

## Gas–Surface Chemical Reactions at High Collision Energies?

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**Abstract:** Most gas–surface chemical reactions occur via reaction of adsorbed species to form a thermal-energy ( $\sim kT$ ) product; however, some instances exist where an energetic projectile directly reacts with an adsorbate in a single-collision event to form a hyperthermal product (with a kinetic energy of a few eV). Here we show for the first time that 30–300 eV  $F^+$  bombardment of fluorinated Ag and Si surfaces produces “ultrafast”  $F_2^-$  products with exit energies of up to 90 eV via a multistep direct-reaction mechanism. Experiments conclusively show that the projectile F atom ends up in the fast molecular product despite the fact that the impact energy is far greater than typical bond energies.

### Introduction

Gas–surface reactions typically proceed via the Langmuir–Hinshelwood mechanism, where atoms or molecules adsorb onto a surface, diffuse around, and subsequently react to form a product molecule that leaves the surface (desorbs) at thermal energies ( $\sim kT$ ).<sup>1</sup> However, another class of reactions exists where an adsorbate directly reacts with an impinging gas molecule (or energetic projectile) through a collision-based mechanism to form a “fast” product—the so-called Eley–Rideal (ER) mechanism.<sup>2–6</sup> ER products are distinct because they are frequently excited (rotation–vibration) and tend to leave the surface at hyperthermal energies (up to a few eV) in specific directions that correlate with the incoming projectile geometry.<sup>7</sup> Our current understanding of ER reactions, from the perspective of detailed collision dynamics and energy transfer, is largely qualitative. Most observations suggest that a translationally hot product can be generated in two limiting situations: (i) a light atom strikes a heavy adsorbate, becoming trapped in the attractive well of the heavy-atom recoil as it leaves the surface or (ii) a heavy projectile scatters off the surface and abstracts (“scoops up”) a lighter atom on the outgoing trajectory path. Therefore, ER products would seem to form in single-collision events only when (i) the partners are mismatched in mass and (ii) the post-collision kinetic energy of each fragment that makes up the product molecule must be less than typical bond energies (otherwise the product molecule would not remain intact as it leaves the surface). As such, ER reactions should not occur at

high impact energies. Here, we present experimental evidence and theoretical support for a new class of ER reactions at high impact energies (up to 300 eV) that involve equal-mass partners and multiple collision events and form “ultrafast” products (up to 90 eV) that surprisingly remain intact after leaving the surface.

Specifically, we have used  $F^+$  projectiles (30–300 eV), which undergo ER abstraction of F atoms from fluorinated Ag and Si surfaces, to form  $F_2^-$  products with substantial kinetic energies (up to  $\sim 90$  eV). Energy analysis of  $F_2^-$  leaving the surface reveals two distinct exit channels: one low-energy component attributed to sputtering and another higher-energy component that directly correlates with the  $F^+$  incident energy. The fast- $F_2^-$ -exit component *only* occurs for  $F^+$  bombardment, indicating that the product must contain the projectile F atom. Molecular dynamics also predicts fast- $F_2^-$  formation *at the observed experimental energy* through a direct-collision sequence that results in two F species in close proximity leaving the surface with large, yet comparable, exit velocities.

Experimental evidence for ER mechanisms can take several forms:<sup>2</sup> (i) nonthermal translational energies of products, (ii) product energies that depend on the projectile energy (i.e., momentum memory), (iii) rotationally and/or vibrationally excited products, and (iv) product distributions that depend on impact geometry or peak at off-normal angles. Documented examples of ER mechanisms usually involve projectiles at “low” collision energies accessible by molecular-beam methods.<sup>8</sup> Notable examples include D- and Cl-atom abstraction by H atoms from D/Cu(111),<sup>9</sup> Cl/Au(111),<sup>10</sup> and D/Si(100)<sup>11</sup> as well as proton “pickup” from Pt(111) by  $N(C_2H_4)_3N$ .<sup>12</sup> Other studies with low-energy ion beams ( $< 50$  eV) have demonstrated direct abstraction of protons from pyridine-covered Ag(111) (pyridine

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- (1) Weinberg, W. H. *Dynamics of Gas–Surface Interactions*; Rettner, C. T., Ashford, M. N. R., Eds.; Royal Society of Chemistry: London, 1991.
- (2) Maazouz, M.; Barstis, T. L. O.; Maazouz, P. L.; Jacobs, D. C. *Phys. Rev. Lett.* **2000**, *84*, 1331.
- (3) Kratzer, P. *J. Chem. Phys.* **1997**, *106*, 6752.
- (4) Dinger, A.; Lutterloh, C.; Kuppers, J. *Chem. Phys. Lett.* **1999**, *311*, 202.
- (5) Kim, J. Y.; Lee, J. *Phys. Rev. Lett.* **1999**, *82*, 1325.
- (6) Yi, S. I.; Weinberg, W. H. *Surf. Sci.* **1998**, *415*, 274.
- (7) Rettner, C. T.; Auerbach, D. J. *Science* **1994**, *263*, 365.

(8) Rettner, C. T.; Auerbach, D. J.; Tully, J. C.; Kleyn, A. W. *J. Phys. Chem.* **1996**, *100*, 13021.

(9) Rettner, C. T.; Auerbach, D. J.; Lee, J. *J. Chem. Phys.* **1996**, *105*, 10115.

(10) Rettner, C. T. *J. Chem. Phys.* **1994**, *101*, 1529.

(11) Buntin, S. A. *J. Chem. Phys.* **1998**, *108*, 1601.

(12) Kuipers, E. W.; Vardi, A.; Danon, A.; Amirav, A. *Phys. Rev. Lett.* **1991**, *66*, 116.

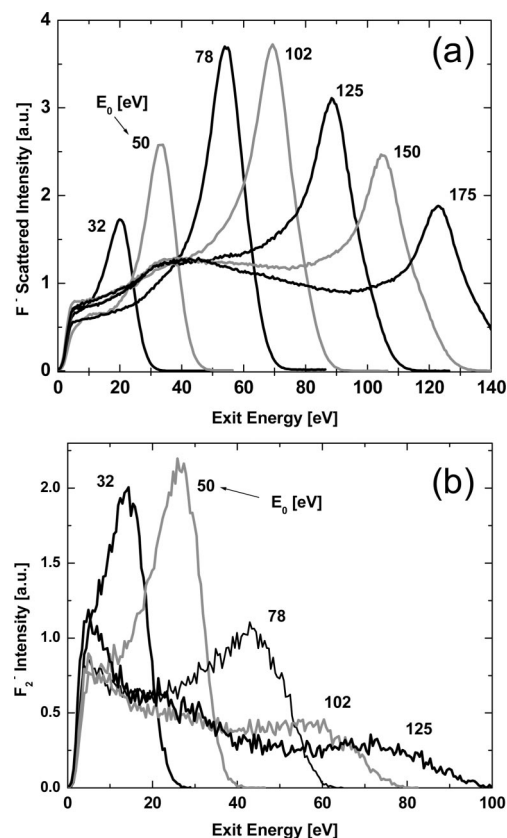
projectiles);<sup>13,14</sup> H, F, CH<sub>3</sub>, and C<sub>2</sub>H<sub>3</sub> groups from self-assembled monolayers by pyrazine and pyrene;<sup>15</sup> O from Ag(111) by NO<sup>+</sup>,<sup>2</sup> and CO and CO<sub>2</sub> from Pt(111) by Cs<sup>+</sup>.<sup>16</sup> Energetic O<sup>+</sup> (10–60 eV) has also been shown to remove O atoms from oxidized Si to form fast O<sub>2</sub><sup>-</sup> (~8 eV).<sup>17</sup> In all of these cases, product energies are comparable to or a few times greater than the bond energy; this situation is understandable because the relative kinetic energy of the fragments that make up the final molecule cannot be greater than typical bond energies. In fact, a single collision event, when it occurs at high energy, can never result in a scattered projectile and recoil with small relative kinetic energies (i.e., relative to the center-of-mass of the product molecule). To date, no ER mechanisms that result in highly energetic products (> 10 eV) have been observed. The reason may be found in the collision cascade: when the collision energy is raised, gas–surface reactions transition into hard-sphere scattering processes in which the projectile cascade sputters atoms and clusters from the surface.<sup>18</sup> At such energies, chemical “reactions” per se become secondary compared to momentum-driven sputtering processes; direct reactions (even if they occur through multiple collisions) are simply washed out. However, we show here that direct reactions do occur at high impact energies, yielding highly energetic (10–100 eV) products; furthermore, these experiments suggest that ultrafast products should be formed in many other collision systems.

## Experimental Section

Scattering experiments were conducted in a custom-built, low-energy ion scattering system that has been described elsewhere.<sup>19</sup> Briefly, the system utilizes an inductively coupled plasma (ICP)-source, high-voltage beamline (20 keV) with a 60° magnetic mass filter and deceleration optics to deliver high fluxes of isotopically pure species at low energies (20–1500 ± 2 eV fwhm) onto a grounded target under UHV conditions. The ion-beam energy and spatial profile were characterized with a 180° electrostatic sector and 2D wire sensor at the target position. For F<sup>+</sup> and <sup>22</sup>Ne<sup>+</sup> beams, the ICP was run at 2 mTorr/600 W with pure Ne or CF<sub>4</sub>/O<sub>2</sub> mixes. Scattered species were analyzed with a triply differentially pumped detector system with an electrostatic sector and quadrupole mass filter to measure the energy distribution and charge state of each species leaving the target. Experiments were conducted at a laboratory angle  $\theta_L = 90^\circ$  in specular reflection with beam currents in the 1–10  $\mu$ A range over 2 mm. Product spectra were recorded under steady-state scattering conditions at room temperature; all of the samples were sputter-cleaned with 5 keV Ar<sup>+</sup>, and the target surface could be flooded with XeF<sub>2</sub> gas through a doser pipe situated ~1 cm from the surface.

## Results and Discussion

Typical spectra for F<sup>-</sup> and F<sub>2</sub><sup>-</sup> leaving an Ag surface under F<sup>+</sup> bombardment at various projectile energies ( $E_0 = 30$ –175 eV) are shown in Figure 1a,b, respectively. Intensities were normalized by beam current and scattering cross section (F<sup>-</sup> data only) for an F + Ag collision at  $\theta_L = 90^\circ$  using the



**Figure 1.** Energy distributions of (a) F<sup>-</sup> and (b) F<sub>2</sub><sup>-</sup> leaving the surface when Ag is bombarded with F<sup>+</sup> projectiles at various energies (shown as  $E_0$ ) for  $\theta_L = 90^\circ$ .

Thomas–Fermi–Molière (TFM) potential.<sup>20,21</sup> Several trends in the data are worth noting: (i) F<sub>2</sub><sup>-</sup> is produced, (ii) two distinct peaks can be seen for both F<sup>-</sup> and F<sub>2</sub><sup>-</sup>, (iii) the low-energy peak (~10 eV) for each ion appears to be invariant with projectile energy (reminiscent of cascade sputtering<sup>18</sup>), and (iv) the high-energy F<sup>-</sup> and F<sub>2</sub><sup>-</sup> peaks shift upward as the impact energy is increased. The charge-exchange picture of F scattering in this case is efficient Auger or resonant neutralization of the projectile on the incoming path and hard collision (which may lead to F\*, F<sup>+</sup>, or F<sup>-</sup>) followed by electron capture (or detachment) on the outgoing path. Copious F<sup>-</sup> is not unexpected because the anion level of F shifts<sup>22</sup> well below the Fermi level of the target as a result of image-charge effects when  $R_{\min} < 4 \text{ \AA}$ . The intensity of negative ions leaving the target surface (relative to that of F<sup>+</sup>) was quite large (>2–3 orders of magnitude) for all impact energies. In general, the F<sup>-</sup> yield (total negative ions) goes through a maximum. This behavior is due to perpendicular velocity effects<sup>23</sup> at low  $E_{\text{exit}}$  (i.e., more anions survive because of shorter contact time on the outgoing path) and cross-section/subplantation<sup>24</sup> effects at higher  $E_0$  (i.e., the projectile preferentially scatters forward and/or penetrates deeper into the target, so the 90° flux is lower).

(13) Wu, Q.; Hanley, L. J. *Phys. Chem.* **1993**, *97*, 8021.

(14) Wu, Q.; Hanley, L. J. *Phys. Chem.* **1993**, *97*, 2677.

(15) Morris, M. R.; Riederer, D. E.; Winger, B. E.; Cooks, R. G.; Ast, T.; Chidsey, C. E. D. *Int. J. Mass Spectrom. Ion Processes* **1992**, *122*, 181.

(16) Kim, J. H.; Lahaye, R. J. W. E.; Kang, H. *Surf. Sci.* **2007**, *601*, 434.

(17) Quinteros, C. L.; Tzvetkov, T.; Jacobs, D. C. *J. Chem. Phys.* **2000**, *113*, 5119.

(18) Sigmund, P. *Phys. Rev.* **1969**, *184*, 383. Thompson, M. W. *Phil. Mag.* **1968**, *18*, 377.

(19) Gordon, M. J.; Giapis, K. P. *Rev. Sci. Instrum.* **2005**, *76*, 083302.

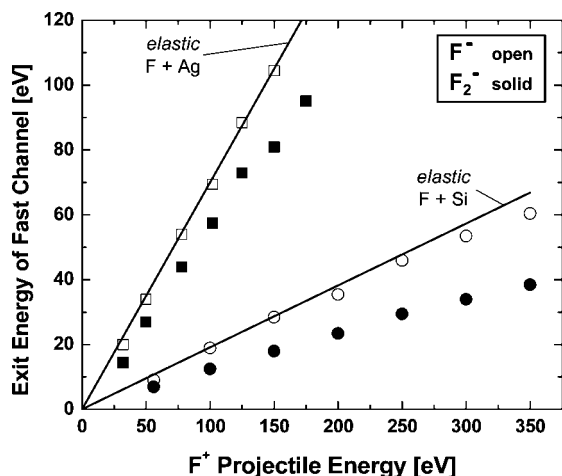
(20) Gordon, M. J.; Mace, J.; Giapis, K. P. *Phys. Rev. A* **2005**, *72*, 012904.

(21) Mace, J.; Gordon, M. J.; Giapis, K. P. *Phys. Rev. Lett.* **2006**, *97*, 257603.

(22) Ustaze, S.; Guillemot, L.; Esaulov, V. A.; Nordlander, P.; Langreth, D. C. *Surf. Sci.* **1998**, *415*, L1027.

(23) Maazouz, M.; Guillemot, L.; Esaulov, V. A. *Phys. Rev. B* **1997**, *56*, 9267.

(24) Rabalais, J. W. *Principles and Applications of Ion Scattering Spectrometry: Surface Chemical and Structural Analysis*; John Wiley and Sons: Hoboken, NJ, 2003.

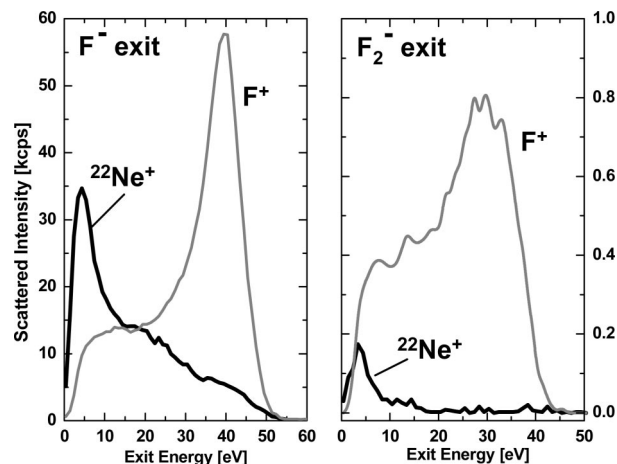


**Figure 2.** Exit energies of fast  $F^-$  and  $F_2^-$  off Ag and Si along with binary elastic predictions for  $F + Ag$  and  $F + Si$  at  $\theta_L = 90^\circ$ .

Although yield data are informative, energy distributions of species leaving the target are more useful in determining the actual scattering mechanism. For instance, both  $F^-$  and  $F_2^-$  leaving the surface have well-defined, high-energy peaks that appear to scale with the incoming projectile energy. These peak locations are summarized in Figure 2, along with the elastic prediction<sup>20,21</sup> for a single-scatter  $F + Ag$  or  $F + Si$  collision giving a  $90^\circ$  exit. As shown, the fast- $F^-$  exit is in excellent agreement with elastic binary collision theory; similar results for  $F^+$  exits off the same surfaces have been shown previously.<sup>21</sup>

However, the most notable feature in the data is the *highly nonthermal*  $F_2^-$ , which is suggestive of a direct (ER) mechanism. This peak could originate from (i) “sputtering” of  $F_2$  off the surface by the projectile cascade or (ii) ER-like abstraction (i.e., the projectile F atom ends up in the fast- $F_2^-$  exit via direct or scattering-mediated abstraction of a surface-bound F). Process (i) can be eliminated on several grounds. The high exit energy ( $\gg$  surface binding energy), the shift in the distribution maximum with  $E_0$ , and the lack of a high-energy tail are all contrary to standard sputtering theories and experiment.<sup>18</sup> Thus, it seems that direct reaction [process (ii)] could be responsible for the fast  $F_2^-$ . To test this hypothesis further, the target was flooded with  $XeF_2$  gas from a doser pipe during  $F^+$  or  $^{22}Ne^+$  bombardment. In these experiments, the scattering chamber pressure was increased from  $<10^{-9}$  to  $7 \times 10^{-7}$  Torr by leaking in  $XeF_2$  to saturate the target surface with fluorine. We specifically chose  $^{22}Ne^+$  projectiles instead of  $^{20}Ne^+$  to remove all possibilities of  $^{20}Ne^+$  contamination in the  $F^+$  beam or “false counting” of mass 20 when the quadrupole in the scattered-product detector was set to mass 19.

Figure 3 summarizes typical ion-energy distribution functions for the  $XeF_2$  dosing experiments for a 60 eV projectile. It can be clearly seen that fast  $F_2^-$  is absent for the  $^{22}Ne^+$  projectile case. The data also show that (i)  $F^+$  and  $^{22}Ne^+$  generate similar amounts of low-energy sputtered  $F^-$  when the surface is fluorinated, (ii) more low-energy  $F^-$  is generated when the surface is flooded with thermal F (i.e.,  $XeF_2$  dosing) than for  $F^+$  projectiles alone, and (iii) small amounts of  $F_2^-$  at low energy (3–5 eV) are sputtered from the surface by  $^{22}Ne^+$ . All of these trends make sense with respect to increased sputtering due to higher surface fluorination, sputtering that is projectile-insensitive (only momentum is at play), and production of fast  $F_2^-$  via an ER mechanism. This experiment eliminates the possibility of scattering-mediated abstraction,<sup>17</sup> where the incoming pro-



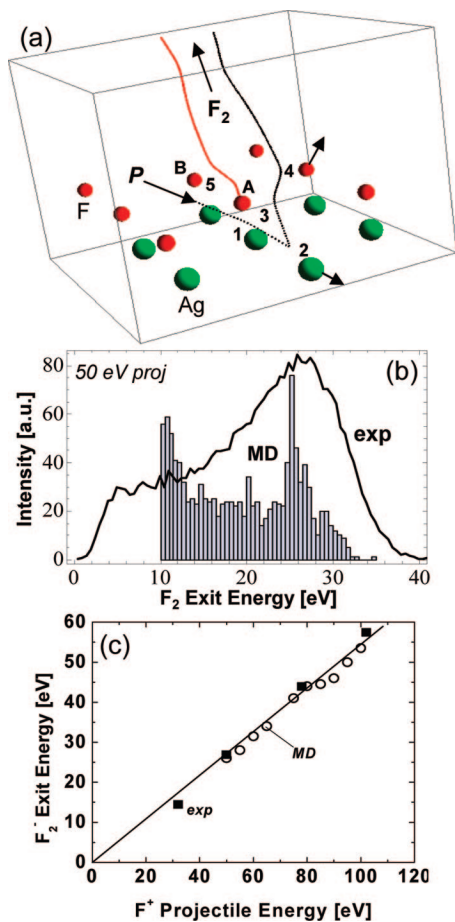
**Figure 3.**  $F^-$  and  $F_2^-$  product energy distribution functions for  $F^+$  and  $^{22}Ne^+$  projectiles when an Ag surface is flooded with thermal  $XeF_2$ .

jectile creates an F recoil that directly “scoops up” another F on the outgoing path. Such a mechanism should be operable for both  $F^+$  and  $^{22}Ne^+$  projectiles; however, this is not seen. By the process of elimination, it appears that fast  $F_2^-$  is formed through an ER-type direct reaction where the projectile F atom ends up in the  $F_2^-$  exit.

Additional support for a direct mechanism comes from molecular dynamics (MD) simulations.<sup>25</sup> Figure 4a shows a trajectory “history” that generates a fast, vibrationally excited  $F_2$  exit when F hits a fluorinated Ag surface at 50 eV. Fast  $F_2$  is made via five steps: (i) projectile **P** (black) hits F atom **A**, after which **P** forward-scatters and **A** recoils (red); (ii) **P** collides hard with an Ag atom and scatters at  $\sim 95\text{--}100^\circ$ ; (iii) **P** nudges the moving F atom **A** again; (iv) **P** deflects off another F, leaving the surface; and (v) the moving F atom **A** nudges another surface F atom **B** and leaves with a velocity vector similar to that of **P**. The two exiting F atoms combine and leave the surface in a vibrationally hot state (the trajectory oscillation should be noted: further timesteps clearly show the  $F_2$  vibration). This collision sequence is clearly direct (Eley–Rideal), retains a considerable portion of the projectile momentum (i.e., **P** hits its final partner two times), and the resulting  $F_2$  molecule contains the projectile F atom. The role of the surface in this case is to act as a kinematic mediator that enables the fast- $F_2$  channel by preparing the trajectory and energy of the projectile and its final partner. For the case shown (and similar direct sequences), the  $F_2$  final energy falls in the 24–28 eV range for a 50 eV projectile.

When all of the MD trajectories resulting in  $F_2$  are binned according to the final  $F_2$  energy (Figure 4b), a large peak near 26 eV is seen, exactly matching that measured in our experiments. The fast- $F_2$  peak width difference between the experimental and MD results is easily explained by the finite-energy width of the  $F^+$  projectile beam in the experiment ( $50 \pm 2$  eV

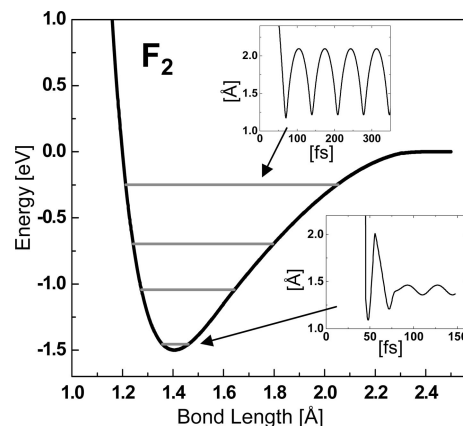
(25) MD was carried out using a superposition of modified Morse–Molière potentials for  $F + F$  and  $F + Ag$ . At each  $E_0$ ,  $10^7$  primaries were launched at the F-on-Ag target [one F and two Ag(111) layers] with  $45^\circ$  incidence versus the surface normal, random impact parameter, and random azimuth. The cascade was followed until all species had kinetic energies of  $<10$  eV. An “intact”  $F_2$  was defined as  $E_{tot}^{F_2} = K_{tot}^{F_2} + U_{tot}^{F_2} < 0$ , where  $K_{tot}^{F_2}$  is the kinetic energy of  $F_2$  in the center-of-mass system and  $U_{tot}^{F_2}$  is the potential energy. Total energies for F and  $F_2$  from density-functional theory (DFT) calculations were  $-99.7208$  and  $-199.4968$  hartree, respectively; the optimized bond length for  $F_2$  was found to be 2.6549 bohr. See the Supporting Information for details.



**Figure 4.** Fast  $F_2$  formation. (a) MD trajectory history for a 50 eV  $F^+$  projectile (P; black line) reacting directly with a fluorinated Ag surface to generate  $F_2$  at a high exit energy (27 eV). See the text for the collision sequence. (b) Experimental  $F_2^-$  exit energy (solid) and MD (histogram) results for  $F_2$  leaving the surface for 50 eV incident F (see ref 25). (c) Fast- $F_2^-$  peak location for various  $F^+$  impact energies on fluorinated Ag: (solid) experimental and (open) MD results. The solid line is to guide the eye only.

fw)hm). Differences at low  $F_2$  exit energies are related to electron detachment from  $F_2^-$  at low exit velocities, i.e., a slow  $F_2^-$  leaving the surface easily loses its electron back to the surface and is not seen in the experiment (i.e., perpendicular velocity effects). As added evidence, the fast  $F_2$  peak from MD calculations was tallied for different impact energies; Figure 4c demonstrates that this “direct” collision sequence from MD agrees extremely well with experiment. We should mention that a scattering-mediated abstraction reaction (i.e., projectile F hits a surface F, which then “scoops up” another F on the exit) was found via MD; however, this collision sequence was eliminated given that the negative control experiment with  $^{22}\text{Ne}^+$  and  $\text{XeF}_2$  on Ag (see Figure 3) did not give fast  $F_2^-$ .

Finally, it is worth commenting on the intensity of scattered  $F_2^-$  as a function of  $F^+$  impact energy. The decreasing  $F_2^-$  yield at high  $E_0$  results from increased vibrational excitation of ER-created  $F_2^-$ , leading to autodetachment<sup>17</sup> (in which case the  $F_2$  neutral would not be seen), or complete dissociation of vibrationally hot  $F_2^{0/-}$ . The MD results for fast exits consistently



**Figure 5.** Vibrational excitation of fast  $F_2$  leaving a fluorinated Ag surface for 50 eV  $F^+$  impact, as determined from MD. The potential energy curve and associated vibrational levels (classical) of four different exits are shown. The insets show the  $F_2$  bond length vs time for two specific fast- $F_2$  exits.

show rotation and vibration in the  $F_2$  product. For instance, Figure 5 gives a summary of the results for four vibrationally excited fast  $F_2$  molecules leaving the surface for 50 eV  $F^+$  impact as a result of direct reactions similar to that shown in Figure 4a. The insets show the F–F bond length of the final  $F_2$  product as a function of the collision time; short times (<50–100 fs), where the bond length is physically impossible (>2.1–2.2 Å), are associated with the projectile approach to the surface and “pre-molecule-formation” collisions (see Figure 4a). These classical trajectory calculations predict a wide range of vibrational excitation in the  $F_2$  product, all the way up to the dissociation limit. In addition, the anharmonicity in the potential energy curve near the dissociation threshold becomes apparent in the temporal variation of the F–F bond length (Figure 5, upper inset). Although the potential energy curve changes when the  $F_2$  becomes an anion, it is highly probable that the fast  $F_2^-$  product is vibrationally excited.

## Conclusion

In summary, we have shown that Eley–Rideal abstraction involving  $F^+$  projectiles and fluorinated Ag and Si surfaces can occur at high impact energies (30–300 eV), resulting in hyperthermal  $F_2^-$  ions leaving the surface at energies of tens of electron volts. Energy analysis of the  $F_2^-$  products as well as bombardment of externally fluorinated surfaces with  $^{22}\text{Ne}^+$  rather than  $F^+$  shows that  $F^+$  projectiles are required for fast- $F_2^-$  formation. MD results also show that a direct-reaction sequence involving multiple collisions can form an  $F_2$  product with a high translational energy that correlates exactly with experiment.

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**Supporting Information Available:** Details of MD and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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