

Ion Pickup of Large, Surface-Adsorbed Molecules: A Demonstration of the Eley–Rideal Mechanism

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Abstract: Surface collisions of polycyclic aromatic hydrocarbon ions can be made to produce abundant pickup of large, surface-adsorbed species in a tandem time-of-flight mass spectrometer. Attachment of C_1H_n – C_6H_n to naphthalene and phenanthrene ions occurs with collision energies between 40 and 160 eV. Formation efficiency for these ion–adsorbate attachment reactions can be as high as 0.8%. Surface collisions produce no measurable shift in our flight times nor distortion in peak shapes for these species; this indicates the reaction time on the surface must be less than 160 ns. Theoretical calculations show that these reactions are direct (<100 fs residence on the surface) and thus proceed by an Eley–Rideal mechanism.

More than 50 years ago, Eley and Rideal¹ proposed that gas–surface reactions could proceed by direct pickup of species from the surface by a gas-phase molecule. Evidence has accumulated that almost all gas–surface reactions follow instead the Langmuir–Hinshelwood mechanism,² whereby the reactants are first adsorbed on and equilibrate with the surface prior to reaction followed by desorption. The question has been hotly debated whether the Eley–Rideal mechanism applies to any known gas–surface reaction. Recently, Kuipers et al.³ have reported the abstraction of a proton from a hydrogen-covered Pt(111) surface by bombardment with a 2–9-eV beam of $N(C_2H_4)_3N$. They found the time-of-flight distribution of the adduct changed with different initial precursor kinetic energies, clearly indicating an Eley–Rideal mechanism for reaction. Other more indirect evidence for an Eley–Rideal mechanism has been presented.⁴ In this paper, we report additional examples of an Eley–Rideal reaction involving ion–adsorbate attachment.

Cooks and co-workers^{5–9} first demonstrated that ions can be made to react with surface-adsorbed molecules upon collision with a surface. Pickup of one to four hydrogens^{5–7} and carbon species up to C_4H_n ^{8–10} have been observed for several precursor ions colliding with a variety of surfaces. The source of these adsorbates has been attributed to vacuum pump oil present on these surfaces. More recently, well-characterized organic monolayer surfaces have been used;^{11,12} with a perdeuterated thioalkane–gold surface, attachment of CD_3 to the molecular ion of pyrazine, $(C_4H_4N_2)^{++}$, was observed,¹¹ a clear demonstration of these ion–adsorbate reactions. Ion fragmentation, called surface-induced dissociation (SID), also occurs,^{5–18} and Cooks has pioneered its development for structural elucidation of ions by tandem mass spectrometry.¹⁹

Here, we show that species as large as C_6H_{0-4} can be attached to polycyclic aromatic hydrocarbon (PAH) ions upon surface bombardment in a tandem time-of-flight mass spectrometer. Theoretical calculations indicate that these reactions are direct (<100 fs residence time on the surface) and thus proceed by an Eley–Rideal mechanism. Our calculations are consistent with experimental results reported here and elsewhere and provide detailed insight into ion–adsorbate attachment reactions.

A reflectron time-of-flight mass spectrometer (R. M. Jordan Co.) modified with an in-line stainless-steel collision surface was used in these experiments (Figure 1). SID spectra are measured with the surface inserted into the reflectron; ions are made to undergo collisions by reducing the potential on the surface to below that of the ion acceleration energy (~ 2.6 kV). Ions produced at the surface are subsequently accelerated (~ 2.6 kV), with mass separation taking place based on their flight times to the detector.

Use of a similar instrument for ion–surface collisions has been reported recently by Whetten and co-workers.²⁰

The sample (Aldrich), introduced through a gas-phase inlet system, was photoionized by using 266-nm photons from a Nd:YAG laser (Continuum Model 661-30); laser power ($\sim 10^6$ W/cm²) was reduced so that parent ions were formed exclusively. Similar results are obtained with higher laser power (up to 10^8

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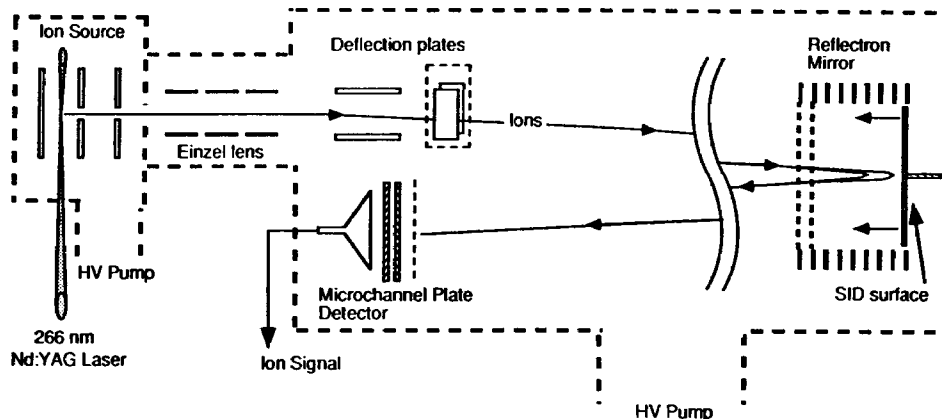


Figure 1. Schematic of the tandem time-of-flight mass spectrometer for measuring surfaced-induced dissociation spectra.

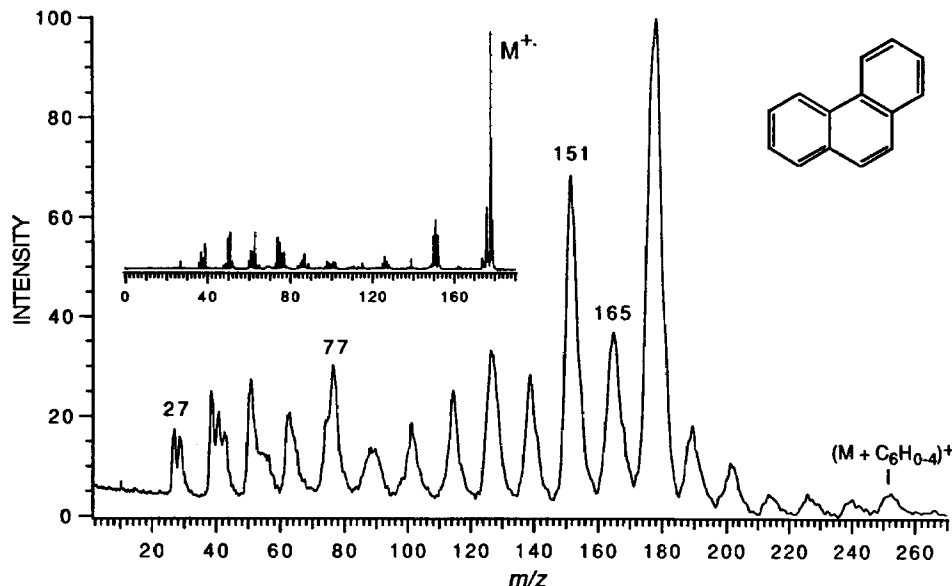


Figure 2. Surface-induced dissociation spectrum of the molecular ion of phenanthrene, $(C_{14}H_{10})^{+}$, with 120 eV collision energy; high power, 266-nm multiphoton ionization spectrum inset.

W/cm^2) by using a pulsed deflection lens to select only the parent ion. Source pressure with sample introduction is $\sim 4 \times 10^{-7}$ Torr. The main flight chamber with the collision surface was maintained at $\sim 2 \times 10^{-8}$ Torr.

Molecular ions of PAHs can be made to undergo extensive fragmentation upon collision with a stainless-steel surface. We find the dissociation of the molecular ion of phenanthrene, $(C_{14}H_{10})^{+}$, with collision energies between 0 and 200 eV produces fragmentation comparable to that reported by Schey et al.¹⁵ for its isomer, anthracene, although fragmentation appears more extensive, consistent with higher internal energy deposition with our near-normal collisions. With 120-eV collisions (Figure 2), the principal dissociation is loss of acetylene (appearance potential ~ 16 eV), the formation of which is ~ 8 eV above the ionization potential, indicating substantial internal energy deposition at this collision energy.²¹ We are unable to resolve loss of H or H_2 from undissociated molecular ions, although broadening in this peak indicates the presence of these ions.

In addition to dissociation and neutralization, we observe abundant pickup by the molecular ion of $C_1H_n-C_6H_n$ with collision energies between 40 and 160 eV; the maximum intensity for these attachment reactions occurs around 120 eV (Figure 2). At this energy, pickup of $C_1H_n-C_4H_n$ is substantially higher than observed previously;⁸⁻¹⁰ attachment of C_3H_n and C_6H_n has not been reported before. The total ion abundance of these reactions is 11% that of fragmentation, and 0.8% of the uncollided precursor ion

abundance, i.e., 0.8% formation efficiency.

We find these same attachment reactions for naphthalene molecular ions, $(C_{10}H_8)^{+}$. No ion signal is observed above the $(M + C_6H_4)^{+}$ ion (m/z 204 for naphthalene). This indicates that secondary ion emission (i.e., sputtering) of surface adsorbates does not contribute measurable ion signal to the higher mass $C_3H_n-C_6H_n$ attachment reactions observed with phenanthrene molecular ions, i.e., this ion signal originates exclusively from ion-adsorbate reactions. The origin of these higher mass adducts is not known. Replacing the polyphenyl ether, used as oil in our untrapped diffusion pumps, results in the elimination of the $C_4H_n-C_6H_n$ adduct attachment reactions, indicating cracked poly(phenyl ether) as a likely source for these adducts. We do not exclude hydrocarbon contamination from the mechanical backing pumps, the presence of which is indicated by m/z 29, 43, and 57 produced by sputtering,⁸ as a possible source.

Mass assignments for these adduct ions are determined by their flight times relative to those of the precursor and SID product ions. By comparing our measured flight times for the parent ion (and loss of H) to calculated values,²² we find that nearly all kinetic energy perpendicular to the surface is lost in the ion-surface collision. Similar results have been reported for C_{60}^{+} by Whetten and co-workers.²⁰ Thus, the kinetic energy perpendicular to the surface for $(M + C_6H_n)^{+}$ is implicitly assumed to be the same as that of the SID product ions, i.e., near zero. Note that 40 eV

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(22) Calculations performed using MacSimion, Version 1.1, D. McGilvery and R. Morrison, Centre for High-Resolution Spectroscopy and Opto-Electronic Technology, Monash University, Melbourne, Australia.

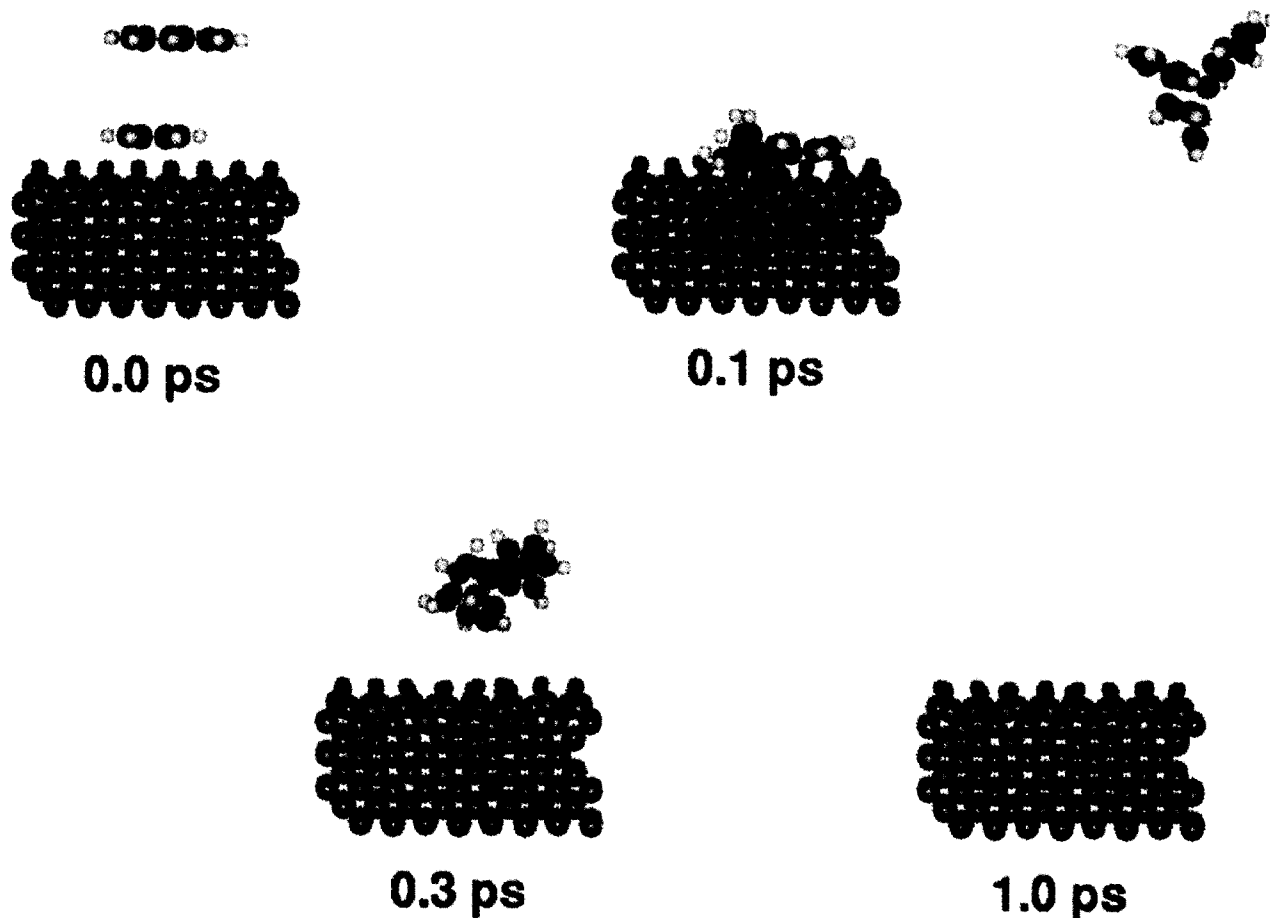


Figure 3. Sequence of time snapshots of a phenanthrene molecule hitting a benzene molecule adsorbed on a hydrogen-terminated diamond surface. The system is viewed from the side. There are periodic boundary conditions in the horizontal directions and the bottom two layers are held rigid in order to maintain crystallinity. The carbon atoms are represented by the larger spheres (gray, red, and blue) and the hydrogen atoms by smaller spheres (gray and yellow). The gray spheres are the substrate, the red spheres represent the physisorbed benzene molecule, and the blue spheres indicate the bombarding phenanthrene molecule. The phenanthrene molecule has 80 eV of kinetic energy at 0.0 ps. The closest approach to the surface occurs at 0.1 ps.

of initial kinetic energy changes our assigned mass by <5 Da. Because this ion is observed with 40-eV collisions, we feel confident in assigning this mass as $(M + C_6H_n)^+$.

An upper limit to the ion residence time on the surface is obtained from both the temporal profile and flight time of these adduct ions. For the $(M + C_6H_n)^+$ ion, the temporal width is 160 ns (fwhm); a longer ion residence time would produce a broader peak with unsymmetrical tailing to higher mass.²³ Note that unresolved masses differing by one hydrogen atom appear to be the major contribution to the peak widths for these ion-adsorbate attachment reactions. Thus, the actual residence time for a single mass is substantially lower. To resolve these individual ions, a 5-fold improvement in resolution is required.

The reaction time on the surface can be determined from the absolute flight time of the smaller adsorbates, for which the m/z ratios have been measured directly with unit mass resolution on quadrupole instruments; by comparison to Cooks' results⁸ for C_1H_n to C_3H_n attachment to PAHs, we are within a few daltons of the expected mass. For example, Cooks finds predominate C_2H_n attachment ions at $(M + 21)^+$ and $(M + 24)^+$. Our corresponding peak occurs at m/z 201, or $(M + 23)^+$, and is 150 ns wide (m/z 199–203). Less than 2% of the integrated ion signal remains 160 ns past m/z 202, or $(M + 24)^+$, indicating a substantially shorter

ion reaction time on the surface.²⁴

To understand the reaction mechanism of the attachment of the C_6H_n species to phenanthrene, we have performed molecular dynamics (MD) calculations of the reaction event. Briefly, MD calculations involve integrating the classical equations of motion for all the atoms of interest. The MD technique yields a time sequence of the microscopic reaction.

An interaction potential for the system is critical to MD calculations. Recently, a many-body interaction potential for reactions between hydrocarbon species was developed by Brenner.²⁵ The interactions are based on the Tersoff²⁶ formulation, where the attractive contribution between any pair of atoms is determined by the composition and geometrical arrangement of the surrounding atoms. Thus, the bonding nature (sp , sp^2 , or sp^3) is determined by the local environment of the neighboring atoms and can change during the reaction event.

Our calculations model a benzene and a phenanthrene molecule striking a benzene molecule lying on a hydrogen-terminated diamond surface. Because only C and H atoms are present, the Brenner interaction potential should be appropriate. The main goals of this calculation are to demonstrate that aromatic hydrocarbon molecules with ~ 100 eV of kinetic energy can pick

(23) The expected pseudo-first-order desorption of a surface-equilibrated ion-adsorbate species should produce an exponential decrease in ion signal with time.

(24) A 160-ns delay corresponds to a ~ 5 -Da shift to higher mass.

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up benzene-like species from the surface and to elucidate the reaction mechanism. Our limited set of initial conditions is sufficient to achieve these goals.

To investigate effects of collision energy, a benzene molecule, in both a flat and a side-on configuration, was sent toward the bare, hydrogen-terminated surface. For kinetic energies below 30 eV, the molecule reflected intact. At about 40 eV, the molecule reacted with the surface and stuck. Analogous calculations for a phenanthrene molecule in a flat configuration indicate that it bounces for kinetic energies below 80 eV and reacts at about 90 eV. Note that the transition from bouncing to sticking occurs at total collision energies corresponding to approximately 6 eV per carbon atom. This value is eminently reasonable, given that the C-C bond strength in aromatic hydrocarbon species is ~ 5 eV.

The pickup reactions were simulated by bombarding a benzene molecule lying on the surface with both benzene and phenanthrene molecules with 30–40 and 80–90 eV of kinetic energy, respectively. Both projectile molecules were oriented horizontal to the surface. A sample trajectory for phenanthrene is shown in Figure 3. Initially, the phenanthrene molecule is 7–8 Å above the surface with 80 eV of kinetic energy. At approximately 100 fs, maximum contact with the surface occurs, causing considerable distortion in all the species. A direct reaction (Eley-Rideal mechanism) involving four pairs of C atoms from the two molecules takes place, followed by desorption of the complex from the surface with 17 eV of translational kinetic energy.²⁷ Our calculations do not

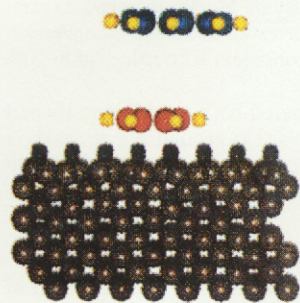
indicate the specific nature of the complex but do show lifetimes greater than 1.6 ps, the duration of our calculations. The reflected complex has 12 eV of internal energy, which is sufficient for subsequent rearrangement¹⁴ or loss of H₂ as observed experimentally. The energy deposition corresponds to a 15% conversion of translational to internal energy, consistent with values of 8–20% measured by Cooks⁵ for SID.

In conclusion, we have demonstrated both experimentally and via molecular dynamics calculations that aromatic hydrocarbon molecules with energies on the order of tens of electron volts can pick up large, surface-adsorbed species. Our calculations indicate these reactions occur in less than 100 fs, clearly indicating an Eley-Rideal mechanism.

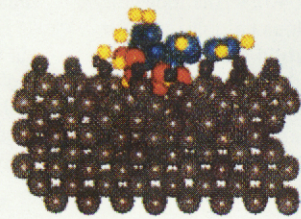
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Registry No. (C₁₄H₁₀)⁺⁺, 34504-68-2; (C₁₀H₈)⁺⁺, 34512-27-1; benzene, 71-43-2.

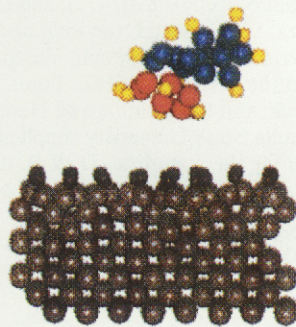
(27) The interaction potential used for these calculations does not include the van der Waals interaction that exists between the benzene molecule and the H-terminated diamond surface. Because the complex desorbs with 17 eV of kinetic energy, this approximation should not significantly alter our results.



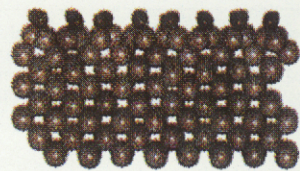
0.0 ps



0.1 ps



0.3 ps



1.0 ps