Reactive ion scattering from ice in a molecular dynamics perspective

R.J.W.E. Lahaye

Department of Physics, Sungkyunkwan University, Suwon, 440-746, South Korea

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ABSTRACT

This is a study into the scattering dynamics of the alkaline ions Cs^+, K^+, Na^+, and Li^+ from an ice surface, and the process of abstracting water molecules by the scattered ions to form ion–water clusters as a result of the ion–dipole attraction. In a classical molecular dynamics computer simulation a semi-empirical ion–water interaction potential and a modified version of the TIP3P ice model are employed.

The thickness of the ice structure at the surface greatly affects the abstraction efficiency. From a thin ice overlayer all alkaline ions exhibit similar scattering probabilities, but Cs^+ abstracts water molecules most efficiently; its lower speed facilitates a mechanism where the Cs^+ in its outgoing trajectory pulls water molecules out of the ice structure. From a thick ice structure the scattering probabilities decrease dramatically due to an effective energy transfer to the ice structure. A more grazing angle of incidence reduces the energy transfer and enhances the scattering probabilities for the lighter alkaline ions. The deprived formation of ion–water clusters in the simulations confirms that from thick ice the cluster formation probability is reduced by at least three orders of magnitude.

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1. Introduction

Reactive ion scattering (RIS) is a surface detection technique, which is designed to identify neutral species on surfaces [1–7] and is able to monitor real time dynamics [8,9]. A beam of Cs^+ ion projectiles at low incidence energies (10–100 eV) prevents unwanted damage to the surface and the adsorbed species. After the collision with the surface, the scattered ions can pick up neutral species (X) from the surface to form Cs^+–X clusters as a result of the ion–dipole attraction; a subsequent mass selective detection of the scattered charged clusters allows an accurate determination of the surface species. Because the alkaline ion has a closed shell electron configuration, it is chemically inert. Therefore processes such as charge transfer are negligible and the interaction with the surface and adsorbates is of physical nature.

Research on ice surfaces has gained increasing attention over the past few decades. In higher atmospheric regions ice particles are considered to be an important catalyst of chemical reactions, which are of vital interest to biological systems on Earth; the atmospheric conditions depend for a great part on the existence of ice at high altitudes and in the polar regions, and minute changes have alarming effects on the environmental balance of the atmosphere [10–14]. Recent findings back up a theory that the early development of life has happened in ice or at ice interfaces [15,16]. Ice grains in interstellar regions are of interest to processes which are involved in the formation of protoplanetary disks in dense molecular clouds [17–21].

New challenges arose when ice surfaces became the target of investigation by Cs^+–RIS [3,4,6,22]. The preparation of ice interfaces and ice surfaces under laboratory conditions permits Cs^+–RIS as a probe for characterizing the chemical properties of microscopic ice particles similar to those in polar, stratospheric, and even interstellar regions [23]. Because the ice surface is rather soft and the Cs^+ ion is relatively heavy, surface damage [24] and RIS detection sensitivity are of major concern. Also, the scattering dynamics depends much on the ice thickness, as the flux of scattered ions drops by several orders of magnitude when increasing the thickness of the adsorbed ice overlayers [4]. Nevertheless, experimental results have indicated that these complications do not jeopardize the qualities of Cs^+–RIS as a valuable detection technique for ice surfaces [23,25].

Theoretical studies have unravelled essential parts of the RIS scattering dynamics, in particular for Cs^+ scattered from metal surfaces [26,27]. In brief, the Cs^+–adsorbate cluster formation is most efficient when the projectile scatters away from the surface at a low enough velocity, so that the adsorbate can be dragged along in the outgoing trajectory. The theoretical analysis brought forward novel features, such as the dependence of the abstraction efficiency on the masses of both the adsorbate and projectile. The scattering dynamics from the soft ice structure, however, is too different for simply extrapolating conclusions.

In present work I have modeled the RIS scattering dynamics of alkaline ions from an ice surface and weighed the merits of Cs^+ ions against K^+, Na^+, and Li^+ as projectile ions. I have employed a classical molecular dynamics simulation, using empirical potentials for the ion–water and for the water–water interactions. Both thick and thin crystalline I_h ice are modelled, where this refers to the relevance of the underlying substrate on which the ice is grown; unlike for thin ice, for

E-mail address: lahaye@skku.edu.

Table 1
Values of the potential parameters for the water–water interaction of the TIP3P model, for the intramolecular water potential, and for the alkaline ion–water interaction. Units are in Ångström and electronvolts, e is the elementary charge.

TIP3P		H$_2$O		Alkaline$^+$-H$_2$O	
q_O	$-0.834e$	R	0.9572	A	5000.0
q_H	$+0.417e$	Θ	104.52	α_{Cs}	3.3322
D	$6.597 \cdot 10^{-3}$	E_s	$459.55 \cdot 10^{-3}$	α_K	3.9598
ρ	3.5364	E_b	$197.7 \cdot 10^{-3}$	α_{Na}	4.6059
$\frac{e^2}{4\pi\varepsilon_0}$	14.4			α_{Li}	5.1597

thick ice a solid substrate underneath the ice layers has no effect on the surface scattering dynamics. For the scattering dynamics in current work thin ice implies a single bilayer of water molecules supported by a rigid solid, whereas two bilayers are sufficient to simulate thick ice.

2. Computational method

The model for the scattering from ice is derived from the existing TIP3P model, which facilitates the conditions for the ice structure. In the next paragraphs I discuss the modifications to this model to accommodate for the ion scattering dynamics in the hyperthermal energy regime (1–50 eV) and introduce a semi-empirical alkaline ion–water potential.

2.1. Ice model

The TIP3P model for crystalline I$_h$ ice has been presented and studied by Jorgensen et al. [28]. The water molecules interact with one another via a Coulomb potential between the electric charges at each of the three atoms in the molecule, and a Lennard-Jones type potential between the oxygen atoms. The water–water interaction potential is given in Eq. (1), in which q_i, q_j, and r_{ij} are the charges of, and distances between the atoms in two water molecules. The Lennard-Jones potential between two oxygen atoms has a well-depth D at equilibrium distance ρ. Table 1 lists the values of all parameters.

$$V = \sum_{i,j \in \{H_2O\}} \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} + D\left[\left(\frac{\rho}{r_{OO}}\right)^{12} - 2\left(\frac{\rho}{r_{OO}}\right)^6\right] \tag{1}$$

The range of the water–water potential is reduced by multiplying the potentials in Eq. (1) with the switching function [29] of Eq. (2). For $x = 2(r - 9.5)$, this function and its derivatives smoothly drop to zero for r between 9.5 and 10 Å.

$$f(x) = \begin{cases} 0 & x > 1 \\ (1-x)^3 \left(1 + 3x + 6x^2\right) & 0 < x < 1 \\ 1 & x < 0 \end{cases} \tag{2}$$

Ice models generally apply periodic boundary conditions to simulate infinite dimensions [30–33]. In case of scattering at hyperthermal energies, a single projectile would cause periodic impact effects on the ice surface, which is undesirable. Instead, the surface of our ice slab has a large enough area of *active* water molecules, embedded in a structure of *rigid* water molecules. Fig. 1 shows such an ice structure with two bilayers of active molecules. The rigid molecules never move from their equilibrium positions, as if they have an infinite mass. These fixed molecules provide the long range potential field for the active molecules, cut off by the switching function of Eq. (2).

The original TIP3P model treats water molecules as rigid bodies, which requires non-trivial techniques in solving the equations of motion, such as a self-consistent evolution of the rotation-quaternions at each time step [34]. I have streamlined the numerical procedure by adding OH-stretching and HOH-bending degrees of freedom to the active water molecules, taking for granted a somewhat higher demand on computational resources. The interaction potentials for the internal
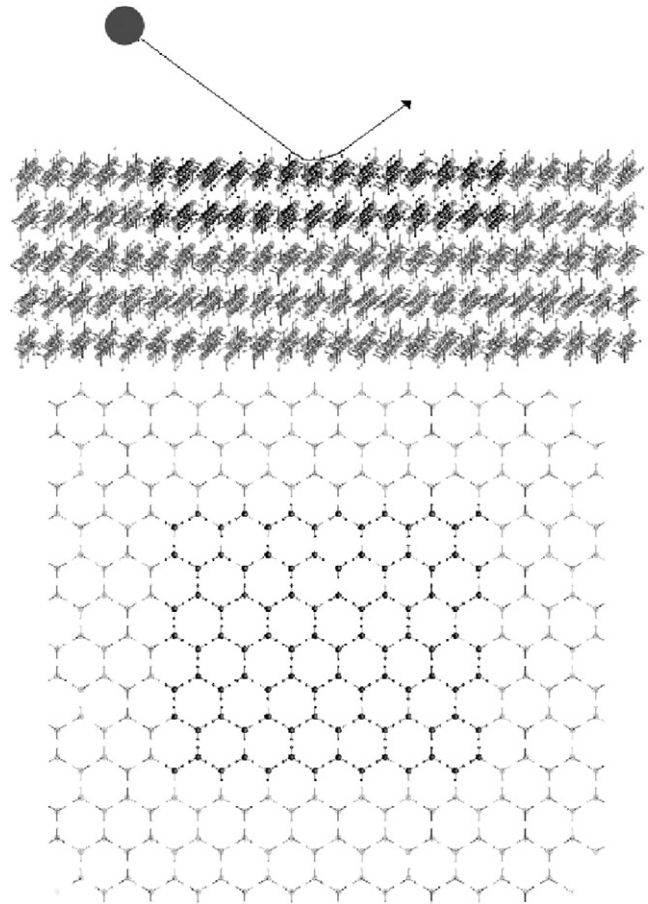

Fig. 1. A side view of the ice structure with an artistic impression of a scattering trajectory (upper panel) and a top view of the ice structure (lower panel). The active water molecules are black and the fixed water molecules light-gray. This example has two active bilayers of water molecules, with 196 (14×14) molecules in each active bilayer. Three bilayers of fixed molecules are underneath and five rows at each side.

motions maintain the geometry of the water molecule without affecting the overall dynamics [35]. Harmonic potentials in Eq. (3) are adequate as an approximation of the internal degrees of freedom. The potential parameters are extracted from the energies of the normal vibrational modes in an isolated water molecule [36]. The parameters k_s, k_b, E_s, and E_b are the harmonic constants and energies of the OH-stretching and HOH-bending motions, R is the hydrogen-oxygen equilibrium distance, Θ is the equilibrium angle between the two hydrogens with respect to the oxygen, and M represents the masses of the oxygen and hydrogen, according to the subscripts. The values of R and Θ are taken from the water molecule in the TIP3P model. The harmonic potentials were verified by a Fourier analysis of the vibrations in the substrate: the molecule's center of mass vibrates at frequencies between 1 and 5 THz, whereas the intramolecular vibrations are in a higher frequency domain between 15 and 30 THz, similar to observations in experiments [37–39].

$$V_{OH}(r) = \frac{1}{2} k_s (r - R)^2$$

$$k_s = \frac{M_O M_H}{M_O + M_H} (E_s / \hbar)^2$$

$$V_{HOH}(\theta) = \frac{1}{2} k_b R^2 (\theta - \Theta)^2 \tag{3}$$

$$k_b = \frac{1}{2} \frac{M_O M_H}{M_O + M_H(1 - \cos\Theta)} (E_b / \hbar)^2$$