Water Cluster Collisions with Graphite Surfaces: Angular-Resolved Emission of Large Cluster Ions

Patrik U. Andersson and Jan B. C. Pettersson*,†

Department of Chemistry, Physical Chemistry, Göteborg University, S-41296 Göteborg, Sweden

Received: April 16, 1998; In Final Form: July 17, 1998

We present experimental studies of negative cluster ions formed during scattering of $(H_2O)_n$ ($\bar{n} \leq 4600$) from graphite surfaces. Angular distributions are measured using surface temperatures of 1280−1450 K and an incident cluster velocity of 1380 m/s. Large cluster ions are found to be emitted in sharply peaked distributions close to the tangential direction, except for normal incidence which produces distributions that are peaked in the surface normal direction. Time-of-flight measurements, combined with energy analysis of the emitted negative ions, are used to determine the final velocity and size of the cluster ions. The clusters are concluded to conserve 65−85% of their velocity parallel to the surface plane during a surface interaction, while the velocity component in the normal direction is 75−100 m/s independent of incident angle. The clusters undergo considerable fragmentation in surface contact, and 15−25% of a cluster survives as one unit for an initial cluster size of a few thousand molecules. The experimental findings are compared with results from earlier studies, and the detailed collision dynamics and conditions under which cluster charging takes place are discussed.

1. Introduction

A variety of processes may occur when clusters collide with solid surfaces, and the subject has recently received considerable attention. Two factors of particular importance for the outcome of a cluster−surface collision are the cluster size and the energy available for the cluster in surface contact. The initial kinetic energy of the cluster is often the dominating energy term, but the surface temperature and internal excitation of the cluster may also play a role when the collision energy is low. At surface impact, cluster collision energy is rapidly transferred to the surface and to internal cluster modes. When the collision energy is comparable to the binding energy of the cluster, the surface collision results in processes such as cluster fragmentation and scattering of surviving cluster fragments. In this energy regime collisions of van der Waals clusters with surfaces have been studied experimentally using neutral cluster beam techniques[1−8] and theoretically by molecular dynamics simulations.[9−16] The behavior of hydrogen-bonded clusters under similar conditions has also been investigated experimentally[17−22] and theoretically.[21,23] For higher collision energies the rapid compression of the cluster at impact may provide extreme conditions of high density and temperature,[24−26] and classical trajectory calculations have been used to investigate chemical reactions that occur inside the cluster[27−32] or at the cluster−surface interface.[33] The use of cluster ions in surface impact experiments allows for size selection and better control of the collision energy, and deposition, scattering, and dissociation of cluster ions have recently been studied.[34−37] Surface deposition of size-selected clusters is also being investigated for material processing applications, including the production of high-quality thin films.[38,39]

Cluster impact with high kinetic energy is known to result in electron emission and dissociative ionization of cluster components.[40−43] A few studies have shown that charged particles may also be emitted during surface impact with low kinetic energies,[17−22,44,45] and the further characterization of this phenomenon is the subject of the present study. In previous work Vostrikov and co-workers[17−21] studied the scattering of neutral water clusters with a velocity of 1300 m/s from different surfaces and observed large cluster ions in the scattered flux, with different ratios between positive and negative cluster ions depending on the surface material used. The probability for cluster ionization in a surface collision was found to typically increase from 10^{-7} for a beam with an average cluster size $\bar{n} =$ 300 molecules to 10^{-4} for $\bar{n} = 1500$.[18,20] The ion intensities in general showed a strong dependence on the angle of incidence, θ_i, with a maximum at $\theta_i = 70 \pm 5°$,[17,18] and the results indicated that this maximum in ionization efficiency was correlated with the survival of large neutral cluster fragments.[20,21] In related studies, Even et al.[44] showed that negatively charged particles were emitted during impact of CCl_4 clusters on metal surfaces with an incident velocity of 1600 m/s. Christen et al.[45] investigated scattering of neutral SO_2 clusters from different surfaces and also observed emissions of both negative and positive ions.

We have recently studied the emission of charged cluster fragments during scattering of large $(H_2O)_n$ clusters ($\bar{n} \leq 3700$) from hot graphite surfaces.[22] The incident velocity used in the studies was 1300 m/s, which combined with a large incident angle of 70° from the surface normal direction prevented the clusters from being immediately destroyed at surface impact. Both negative and positive cluster ions were observed in the flux emitted from the surface, and the ionization probability was found to depend on cluster size and surface temperature. For a given incident cluster size, the temperature dependence of the ion emission was well described by the Arrhenius equation, and activation energies of 3.1 ± 0.3 and 0.52 ± 0.02 eV were determined for negative and positive cluster ions, respectively. The large difference in activation energy indicates

† Also at the School of Environmental Sciences, Göteborg University
* Corresponding author. Tel +46.31.772 28 28; Fax +46.31.772 31 07; E-mail janp@phc.chalmers.se.

S1089-5647(98)01889-6 CCC: $15.00
Published on Web 08/27/1998

that the ions are formed by different mechanisms. We proposed[22] that negative ions are formed by electron transfer from the hot graphite surface, and the activation energy of 3.1 ± 0.3 eV was interpreted as the energy required to transfer an electron from the Fermi level of the graphite surface ($\phi_{graphite}$ = 4.6 eV[46,47]) to a large water cluster with an electron affinity of about 1.4 eV.[48]

Vostrikov et al.[17−21] have previously proposed that H^+-OH^- ion pairs may be formed by autoprotolysis in a water cluster during surface impact, and one of the ions could in a subsequent step be removed leaving a charged cluster fragment to escape from the surface. The activation energy for autoprotolysis in bulk water is 0.58 eV,[49] which is close to the low activation energy of 0.52 eV observed for positive ions in our earlier study.[22] We therefore tentatively proposed that the positive cluster ions are formed by dissociative ionization in the cluster, followed by removal of the negative ion during surface contact.

In our previous study[22] of ion emission in water cluster−surface collisions we measured the total flux of cluster ions from a graphite surface. We here extend the studies and investigate the angular-resolved emission of water cluster ions, with the aim to better characterize the cluster−surface collision dynamics. Angular distributions for negative cluster ions are measured using high surface temperatures of 1280−1450 K. The angular distributions are found to be sharply peaked close to the tangential direction, except for normal incidence which produces a distribution that is peaked in the surface normal direction. We conclude that water clusters conserve 65−85% of their velocity parallel to the surface plane during the surface interaction, while the velocity in the surface normal direction is 75−100 m/s independent of incident angle. Mean velocity measurements combined with energy analysis of the emitted negative ions are used to estimate the fraction of water molecules that remain in the cluster. The clusters are found to undergo considerable fragmentation, and 15−25% of a cluster survives as one unit after the surface interaction for an initial cluster size of about 4000 molecules. A detailed picture of the cluster−surface interaction dynamics emerges when the experimental findings are combined with data from earlier studies, and this provides firmer ground for the discussion of the cluster charging mechanisms in operation.

2. Experimental Section

The cluster beam apparatus used in the experiments consists of a three-chamber differentially pumped beam-line followed by a chamber for beam characterization and surface scattering experiments.[22] Water clusters are generated by adiabatic supersonic expansion of water vapor through a nozzle into vacuum. The cluster beam source is connected to an external water reservoir, and the two parts are separately heated. The water used in the experiment had a resistivity larger than 10^5 Ω m (Milli-Q quality) and was taken from a water purification system (Millipore) where the feedwater is pretreated by deionization. The source pressure is controlled by heating the water reservoir up to 210 °C, which gave stagnation pressures of 0−18 bar and corresponding average cluster sizes $\bar{n}$ = 1−4600. The water vapor is expanded into the first chamber of the apparatus through an 18 mm long capillary with a diameter of 0.3 mm. The first chamber (working pressure of 4×10^{-3} mbar) is pumped by a roots pump and liquid nitrogen cooled walls. The flux is let into the second chamber (5×10^{-6} mbar) through a skimmer with a diameter of 1 mm at a distance of 10−25 mm from the source opening. The cluster beam is chopped (duty time 50%, frequency 163 Hz) in the third chamber before it reaches the ultrahigh-vacuum (UHV) chamber.

The UHV chamber contained a graphite surface and a rotatable collector for angular-resolved measurements of charged particles emitted from the surface. The UHV chamber was in the present experiments pumped by a diffusion pump and liquid nitrogen cooled walls, giving a working pressure of typically 1×10^{-8} mbar. The surface was of highly oriented pyrolytic graphite (Grade ZYB type, Union Carbide Corp.) with a mosaic spread of the *Z* axes of the crystallites of 0.8°, and its dimensions were 25×3 mm^2. It could be heated to 1500 K by an ac current (0−45 A) through the sample. The surface could be removed from the beam to allow for beam characterization with a fixed detector.

The cluster size distribution in the beam was determined using the retarding potential method introduced by Hagena and coworkers,[50,51] and the experimental procedure has been described elsewhere.[22] Clusters were ionized by electron impact using a standard axial molecular beam ionizer (Extranuclear Laboratories Inc., model 041-1), and the formed ions continued in the direction of the neutral cluster beam toward a Faraday cup detector. A low electron energy of 30 eV was used in order to limit effects of cluster fragmentation and the formation of multicharged clusters.[22] Experiments using an even lower electron energy of 20 eV gave very similar distributions. Time-of-flight measurements in the beam were carried out by chopping the beam at 50% duty cycle and taking the time derivative of the observed rise in signal after the opening of the chopper. The mean cluster velocity was determined from the time-of-flight measurements to be 1380 ± 20 m/s independent of cluster size, and the translational energy of a water cluster containing *n* water molecules was therefore equal to 0.18*n* eV. The cluster size distribution was measured by linearly varying the voltage of a grid downstream the electron impact region, while the transmitted ionic flux was monitored. The transmitted signal was measured with a Faraday cup using a lock-in amplifier to discriminate from background ions. For a given applied voltage U_{grid}, the measured transmitted signal corresponds to all clusters with a translational energy larger than eU_{grid}. We estimate that the method gives an energy resolution of 1 eV. The cluster ion distribution can then be determined by differentiating the signal with respect to the applied voltage. The distribution of neutral clusters was finally obtained after correction for a $n^{2/3}$ dependence of the ionization cross section on cluster size.

The distance between the surface and the rotatable collector used for detection of cluster ions was 65 mm. The flat collector surface was made of steel and had the dimensions 48×4 mm^2, and the surface normal of the collector was directed toward the center of the graphite surface. To produce a well-defined field, a cylinder with a radius of 55 mm surrounded the surface, and the solid cylinder was in the scattering plane replaced by a grid with 90% transmittance. An additional grounded cylindrical tube with radius 73 mm surrounded the complete collector setup. The detector construction gives an in-plane angular resolution of ±2° and an out-of-plane resolution of ±14°. Collector signals were averaged in a multichannel analyzer for time-of-arrival measurements, while a phase-locked amplifier was used for measurements of angular distributions.

3. Results

One major goal for this study is to characterize the angular-resolved emission of cluster ions formed during scattering of large neutral water clusters from graphite. In an earlier study of water cluster collisions with graphite,[22] we measured the total flux of ions from the surface, and the largest emitted currents

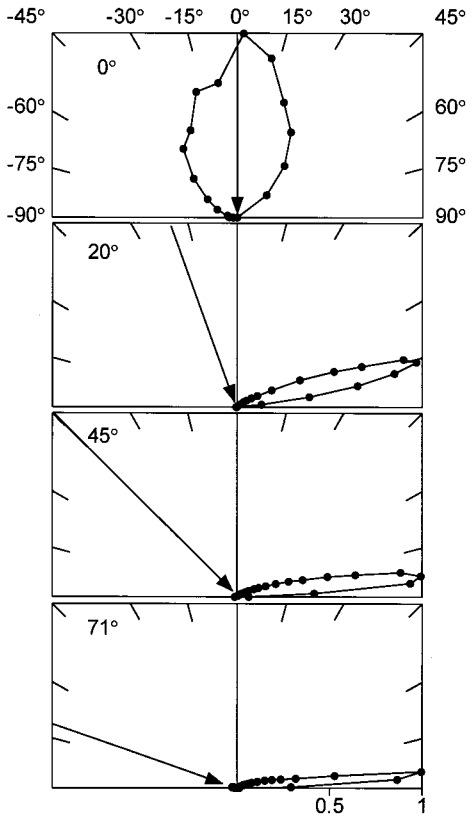

Figure 1. Normalized angular distributions for negatively charged cluster ions emitted during scattering of $(H_2O)_n$ from a hot graphite surface. The arrows indicate the incident beam direction, and the angle between the cluster beam and the surface normal direction is given in each panel. The surface temperature was 1450 K, and the average cluster size in the incident beam $\bar{n} = 3210$ (0°), 3730 (20°), 4530 (45°), and 4570 (71°).

were observed for negative cluster ions at relatively high surface temperatures. In the present study, we therefore concentrate on the emission of negative cluster ions at surface temperatures of 1280−1450 K, where the signal levels are high enough to allow for angular-resolved detection with good sensitivity.

The characteristics of the water cluster size distributions in the incident beam were similar to the ones used in previous studies.[8,22] By using source pressures of 0−18 bar, distributions with $\bar{n} \leq 4600$ and a full width at half-maximum (fwhm) of $\sim\bar{n}$ were produced. The concentration of ions in the incident beam was confirmed to be below the detection limit (1×10^{-15} A). The mean velocity of the incident beam was 1380 ± 20 m/s, and the velocity spread in the beam was $\Delta v/v \leq \pm 4\%$ (fwhm). The effect of cluster size on the mean velocity was within the given error limits.

Angular distributions of emitted negatively charged particles were measured for different surface temperatures and cluster sizes, using incident angles, θ_i, of 0, 20, 45, and 71° from the surface normal direction. The experiments were performed under field-free conditions in order not to influence the direction of the emitted ions; i.e., the surface, the grid, and the collector were all kept at zero voltage. The flux of emitted positive ions was also confirmed to be negligible compared to the negative signal under the conditions used here. Figure 1 illustrates the effect of incident angle on the angular-resolved emission of negatively charged clusters at a surface temperature of 1450 K. The distribution observed for $\theta_i = 71°$ is very narrow and peaks at 85°, close to the tangential direction. When the incident angle is changed to 45°, the peak position of the angular distribution is only slightly shifted while the width is increased. For an

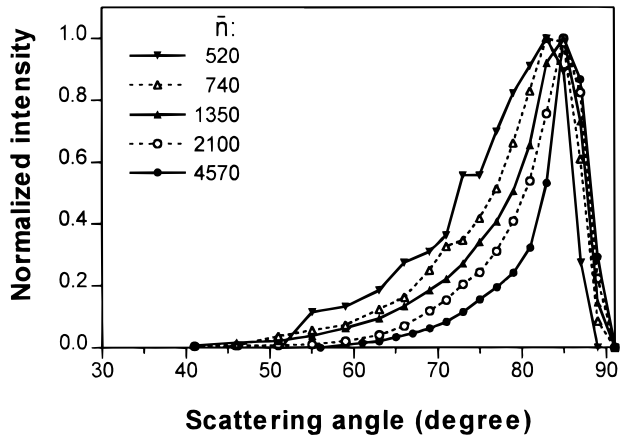

Figure 2. Effect of incident cluster size on angular distributions for negative cluster ions emitted during $(H_2O)_n$ scattering from graphite. The average cluster sizes in the incident beam, $\bar{n}$, are indicated in the figure. The incident angle was 71°, and the surface temperature was 1450 K.

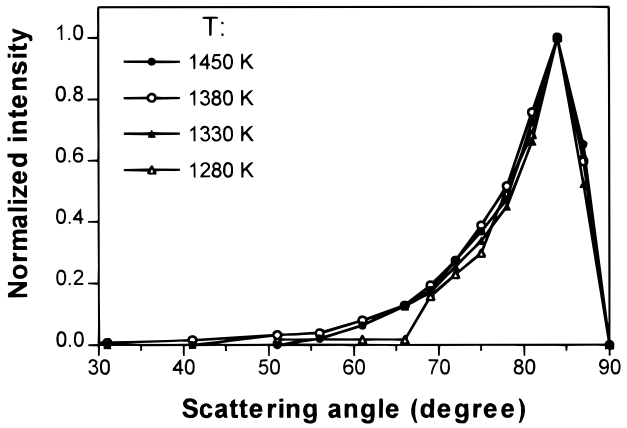

Figure 3. Effect of surface temperature on angular distributions for negative cluster ions emitted during $(H_2O)_n$ scattering from graphite. The surface temperatures are indicated in the figure. The incident angle was 71°, and the average cluster size in the incident beam $\bar{n} = 1630$.

incident angle of 20° the distribution peaks at 76°, which corresponds to a surprisingly large shift of 56° from the specular direction. Finally, a broad distribution that is peaked in the normal direction is observed in the case of normal incidence.

The influence of incident cluster size on the angular-resolved emission of negative ions is illustrated in Figure 2 for $\theta_i = 71°$. The angular distributions all display a sharp peak in the angular range 80−85°, and the intensity rapidly decreases when moving toward the surface normal direction. As the incident cluster size increases, the distributions become increasingly narrow and shifted toward the tangential direction. Figure 3 shows the effect of surface temperature for $\bar{n} = 1630$ and $\theta_i = 71°$. In contrast to the effect of incident cluster size, the surface temperature does not have an observable influence on the angular distributions in the temperature range 1280−1450 K.

The initial cluster size and surface temperature have strong effects on the *intensity* of emitted ions, as illustrated in Figures 4 and 5. The relative particle flux in the incident beam changes with source pressure, and the data in Figure 4 have been corrected for these changes based on measurements with the retarding field detector. Figure 4 shows that an average cluster size of approximately 350 is required to obtain an observable ion signal, and the signal then increases with cluster size. The intensity of negative ions is largest for $\theta_i = 71°$, while the signals are lower and comparable for incident angles of 20 and

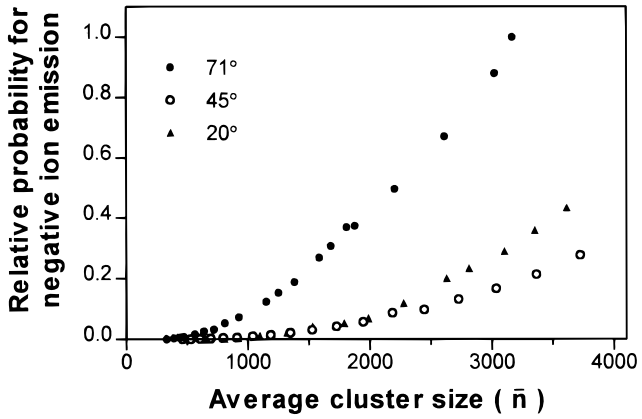

Figure 4. Effect of average incident cluster size on the relative probability for emission of negative cluster ions during scattering of $(H_2O)_n$ from graphite. The incident angles were 20° (▲), 45° (○), and 71° (●), and the measurements were performed in the scattering direction of highest intensity. The data have been corrected for changes in relative particle flux with cluster source pressure, based on measurements with the retarding field detector.

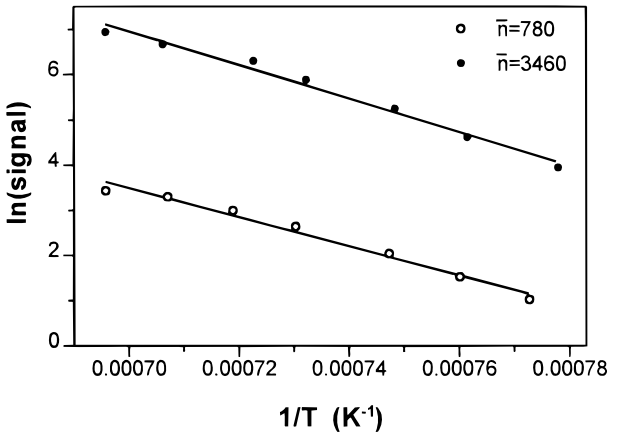

Figure 5. Temperature dependence for the emission of negative cluster ions during scattering of $(H_2O)_n$ from graphite. Activation energies of 2.8 ± 0.4 and 3.2 ± 0.4 eV (95% confidence limits) were determined for an incident beam with $\bar{n} = 780$ (○) and $\bar{n} = 3460$ (●), respectively. The measurements were performed in the scattering direction of highest intensity.

45°. The same trend was observed for the $(H_2O)_n$/surface systems studied by Vostrikov and co-workers,[17,18,20] but the effect of changing the incident angle was larger in their studies. The surfaces used were polished metals (gold, steel, duralumin), Ge(100), Ge(110), and fiberglass laminate. They observed an onset of ion emission at $\bar{n} = 330$, which is close to the value observed here. Figure 5 illustrates the surface temperature dependence of the ion emission. The intensity increases rapidly with surface temperature for the two cluster sizes displayed, and the increase in emission rate can be described by the Arrhenius equation. In the surface temperature range 1280−1450 K, activation energies of 2.8 ± 0.4 and 3.2 ± 0.4 eV are determined for $\bar{n} = 780$ and 3460, respectively. The values are comparable to the value of 3.1 ± 0.3 eV determined for the total negative ion flux from the surface in our previous study.[22]

We have also performed time-of-flight measurements in the scattering peak direction to determine the mean velocity of the emitted ions, and the results for different incident angles are given in Table 1. The data show that clusters leave the surface maintaining 65−85% of their initial velocity parallel to the surface. On the other hand, the final velocity component in the surface normal direction (z direction) is 75−100 m/s for all incident angles, and in case of $\theta_i = 20$ and 45° the clusters have thus lost a substantial amount of their initial kinetic energy. We have also determined the average final kinetic energy of the emitted cluster ions by measuring the collector signal as an increasing negative voltage was applied to it. The average kinetic energy was determined from the voltage required to stop 50% of the flux of negative cluster ions; see Figures 2 and 3 in ref 22 for similar measurements for the total emitted flux. The mean final kinetic energies for different incident angles are in the range 8−53 eV, to be compared with an initial kinetic energy of 712 eV for $\bar{n} = 4000$. The combined mean velocity and kinetic energy determinations allow us to estimate the final size of the detected cluster ions, and the values are given in Table 2. The emitted ions are found to have a final size of about 15−25% of the initial cluster size in case of $\bar{n} = 3100-4400$.

TABLE 1: Average Velocity of the Emitted Negative Cluster Ions in the Scattering Direction of Highest Intensity and Velocity Components Perpendicular (z Direction) and Parallel (x Direction) to the Surface Plane[a]

θ_i (deg)	$\theta_{f,peak}$ (deg)	v_f (m/s)	$v_{f,z}$ (m/s)	$v_{f,x}$ (m/s)	$v_{f,x}/v_{i,x}$
20	76	410 ± 25	100 ± 5	400 ± 25	0.85 ± 0.05
45	83.5	670 ± 60	76 ± 10	670 ± 60	0.68 ± 0.06
71	85	880 ± 130	77 ± 12	880 ± 130	0.67 ± 0.10

[a] The incident velocity was 1380 ± 20 m/s, and the surface temperature was 1450 K. The cluster sizes in the incident beam are given in Table 2.

TABLE 2: Average Kinetic Energy and Size of the Emitted Negative Cluster Ions[a]

θ_i (deg)	$\bar{n}_i$	$\langle E_{kin,f} \rangle$ (eV)	$\bar{n}_f$	$\bar{n}_f/\bar{n}_i$
20	3320 ± 150	8 ± 1	500 ± 90	0.15
45	4430 ± 150	29 ± 3	690 ± 180	0.16
71	3120 ± 150	53 ± 3	730 ± 240	0.23

[a] Final cluster sizes were calculated using the measured $\langle E_{kin,f} \rangle$ values and final velocity values taken from Table 1. Measurements were performed in the scattering direction of highest intensity. The incident velocity was 1380 ± 20 m/s, and the surface temperature was 1450 K.

4. Discussion

The experimental results show that the emitted cluster ions conserve a large fraction (65−85%) of their initial velocity parallel to the surface during a collision. The cluster velocity component in the surface normal direction is on the other hand only 75−100 m/s, indicating effective coupling to other degrees of freedom. The large difference in the behavior of the parallel and perpendicular velocity components is not surprising considering the relatively low corrugation of the graphite surface, and the same type of behavior has also been observed in scattering of argon clusters from graphite[5] and Pt(111).[16] The very different behavior of the velocity components also gives rise to the unusual angular distributions observed in the present study, with distributions peaked close to the tangential direction also for incident angles as small as 20°.

Recent work on the production of small fragments during cluster impact on surfaces helps to give a more complete picture of the collision dynamics. Andersson et al.[8] studied the emission of small neutral fragments during collisions of large water clusters with graphite. Angular distributions for monomers and small clusters produced during surface scattering were found to be well described by a model proposed by Vach et al.[5] where fragments thermally evaporate from parent clusters gliding along the surface plane. This was concluded to be the dominating cluster decomposition channel in the surface temperature range

800−1400 K. When the temperature was decreased below 800 K, clusters were instead slowed by friction forces before complete evaporation took place. The picture with large clusters gliding along the graphite surface is also consistent with earlier experimental and theoretical work on argon cluster collisions with graphite[4−6] and Pt(111).[15,16] During the gliding motion on the surface an initially cold cluster is heated by the surface, and the cluster starts to decompose by evaporation of monomers and small fragments. When the cluster reaches a certain temperature, the very extensive fragmentation may force a remaining large cluster fragment to leave the surface.[15,16] The earlier study[8] indicated that in case of water clusters on hot graphite surfaces this takes place at a cluster temperature of 950 ± 100 K. The angular distributions and average final velocities observed for neutral cluster fragments[8] are very similar to the results obtained for negative cluster ions in the present study, and we therefore conclude that emitted charged and neutral clusters have undergone the same type of gliding motion on the surface. The majority of the gliding clusters leave the surface in neutral form, but a small fraction of the clusters become charged in the process.

The cluster fragments that survive the surface interaction will continue to decrease in size due to evaporative cooling during their flight from the surface to the detector. In the present study the flight time to the detector is 70−160 μs depending on the conditions, and on this time scale we expect the temperature to drop to about 180 K since this is typically found in a relaxed water cluster beam.[52] The present study shows that about 15−25% of the initial cluster may reach the detector as one unit, using an average cluster size of about 4000 molecules in the incident beam. The clusters leave the surface with high internal temperatures, and a substantial part of the fragmentation should thus have taken place after they left the surface.

The angular distributions shown in Figures 2 and 3 provide further information about how the large cluster fragments escape from the hot surface. The data in Figure 3 show that the angular distributions do not depend on the surface temperature. This lack of surface temperature dependence fits well into a model where the emission of clusters takes place when a certain cluster temperature is reached, rather than being directly related to the surface temperature. The angular distributions shown in Figure 2 become shifted toward the tangential direction with increasing initial cluster size. Svanberg and Pettersson[15] have recently studied the survival of large fragments in argon cluster collisions with Pt(111) using classical trajectory calculations. The clusters had an initial size of 1000−4000 atoms and collided with the surface at normal incidence with a velocity of 50−300 m/s. The study showed that emitted small cluster fragments have a larger spread in final velocity and on the average higher velocities compared to those of large ones. Cluster fragments with a size less than 500 atoms typically had a final velocity in the range 30−80 m/s, while fragments with more than 1500 atoms had final velocities below 25 m/s. The same effect could explain the results for water clusters in Figure 2. If we assume that the final velocity component parallel to the surface plane is constant independent of cluster size, large fragments would then preferentially come out closer to the surface tangent compared to the case of small fragments. Further characterization of the final cluster velocity distributions will be required to confirm that the parallel velocity of emitted clusters is indeed independent of cluster size.

Svanberg et al. have recently carried out classical trajectory calculations of Ar_n ($n \leq 4400$) collisions with Pt(111),[16] and the simulations provide an estimate of the time scale for cluster−surface interactions under conditions similar to those in the present study. The initially cold (0 K) clusters interacted with the surface during tens of picoseconds before strong evaporation finally forced them away from the surface. We expect that water clusters behave in a similar way on the hot graphite surface, and the clusters should thus interact with the hot surface during tens of picoseconds while they are being heated from 180 to about 950 K. During this process they may, depending on the parallel velocity, glide tens of nanometers in close contact with the surface.

Negatively charged clusters are produced with a low ionization efficiency of 10^{-8}−10^{-3} per surface collision depending on the initial cluster size.[17−22] The ionization probability increases with increasing cluster size, as seen in Figure 4. The broad size distributions in the incident beam, however, make it difficult to conclusively determine the direct relation between size and charging probability, and further work with a wider cluster size range will help to clarify this point. The clusters may become ionized either through charge exchange with the surface or by intracluster ionization of cluster components, or by a combination of the two. We have previously proposed that clusters may pick up electrons from the hot surface.[22] A second mechanism for the production of charged clusters has been proposed by Vostrikov and co-workers[17−21] where an ion pair is formed by autoprotolysis in the cluster, followed by removal of one of the ions in a subsequent step. The present study suggests that the clusters interact with the surface during relatively long times (tens of picoseconds) and reach high internal temperatures in surface contact. These conditions should favor both of the mentioned charging mechanisms. The relatively long interaction time with the hot surface is likely to increase the probability for electron transfer from the surface. Ion pair formation in the cluster should on the other hand be favored by high internal cluster temperatures and by the extensive fragmentation that could help to separate the ions in a subsequent step. As concluded in our previous study,[22] the observed activation energy of about 3 eV for the production of negative cluster ions can be interpreted as the energy required to transfer an electron from the Fermi level of the graphite surface ($\phi_{\text{graphite}} = 4.6$ eV[46,47]) to a large water cluster with an electron affinity of about 1.4 eV.[48] On the basis of this interpretation, we find the electron-transfer mechanism to be the most likely in the case of emission of negative cluster ions. More work is, however, needed to more clearly distinguish between the proposed mechanisms for formation of cluster ions under different conditions.

5. Conclusions

We have characterized the emitted flux of negative cluster ions formed during scattering of neutral water clusters with 1380 m/s from hot graphite surfaces. Large cluster ions are found to be emitted in sharply peaked angular distributions close to the tangential direction, except for normal incidence which produces distributions peaked in the surface normal direction. The incident velocity component parallel to the surface plane is to a large degree (65−85%) conserved during the surface interaction, while the component in the surface normal direction is small (75−100 m/s) independent of incident angle. The surface temperature has no observable effect on the angular distributions in the temperature range 1280−1450 K, while the angular distributions are shifted toward the tangential direction when the initial cluster size is increased. The results are compared with data from earlier studies of water cluster−graphite collisions,[8] and a relatively clear picture of the collisions

dynamics emerges. The water clusters are concluded to glide along the hot surface while being constantly heated. As the cluster temperature increases, evaporation of monomers and small fragments becomes important, and the evaporation finally forces the remaining part of the cluster to leave the surface when a local cluster temperature of 950 ± 100 K is reached. The emitted clusters continue to decrease in size due to evaporative cooling on their way to the detector, and the present study shows that 15−25% of the cluster reaches the detector as one unit for an initial cluster size of 3100−4400 water molecules. Most clusters leave the surface as neutrals, but a small fraction becomes charged during surface contact. Based on the comparison with trajectory calculations for similar systems,[15,16] the clusters are proposed to interact with the hot surface during tens of picoseconds. The present study thus suggests that cluster charging takes place during conditions characterized by relatively long interaction times with the hot surface and high internal cluster temperatures. We conclude that further theoretical work is needed to more clearly distinguish between different charging mechanisms, including electron transfer from the surface[22] and ion pair formation in the heated cluster.[17−21] Further experimental studies with similar systems, including other surface materials, adsorbed overlayers, and the use of clusters of binary mixtures, should also help to evaluate the importance of different charging mechanisms.

Acknowledgment. We gratefully acknowledge the construction work and technical support of Mr. Benny Lönn. This project was supported by the Swedish Natural Science Research Council.

References and Notes

(1) Gspann, J.; Krieg, G. *J. Chem. Phys.* **1974**, *61*, 4037.
(2) Mironov, S. G.; Rebrov, A. K.; Semyachkin, B. E.; Vostrikov, A. A. *Surf. Sci.* **1981**, *106*, 212.
(3) Holland, R. J.; Xu, G. Q.; Levkoff, J.; Robertson Jr., A.; Bernasek, S. L. *J. Chem. Phys.* **1988**, *88*, 7952.
(4) Châtelet, M.; De Martino, A.; Pettersson, J. B. C.; Pradère, F.; Vach, H. *Chem. Phys. Lett.* **1992**, *201*, 563.
(5) Vach, H.; De Martino, A.; Benslimane, M.; Châtelet, M.; Pradère, F. *J. Chem. Phys.* **1994**, *100*, 8526.
(6) De Martino, A.; Benslimane, M.; Châtelet, M.; Pradère, F.; Vach, H. *J. Chem. Phys.* **1996**, *105*, 7828.
(7) Menzel, C.; Knöner, A.; Kutzner, J.; Zacharias, H. *Z. Phys. D* **1996**, *38*, 179.
(8) Andersson, P. U.; Tomsic, A.; Andersson, M. B.; Pettersson, J. B. C. *Chem. Phys. Lett.* **1997**, *279*, 100.
(9) Xu, G.-Q.; Bernasek, S. L.; Tully, J. C. *J. Chem. Phys.* **1988**, *88*, 3376.
(10) Xu, G.-Q.; Holland, R. J.; Bernasek, S. L.; Tully, J. C. *J. Chem. Phys.* **1989**, *90*, 3831.
(11) Pettersson, J. B. C.; Marković, N. *Chem. Phys. Lett.* **1993**, *201*, 421.
(12) Marković, N.; Pettersson, J. B. C. *J. Chem. Phys.* **1994**, *100*, 3911.
(13) Raz, T.; Even, U.; Levine, R. D. *J. Chem. Phys.* **1995**, *103*, 5394.
(14) Raz, T.; Levine, R. D. *J. Chem. Phys.* **1996**, *105*, 8097.
(15) Svanberg, M.; Pettersson, J. B. C. *Chem. Phys. Lett.* **1996**, *263*, 661.
(16) Svanberg, M.; Marković, N.; Pettersson, J. B. C. *Chem. Phys.* **1997**, *220*, 137.
(17) Vostrikov, A. A.; Dubov, D. Yu.; Predtechenskii, M. R. *Chem. Phys. Lett.* **1987**, *139*, 124.
(18) Vostrikov, A. A.; Dubov, D. Yu.; Predtechenskii, M. R. *Sov. Phys. Technol. Phys.* **1988**, *33*, 1153.
(19) Vostrikov, A. A.; Dubov, D. Yu. *Sov. Tech. Phys. Lett.* **1990**, *16*, 27.
(20) Vostrikov, A. A.; Dubov, D. Yu. *Z. Phys. D* **1991**, *20*, 61.
(21) Vostrikov, A. A.; Zadorozhny, A. M.; Dubov, D. Yu.; Witt, G.; Kazakova, I. V.; Bragin, O. A.; Kazakov, V. G.; Kikhtenko, V. N.; Tyutin, A. A. *Z. Phys. D* **1997**, *40*, 542.
(22) Andersson, P. U.; Pettersson, J. B. C. *Z. Phys. D* **1997**, *41*, 57.
(23) Svanberg, M.; Marković, N.; Pettersson, J. B. C. *Chem. Phys.* **1995**, *201*, 473.
(24) Cleveland, C. L.; Landman, U. *Science* **1992**, *257*, 355.
(25) Hendell, E.; Even, U.; Raz, T.; Levine, R. D. *Phys. Rev. Lett.* **1995**, *75*, 2670.
(26) Schek, I.; Jortner, J. *J. Chem. Phys.* **1996**, *104*, 4337.
(27) Schek, I.; Raz, U.; Levine, R. D.; Jortner, J. *J. Chem. Phys.* **1994**, *101*, 8596.
(28) Raz, T.; Schek, I.; Ben-Nun, M.; Even, U.; Jortner, J.; Levine, R. D. *J. Chem. Phys.* **1994**, *101*, 8606.
(29) Raz, T.; Levine, R. D. *J. Phys. Chem.* **1995**, *99*, 7495.
(30) Raz, T.; Levine, R. D. *Chem. Phys. Lett.* **1995**, *246*, 405.
(31) Gupta, M.; Walters, E. A.; Blais, N. C. *J. Chem. Phys.* **1996**, *104*, 100.
(32) Qi, L.; Sinnott, S. B. *J. Phys. Chem. B* **1997**, *101*, 6883.
(33) Beauregard, J. N.; Mayne, H. R. *J. Chem. Phys.* **1993**, *99*, 6667.
(34) Yeretzian, C.; Beck, R. D.; Whetten, R. L. *Int. J. Mass Spectrom. Ion Processes* **1994**, *135*, 79.
(35) Lill, Th.; Busmann, H.-G.; Lacher, F.; Hertel, I. V. *Chem. Phys.* **1995**, *193*, 199.
(36) Yasumatsu, H.; Koizumi, S.; Terasaki, A.; Kondow T. *J. Chem. Phys.* **1996**, *105*, 9509.
(37) Bernhardt, T. M.; Kaiser, B.; Rademann, K. *Z. Phys. D* **1997**, *40*, 327.
(38) Haberland, H.; Insepov, Z.; Karrais, M.; Mall, M.; Moseler, M.; Thurner, Y. *Mater. Sci. Eng. B* **1993**, *19*, 31.
(39) Yamada, I. *Mater. Sci. Eng. A* **1996**, *217/218*, 82.
(40) Baragiola, R. A. *Nucl. Instrum. Methods B* **1994**, *88*, 35.
(41) Beuhler, R. J. *J. Appl. Phys.* **1983**, *54*, 4118.
(42) Hendell, E.; Even, U. *J. Chem. Phys.* **1995**, *103*, 9045.
(43) Töglhofer, K.; Aumayr, F.; Kurz, H.; Winter, H. P.; Scheier, P.; Märk, T. D. *Nucl. Instrum. Methods B* **1994**, *88*, 44.
(44) Even, U.; de Lange, P. J.; Jonkman, H. Th.; Kommandeur, J. *Phys. Rev. Lett.* **1986**, *56*, 965.
(45) Christen, W.; Kompa, K.-L.; Schröder, H.; Stülpnagel, H. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1197.
(46) Ivey, H. F. *Phys. Rev.* **1949**, *76*, 567.
(47) Möller, K.; Holmlid, L. *Surf. Sci.* **1986**, *173*, 264.
(48) Barnett, R. N.; Landman, U.; Cleveland, C. L.; Jortner, J. *Chem. Phys. Lett.* **1988**, *145*, 382; *J. Chem. Phys.* **1988**, *88*, 4429.
(49) Knight, B.; Goodall, D. M.; Greenhow, R. C. *J. Chem. Soc., Faraday Trans.* **1975**, *75*, 841.
(50) Bauchert, J.; Hagena, O. F. *Z. Naturforsch.* **1965**, *20A*, 1135.
(51) Hagena, O. F.; Obert, W. *J. Chem. Phys.* **1972**, *56*, 1793.
(52) Torchet, G.; Schwartz, P.; Farges, J.; de Feuraudy, M.; Raoult, B. *J. Chem. Phys.* **1983**, *79*, 6196.