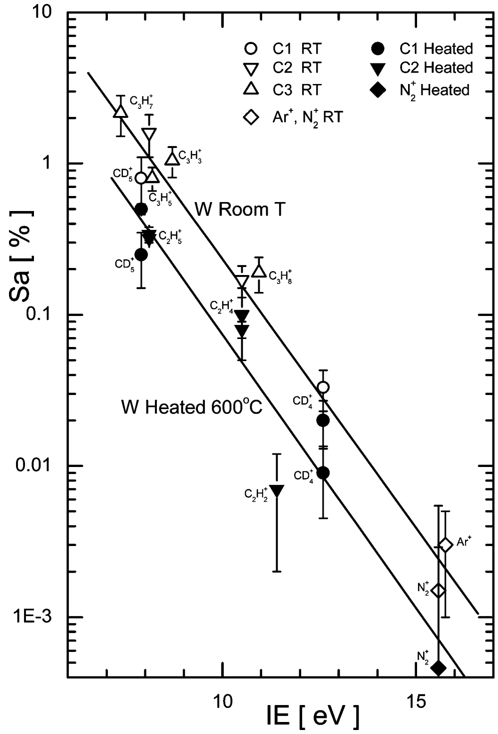

Figure 5. Semilogarithmic plot of the dependence S_a vs IE for tungsten surfaces at room-temperature (open points) and heated to 600 °C (solid points). Incident energy 31 eV, incident angle 30° (with respect to the surface).

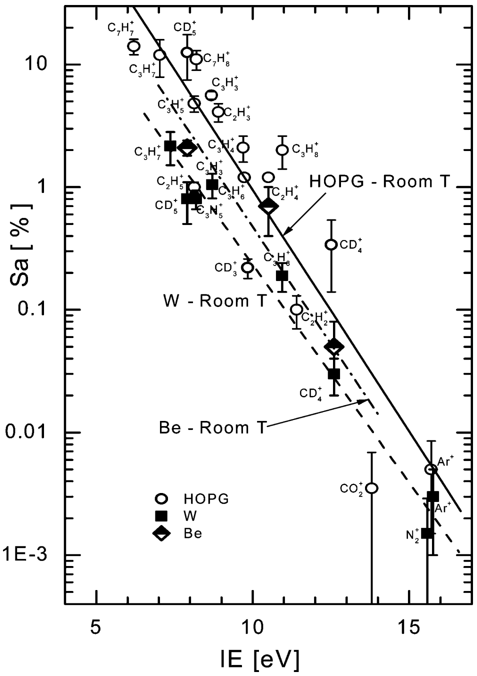

Figure 6. Comparison of the semilogarithmic plots of the dependence S_a vs IE for room-temperature surfaces of carbon (HOPG) (open points, see Figure 3), tungsten (solid points, see Figure 5), and beryllium (semiopened diamonds). Incident energy 31 eV, incident angle 30° (with respect to the surface).

TABLE 7: Values of Parameters *a* and *b* in the Plots Log S_a = *a* − *b*(IE) for Different Surfaces[a]

surface	*a*	*b*
carbon(HOPG), RT	3.9 ± 0.5	0.39 ± 0.04
carbon (HOPG), H	5.4 ± 1.1	0.5 ± 0.1
tungsten, RT	2.9 ± 0.2	0.35 ± 0.02
tungsten, H	2.5 ± 0.4	0.35 ± 0.04
beryllium, RT	(3.9)	(0.39)

[a] Note: RT - room-temperature, H - heated to 600 °C.

ments, are summarized in Table 7. The form of eq 5 is consistent with the general expression for the resonant neutralization transition rate of ions at surfaces developed by Janev and Krstic.[5]

The values of the parameters *b* (slopes) for the room-temperature surfaces are very similar (for HOPG 0.39 ± 0.04, for W 0.35 ± 0.02, for Be the parallel line with HOPG). This similarity is presumably caused by the hydrocarbon coverage of the surfaces. The quality of the underlying surface seems to influence only the absolute value of S_a. For the heated carbon (HOPG) surface, practically devoid of surface hydrocarbons, both values of *a* and *b* are different.

Conclusions

Ion survival probabilities were experimentally determined for a series of C1−C3 hydrocarbon ions and for some nonhydrocarbon ions on room-temperature and heated (600 °C) surfaces of carbon (HOPG), tungsten, and beryllium for ion incident energies up to 50 eV and incident angle of 30° (with respect to the surface plane).

The observed correlation between the logarithm of the survival probability and the ionization energy of the projectile ion as described by empirical relation (eq 5), log $S_a = a - b$ (IE), can be used in estimating the survival probability of any ion of known ionization energy on the particular surface, characterized by the parameters *a* and *b*. Though the error in the estimation may be rather large, eq 5 provides a new, quick way of its estimation for the purpose of plasma modeling or other purposes.

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