What Determines the Sticking Probability of Water Molecules on Ice?

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We present both experimental and theoretical studies of the sticking of water molecules on ice. The sticking probability is unity over a wide range in energy (0.5 eV–1.5 eV) when the molecules are incident along the surface normal, but drops as the angle increases at high incident energy. This is explained in terms of the strong orientational dependence of the interaction of the molecule with the surface and the time required for the reorientation of the molecule. The sticking probability is found to scale with the component of the incident velocity in the plane of the surface, unlike the commonly assumed normal or total energy scaling.

The adsorption of molecules on the surfaces of solids is an important step in many processes, in particular, crystal growth and catalysis. A molecule that collides with a surface of a crystal can get trapped if it loses enough of its kinetic energy to the lattice and thereby becomes attached to the surface. If the energy transfer is not fast enough, the molecule will be reflected back into the gas phase. The probability that the molecule gets attached to the surface is an important parameter in the modeling of various phenomena. An important example is the modeling of polar stratospheric clouds where the predicted formation temperature, size, and lifetime of ice particles is strongly sensitive to the value assumed for the probability that impinging water molecules get incorporated into the ice lattice [1].

In order for a molecule not to be reflected after colliding with a solid surface, it needs to lose the energy associated with the component of momentum normal to the surface, $p_\perp$. Therefore, it would appear that the sticking probability would be greater the smaller $p_\perp$ is. It is, therefore, commonly assumed that the sticking coefficient, S_0, scales with "normal energy"; i.e., various values of the incident energy and angle give a sticking coefficient that maps onto a single curve when plotted as a function of the energy associated with the normal component of the momentum $E_k \cos^2\theta$ where E_k is the kinetic energy and θ is the angle between the direction of incidence and the normal to the surface [see, for example, [2]]. For fixed incident kinetic energy, the sticking probability then increases as the incoming direction of the molecules is moved away from the surface normal. Normal energy scaling has been observed in several systems, but deviations from that behavior have also frequently been seen and are typically expressed as $E_k \cos^n\theta$ where n is less than 2. When the surface is highly corrugated, that is, when there is a large variation of the potential energy as the incident molecule is moved along the surface, the conversion between parallel and perpendicular components of the momentum occurs readily and the sticking probability then scales with the total incident kinetic energy, that is, n becomes zero. Most systems exhibit behavior that can be expressed by an intermediate value of n, that is, the scaling of the sticking coefficient is somewhere in between normal and total energy scaling [3]. The sticking coefficient is usually thought to increase with θ, possibly slower than given by normal energy scaling and, in the limit of total energy scaling, becomes independent of θ.

Some systems have been observed to have a different variation of the sticking coefficient with θ, namely, a *decrease* in S_0 as θ is increased. This includes experimental measurements of ethane on Si(100) [4], Cl_2 on Cl-covered GaAs(110) [5], CO on Ni(100) [6], and Xe [7], ethane [8], and propane [9] on the highly corrugated Pt(110)-(2×1) surface, as well as modeling of CO on Cu(100) [10] and HCl on ice [11]. In some cases this kind of behavior has been described by a negative power of $\cos\theta$ [10] or a linear combination of $\cos^2\theta$ and $\sin^2\theta$ [4,5,9].

Unlike the cases listed above, we report here on studies of a one component system—water molecules sticking on ice. In such a system there is no mismatch in the interaction between the incident molecule and the surface on one hand and the interaction between the molecules within the solid on the other hand. Also, there is no mass difference between the incident molecule and those in the solid, so the momentum transfer efficiency is optimal. After noticing a decrease of the sticking probability at large incident angle in simulations of ice growth, we decided to make a combined theoretical and experimental study of the sticking probability over a wide range in incident energy and angle. The sticking coefficient is found to scale well with only the incident momentum component *along* the surface. That is, molecules with the same velocity along the surface but quite different velocity normal to the surface have roughly the same probability of sticking. The explanation for this

behavior appears to be a strong variation of the molecule-surface interaction energy as the molecule rotates, leading to scattering into the vapor phase if the molecule does not have enough time to adjust its orientation as it moves along the surface.

The experiments were performed in a molecular beam-surface scattering apparatus described in detail previously [12,13]. Crystalline and amorphous ice films were deposited on a 10 mm diameter Pt(111) single crystal using a 300 K quasieffusive H_2O beam that overfilled the Pt(111) sample. The phase (crystalline versus amorphous) of the ice film was determined using a combination of temperature programmed desorption and infrared spectroscopy [14,15]. The sticking measurements were performed by measuring the angle-integrated reflected flux mass spectrometrically using the technique of King and Wells [12,16,17]. A supersonic molecular beam of H_2O is produced by expanding a $\sim 2\%$ mixture of H_2O vapor seeded in ~ 1 atm H_2 through a 100 μm diameter circular orifice. The kinetic energy of the supersonic H_2O beam was varied between ~ 0.5 and 1.5 eV by heating (300–1000 K) the nozzle. These expansion conditions produce relatively narrow ($\Delta E/E \sim 0.2$) energy distributions as determined via standard time-of-flight techniques [18,19]. The resulting H_2O beam has a diameter of ~ 2 mm at the target enabling the incident angle to be varied between 0 and 75 degrees without overfilling the ice film. For the experiments reported here the crystalline ice film temperature was held at 20 K during the sticking measurements. A limited number of experiments were also performed on amorphous ice films, and at higher substrate temperature. The measured H_2O sticking coefficient was found to be

independent of ice film phase, thickness (25 and 100 bilayers), and film temperature (20 K $<$ T $<$ 120 K).

Figure 1 shows the measured sticking coefficient as a function of the incident angle for two values of the incident kinetic energy, 0.5 eV and 1.5 eV. At the lower energy value, the sticking coefficient is unity, within experimental error, for the full range in incident angle but at the higher energy there is a clear drop as the angle is increased beyond ca. 30 degrees. This behavior is clearly very different from normal or total energy scaling (or anything in between those limits). As shown in Fig. 2, the sticking probability is found to scale with the component of the incident velocity that lies in the surface plane, perpendicular to the surface normal.

Also shown in Figs. 1 and 2 are the results of computer simulations of a water molecule impinging on a slab representing the flat, basal plane of hexagonal ice. The simulations are based on classical dynamics [the velocity VERLET algorithm [20]] and make use of a simple pairwise additive interaction potential function for rigid water molecules, the TIP4P potential [21]. The TIP4P potential is known to reproduce quite well the properties of ice. The surface is stable and does not reconstruct, in agreement with He-atom scattering studies [22]. The TIP4P potential has previously been used to study surface premelting of ice [23] and the binding and diffusion of admolecules on the ice Ih surface [24]. It is important to emphasize that a pairwise additive potential function can only give a rough
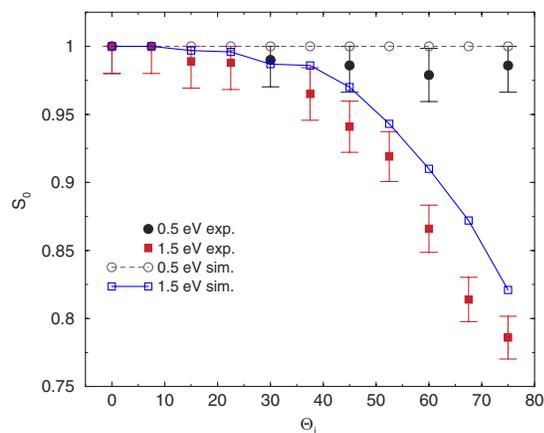

FIG. 1 (color online). Measured and calculated sticking coefficient as a function of incident angle at two different values of the incident kinetic energy. The filled circles and boxes show the experimental results for 0.5 eV and 1.5 eV, respectively. The open circles and boxes show the corresponding results of classical dynamics calculations. At high energy, the sticking coefficient decreases with incident angle, opposite to the commonly assumed normal energy scaling.
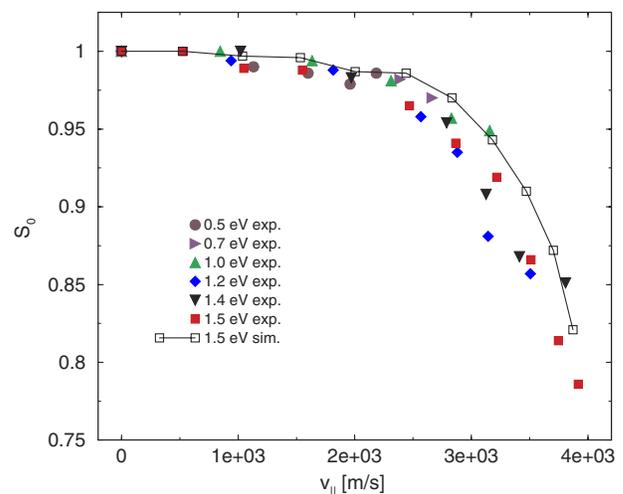

FIG. 2 (color online). Experimental and theoretical results on the sticking probability of a water molecule impinging on an ice surface as a function of the incident velocity component that lies in the surface plane. The incident energy ranged from 0.5 eV to 1.5 eV and incident angle from 0 to 75 degrees. The drop in the sticking probability at large incident energy and angle is found to scale well with the component of the incident velocity in the plane of the surface. The error bars (omitted for clarity) in the experimental measurements are estimated to be ± 0.02. The apparent scatter in the experimental data lies within this uncertainty.

approximation to the intermolecular interaction, particularly at surfaces since the environment is quite different from the liquid for which the potential function was developed. As an example, the molecular dipole moment of water molecules in ice has been estimated from an induction model to be 3.1 D, while the molecular dipole moment of a TIP4P molecule is 2.2 D [25]. However, we believe the TIP4P potential gives a good enough estimate of the intermolecular interactions for the purpose of the present study as the good agreement between experiment and simulation shown in Figs. 1 and 2 indicates.

The simulated slab consisted of 4 bilayers each containing 32 molecules. The molecules in the lowest bilayer were not allowed to move. In order to make the sampling of trajectories for molecules incident on the ice surface more manageable, we have assumed the protons are ordered in an antiferroelectric structure [24]. This leads to a small surface unit cell which can be sampled reasonably well with a few hundred trajectories. Our experiments show that the sticking coefficient is independent of the ice phase (amorphous versus crystalline) so it is probably not necessary to reproduce the surface structure in detail. After the basic parameters of the incident molecules had been specified, such as translational energy, incident angle, and rotational temperature, the initial conditions for the trajectories were generated with a random number generator. The classical trajectory of the incident molecule and the movable molecules in the ice slab were calculated for a time period of 3 ps [20]. At the end of each trajectory, a decision was made as to whether adsorption or reflection from the surface had occurred based on the position of the molecule and its velocity. In order to obtain good statistics, a total of ca. 1000 trajectories were run for each set of incident kinetic energy and angle.

Given the simplicity of the model (the TIP4P potential and antiferroelectric surface), the agreement between theory and experiment is quite good. The reason for the drop in the sticking coefficient at large incident angle and energy results from a strong variation in the molecule-surface interaction as a function of both the lateral position and the orientation of the incident water molecule. This is illustrated in Figs. 3 and 4. There are two stable sites on the antiferroelectric surface, sites A and B, as shown in Fig. 3 [see also [24]]. In the first site, only one of the three close water molecules in the surface layer has a H atom pointing up. The admolecule points its H atoms towards the other two. In the second site, two of the close water molecules have a H atom pointing up and the admolecule points one of its H atoms towards a surface molecule and the other one points away from the surface. The orientation of the admolecule in the two sites is, therefore, quite different. A minimum energy path, calculated using the nudged elastic band method [26], between the two sites is shown in Fig. 3. The molecule needs to reorient as it moves along the path. The energy barrier is rather low, 0.27 eV, which, together with a prefactor of 10^{12} s^{-1} [24], is consistent with an
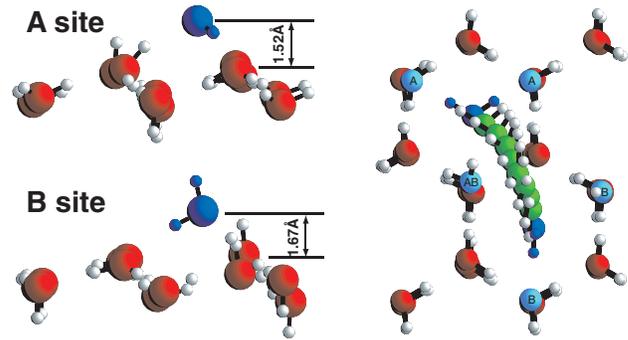

FIG. 3 (color).   Left: side view of the two types of binding sites for a water admolecule (shown in blue) on the surface of antiferroelectric ice, the A and B sites. In the former the admolecule points both of its H atoms towards the surface. In the B site one points towards the surface and the other points away from the surface. Right: on-top view of the minimum energy path between the two sites. The three underlying water molecules are shown in light blue and marked with the site type.

upper bound obtained from experiments [27]. If, however, the molecule is brought from the A site to the location of the B site without reorientation, a large repulsive interaction will tend to push the molecule from the surface, as shown in Fig. 4. If the orientation which is optimal for an
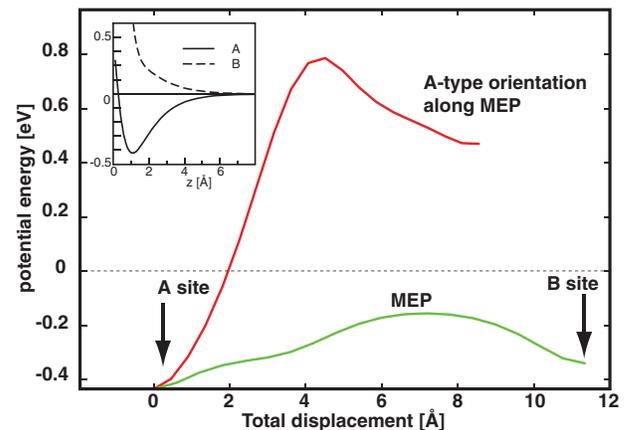

FIG. 4 (color online).   An illustration of the variation of the molecule-surface interaction energy as the H_2O molecule moves from one site to another on the ice surface. The lower energy curve shows the energy along the minimum energy path (MEP) between the A and B sites as a function of the total displacement of all the atoms in the system. The higher energy curve shows the variation in the potential energy as the O atom of the admolecule moves in the same way as in the minimum energy path, but the orientation of the molecule remains fixed as in the A site. This results in a large repulsive barrier. The variation of the potential energy with the distance of the admolecule from the surface is shown in the inset. Here, the orientation of the molecule is fixed at the one giving minimum energy at the A site. If the molecule is brought to the B site with that orientation, the interaction with the surface is purely repulsive. A molecule that does not have time to reorient as it moves from one site to another will, therefore, be subject to a large repulsive interaction with the surface.

admolecule at the A site is maintained as the molecule is brought to the B site, there is a purely repulsive interaction with the surface. A similar but lower repulsive barrier (~0.5 eV) is obtained along the path from an A site to another A site. It is, therefore, essential for the molecule to be able to change orientation as it moves along the surface.

At normal incidence the incoming molecule has time to orient itself as it approaches the surface into the optimal orientation for the site upon which it is impinging. Analysis of the trajectories for normal incidence show that the molecule most likely adsorbs at the site closest to impact. But, at glancing incidence and high incident energy, the molecule is moving fast along the surface and the torque is changing from one location above the surface to another. If the molecule is moving fast enough, it does not have sufficient time to reorient and experiences a repulsive interaction with the surface. We have estimated the time needed for the molecule to reorient by placing a molecule at random above the surface and then carried out classical dynamics calculation until it has gained the right orientation. The average time for reorientation turned out to be about 0.4 ps. The distance between sites on the surface is ca. 3 Å so the velocity at which the molecule does not have sufficient time to reorient is estimated to be on the order of 10^3 m/s. This is in good agreement with the onset of the drop in the sticking coefficient shown in Fig. 2.

In other systems, for example, CO sticking on metal surfaces and ethane sticking on silicon, this orientational corrugation is also important, but the situation is complicated by the fact that in those cases the sticking coefficient is dropping with energy even at normal incidence because of inefficient energy transfer. Here, the orientational effect becomes clearer because of the efficient energy transfer to the lattice which results in an energy independent sticking coefficient near unity at normal incidence. The deviation from unit sticking probability at large energy and angle arises predominantly from the orientational corrugation.

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