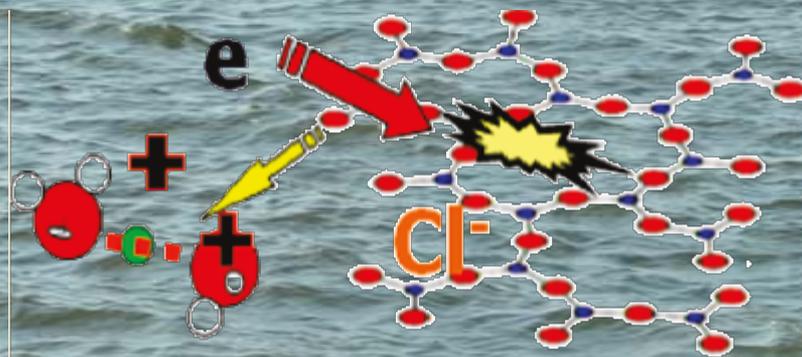


Probing the Interaction of Hydrogen Chloride with Low-Temperature Water Ice Surfaces Using Thermal and Electron-Stimulated Desorption

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Introduction:

1. Heterogeneous processes play an important role in the chemistry occurring in the atmospheric polar regions since many reactions are relatively slow or forbidden in the gas phase.
2. The reactions $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$ and $\text{HCl} + \text{HOCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$ are thought to occur on PSCs.
4. Cl_2 (g) can photodissociate to form Cl atoms which can trigger ozone layer depletion.
3. An important initial step is to determine whether reactants such as HCl are present in ionized or solvated forms versus chemisorbed molecular states.
4. Several studies on the interaction of adsorbates like HCl on low temperature ices ultrahigh vacuum conditions have been done. Kang *et al.* used reactive ion scattering (RIS) and low energy secondary ion mass spectrometry (SIMS) to measure the extent of ionization with temperature and found mostly molecular HCl below 70 K, a mixture of the ionized and molecular forms of HCl from 90 to 120 K, and complete ionization above 140 K.
5. Electron stimulated desorption (ESD) is an extremely sensitive surface specific probe that has been used to study the near-surface structure of ice.
6. In this paper, **the previous and present studies have been expanded in more details concerning the interactions of low concentrations of HCl with low-temperature porous amorphous solid water (PASW), amorphous solid water (ASW), and crystalline ice (CI) surfaces.**

7. Previous studies revealed that (i) the ESD cation yields from PASW,^{*} ASW,[‡] and CI[†] ice as a function of HCl coverage (ii) isotope exchange data from D₂O ices demonstrating HCl autoionization (iii) proton kinetic energy distributions that reflect HCl induced changes in the dangling bond sites, and (iv) TPD measurements demonstrating thermally activated HCl ionization on low-temperature ice.

^{*}PASW – Porous amorphous solid water (80 K)

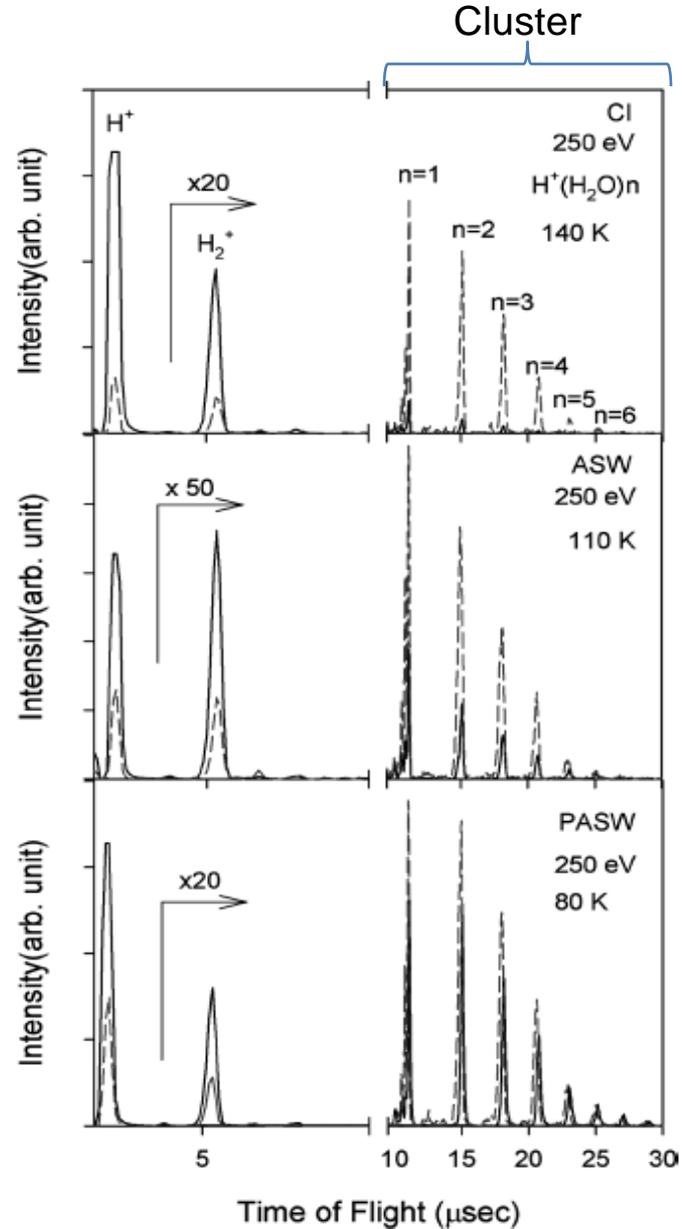
[‡]ASW – Amorphous solid water (110 K)

[†]CI – Crystalline water (140 K)

Experimental:

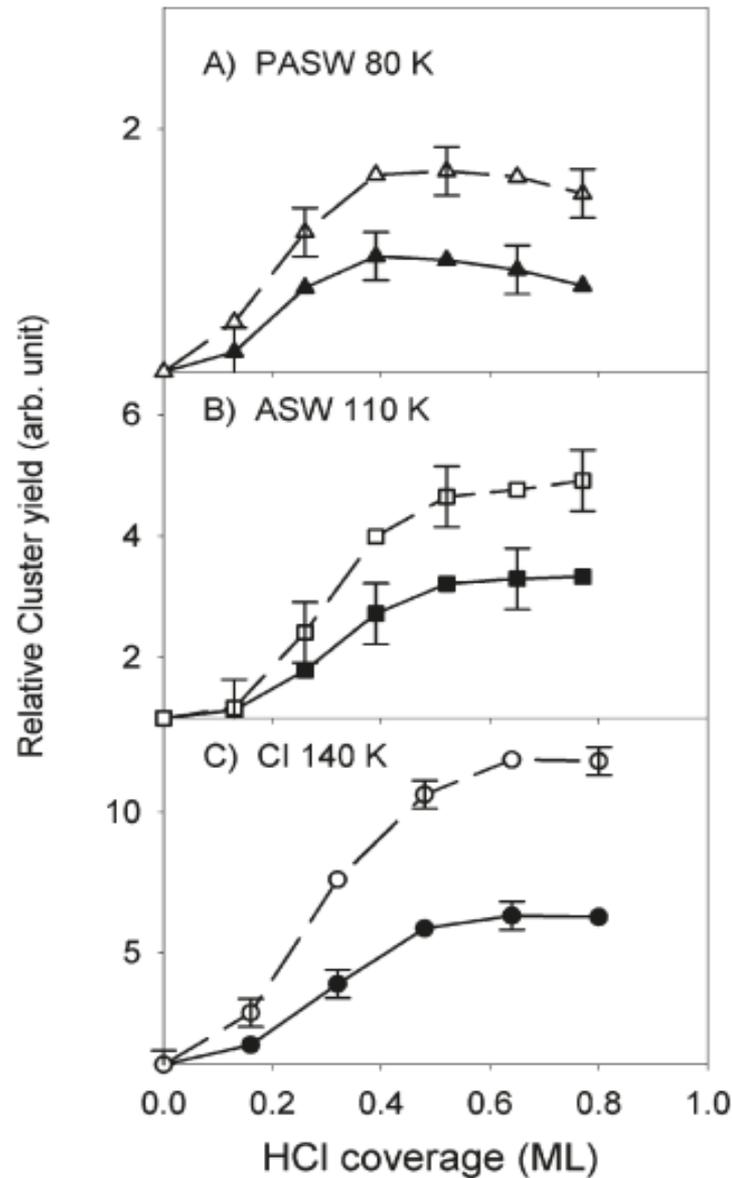
1. The system consists of an ultrahigh vacuum (UHV) chamber with a typical base pressure of 2×10^{-10} torr equipped with a pulsed low-energy electron beam, a quadrupole mass spectrometer (QMS), a time-of-flight (TOF) mass spectrometer, and a cryogenically cooled sample mount.
2. The substrate was a zirconia sample that could be varied in temperature from 80 to 600 K and rotated to face any port in the UHV chamber.
3. The pulsed electron gun was at a 45° incident angle relative to the sample substrate normal and the electron beam energy could be varied from 5 to 250 eV.
4. The electron flux density during a single 200 ns pulse was typically $6 \times 10^{11} \text{ s}^{-1} \text{ cm}^{-2}$.

Results:



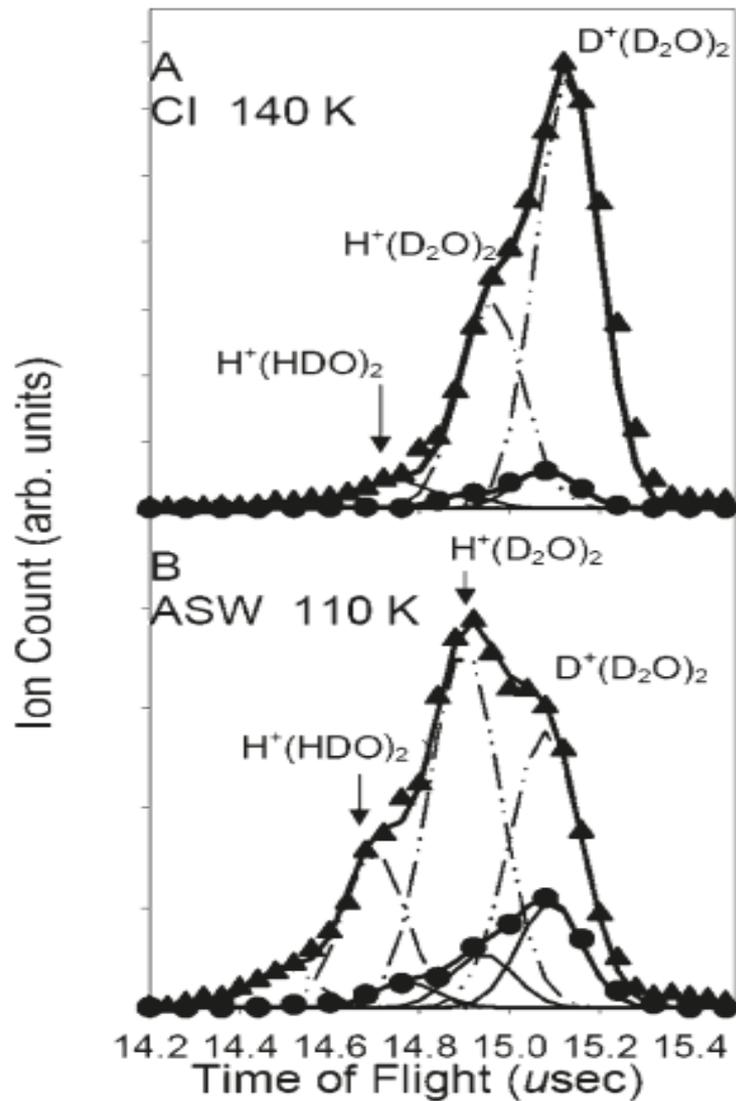
The random orientation of the surface water molecules leads to a low proton yield for PASW

Cations produced and desorbed during 250 eV electron impact of pure (solid line) and HCl (dashed gray line) dosed PASW (bottom panel), ASW (middle panel), and CI (top panel).



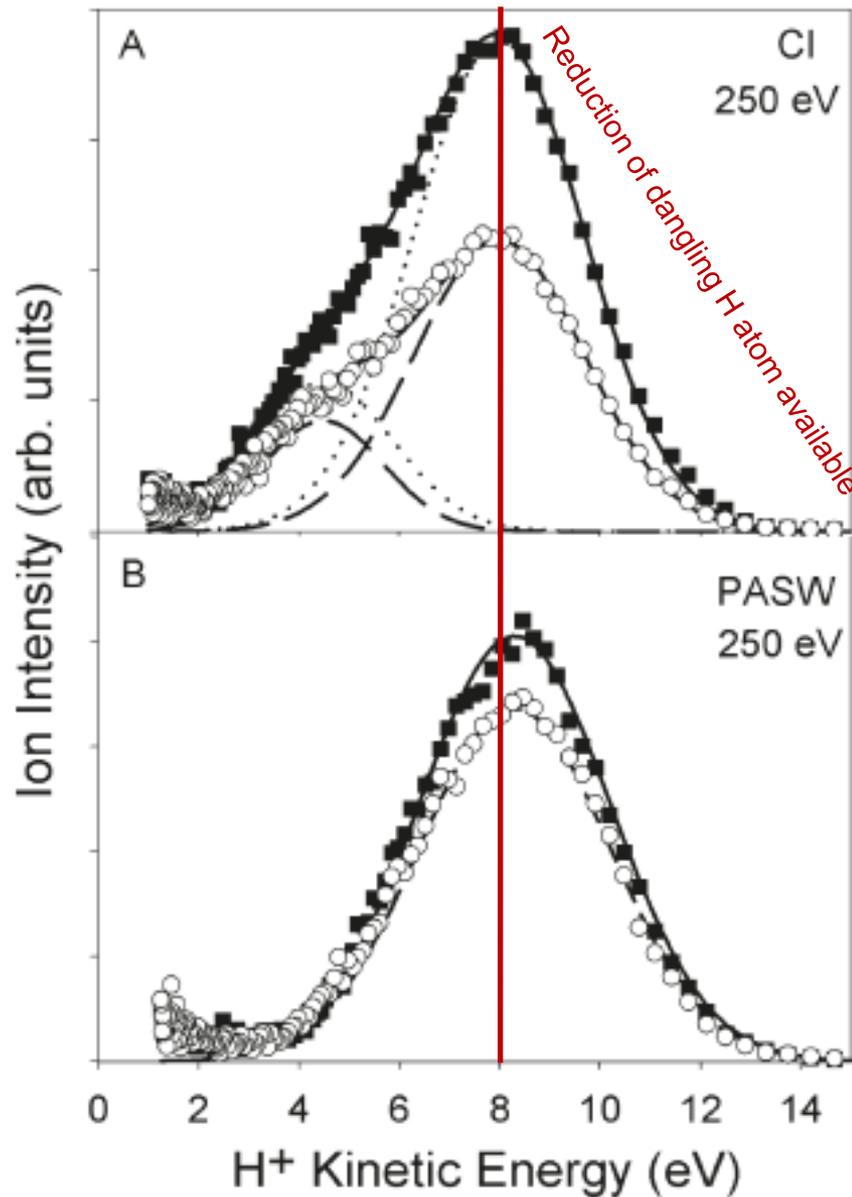
PASW has the highest overall cluster yield

Relative increase in cluster yield with HCl coverage for $H^+(H_2O)$ (filled symbols) and $H^+(H_2O)_2$ (open symbols) for (A) PASW, (B) ASW, and (C) Cl.



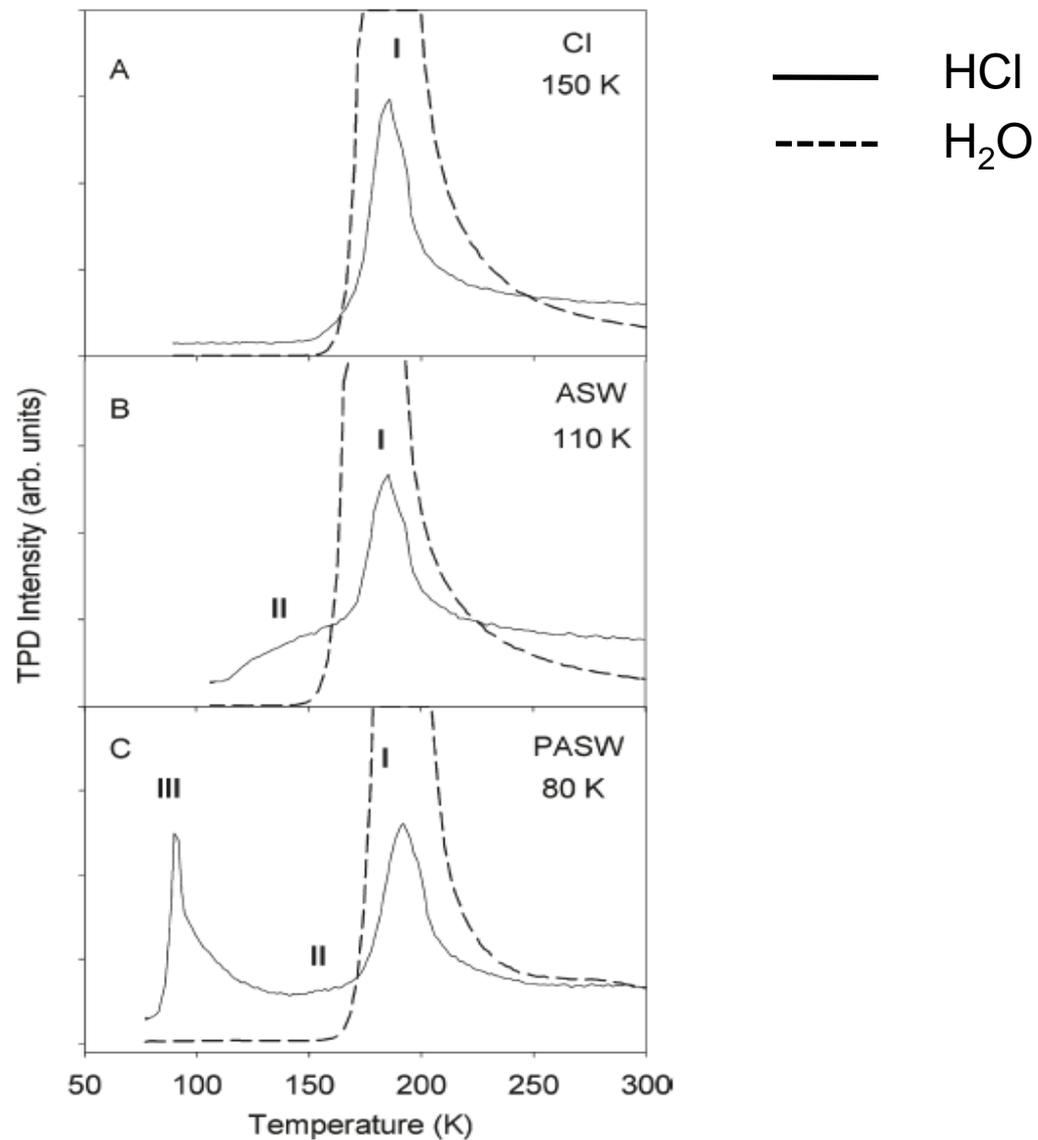
TOF spectra of the protonated water dimer produced during pulsed 250 eV electron bombardment of D_2O ice (50 ML) containing 0.8 ML of HCl dosed at 85 K. The data points for pure ice and HCl dosed ice are shown as circles and triangles, respectively.

No shift for HCl dosing, surface is not charging



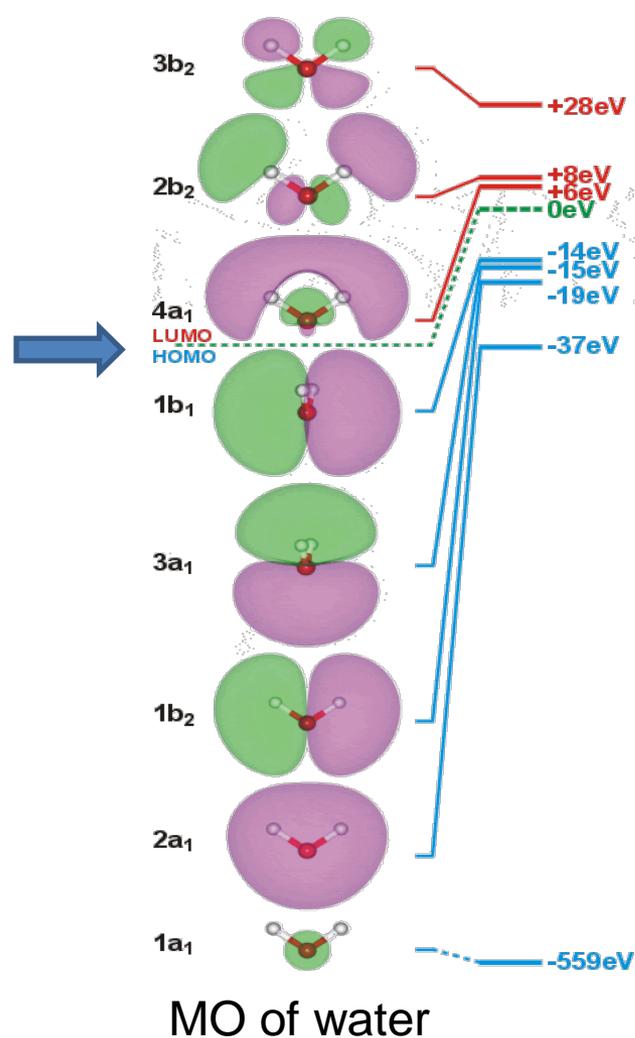
Jacobian transformation, $I(\mathbf{E}) = I(t)t^3/(mL^2)$
I = intensity, t = time, m = mass of the ion, L = length of the flight path

H⁺ kinetic energy distribution from pristine (squares) and HCl dosed (circles)
(A) CI and (B) ASW ice samples collected under field-free conditions.



Temperature programmed desorption spectra of HCl dosed (0.5 ML) on ice at (A) 150 K, (B) 110 K, and (C) 80 K on Cl, ASW, and PASW, respectively.

Discussion:



H⁺ is produced from two hole or 2 hole one electron mechanism.

The primary valence configurations $(3a_1)^{-1}(1b_1)^{-1}(4a_1)^1$ and $(3a_1)^{-2}(4a_1)^1$ are known to produce protons with kinetic energy ranging from 0 and 4 eV. The $(1b_1)^{-2}(4a_1)^1$ configurations produce protons with kinetic energy between 4 and 7 eV while the two-hole $(2a_1)^{-2}$ states leads to the formation of fast protons with kinetic energy greater than 7 eV.

1. Production of $\text{H}^+(\text{H}_2\text{O})_n$ involves this two hole mechanism and Coulomb explosion in the neighboring H_2O molecule.
2. ~ 25 eV threshold energy is required to produce $\text{H}^+(\text{H}_2\text{O})$ from the surface. The mechanism is either intermolecular Coulomb decay or reactive ion scattering.
3. Due to the lack of an ordered hydrogen bonding network in PASW, the holes can localize and are less likely to hop to a screening distance (1-2 nm) before a Coulomb explosion occurs.
4. Above phenomena occurs in the terminal 1-3 water layers of PASW.
5. Upon increase of temp. pore collapses and proton can hop more distance and hence reduces the cluster yield.
6. The addition of HCl decreases the proton yield by reducing the number of dangling hydrogen atoms available. This reduction is due to the formation of a solvation shell around the Cl^- .
7. The activation energy of the ionized HCl desorption feature (I) (slide 8) was found to be 43 ± 2 kJ/mol using the Polanyi-Wigner equation and assuming second-order kinetics and a normal prefactor of $10^{13} \text{ ML}^{-1} \text{ s}^{-1}$.
8. The nature of peak II in slide 8 suggests some interaction of the HCl with either the water ice or the ionized HCl species that seems to remain on or near the ice surface.
9. The lowest temperature peak (III) is most likely physisorbed HCl which is only weakly interacting with the surface.

Conclusion :

1. The surface of the ice becomes disordered as HCl autoionizes and forms contact ion pairs, leading to reduced numbers of dangling bonds at the surface and increased hole localization.
2. The increase in the cluster yield with HCl results from the disorder present at the surface of the ice.

A photograph of a scorpion on a light-colored, textured surface. The scorpion is dark brown or black, with its pincers (pedipalps) raised. The text "Thank you" is overlaid in white, serif font in the center of the image.

Thank you

Polanyi-Wigner equation

$$r_{des} = -\frac{d\Theta}{dt} = v_n \cdot \exp\left(-\frac{\Delta E_{des}^{PW}}{RT}\right) \cdot \Theta^n$$

Further extension:

1. Instead of e^- , fire low energy $^3\text{H}^+$ or $^{14}\text{CH}_x^+$. Those are slow β^- emitters. This can trigger new chemical reaction apart from ion scattering.
2. Charged projectile can initiate chemical reaction given an energy < 5 eV. Since electron is reducing agent we can think of preparing very active nanoparticles inside vacuum chambers at low temperature. Preparing alkali or alkaline earth metal nanoparticle is nearly impossible right now at standard condition but at low temp. and pressure it may be possible.