Chemical Desorption versus Energy Dissipation: Insights from Ab Initio Molecular Dynamics of HCO● Formation

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Abstract

Molecular clouds are the cold regions of the Milky Way where stars form. They are enriched by rather complex molecules. Many of these molecules are believed to be synthesized on the icy surfaces of the interstellar submicron-sized dust grains that permeate the Galaxy. At 10 K thermal desorption is inefficient and, therefore, why these molecules are found in the cold gas has tantalized astronomers for years. The assumption of the current models, called chemical desorption, is that the molecule formation energy released by the chemical reactions at the grain surface is partially absorbed by the grain and the remaining energy causes the ejection of the newly formed molecules into the gas. Here we report accurate ab initio molecular dynamics simulations aimed at studying the fate of the energy released by the first reaction of the H₂O addition chain to CO, H₂ + CO → HCO, occurring on a crystalline ice surface model. We show that about 90% of the HCO formation energy is injected toward the ice in the first picosecond, leaving HCO- with an energy content (10–15 kJ mol⁻¹) of less than half its binding energy (30 kJ mol⁻¹). As a result, in agreement with laboratory experiments, we conclude that chemical desorption is inefficient for this specific system, namely H₂ + CO on crystalline ice. We suspect this behavior to be quite general when dealing with hydrogen bonds, which are responsible for both the cohesive energy of the ice mantles and the interaction with adsorbates, as HCO-, even though ad hoc simulations are needed to draw specific conclusions on other systems.

Unified Astronomy Thesaurus concepts: Astrochemistry (75); Pre-biotic astrochemistry (2079); Interstellar dust processes (838); Solid matter physics (2090)

Supporting material: tar.gz file

1. Introduction

To date, more than 200 types of molecules have been detected in the interstellar medium (ISM) (e.g., McGuire 2018). Of these, all molecules with more than five atoms contain carbon. These are the so-called interstellar complex organic molecules (iCOMs; Herbst & van Dishoeck 2009; Ceccarelli et al. 2017). iCOMs are most commonly observed in galactic star-forming regions (e.g., Rubin et al. 1971; Blake et al. 1986; Cazaux et al. 2003; Belloche et al. 2017; Leffoch et al. 2017; Bianchi et al. 2019) and external galaxies (e.g., Muller et al. 2013; Sewilo et al. 2018). Besides these, iCOMs are also detected toward cold (∼10 K) sources (e.g., Bacmann et al. 2012; Cernicharo et al. 2012; Vastel et al. 2014; Jiménez-Serra et al. 2016). These latter detections are important for (at least) two reasons: first, they challenge the idea that iCOMs are synthesized on lukewarm (30–40 K) grain surfaces by radical–radical combination (Garrod & Herbst 2006; Öberg et al. 2009; Ruaud et al. 2015), and, second, if for whatever reason they are formed on grain surfaces, the mechanism that lifts them off into the gas (where they are detected) must be nonthermal. Different nonthermal mechanisms have been invoked in the literature to explain the presence of gaseous iCOMs in cold environments: cosmic-ray spot heating (Léger et al. 1985; Hasegawa & Herbst 1993) or sputtering (e.g., Dartois et al. 2019); UV-induced photodesorption (e.g., Dominik et al. 2005; Fayolle et al. 2011; Bertin et al. 2013, 2016), codesorption of ices (e.g., Sandford & Allamandola 1988; Ligterink et al. 2018), and chemical (or reactive) desorption (Duley & Williams 1993; Garrod et al. 2007; Minissale & Dulieu 2014; Minissale et al. 2016).

Here, we focus on the last mechanism, the chemical desorption (CD). The underlying idea is that the energy released by strongly exothermic chemical reactions occurring on grain surfaces is only partly absorbed by the grains, while the remaining energy is used to break the bonds between the newly formed species and the surfaces, so that a fraction of the synthesized species is injected into the gas phase. Therefore, CD and the dissipation of the surface-reaction energy are two sides of the same coin, intrinsically linked.

From an experimental point of view, it is extremely difficult, if not impossible, to quantify the energy dissipation. Overall, laboratory experiments showed that CD can be more or less efficient depending on the adsorbate and the substrate. For example, Oba et al. (2018) found high CD efficiencies (∼60%) for H₂S formation on amorphous solid water. On the contrary, lower CD efficiencies for different systems were observed by other authors: Dulieu et al. (2013) found a CD efficiency for the O₂ + D reaction lower than 10%, He et al. (2017) showed that the H₂O addition to O₂ causes the desorption of the product O₂ by no more than 11%, and Chuang et al. (2018) found a CD
efficiency lower than 2% per hydrogen-atom-induced reaction in the hydrogenation of CO toward methanol. In a systematic study of CD in several reactions on different substrates, Minissale et al. (2016) showed that the CD efficiency does indeed depend on three major factors: the reaction formation energy, the binding energy of the adsorbate, and the nature of the substrate. They proposed a general formalism to estimate the CD probability, based on the idea that the energy dissipation can be approximately treated as an elastic collision.

Theoretical calculations are, in principle, capable of simultaneously studying the energy dissipation and CD. Various techniques have been so far used for different systems. Fredon et al. (2017) and Fredon & Cuppen (2018) simulated the relaxation of translationally excited admolecules (CO2, H2O, and CH4) on crystalline and amorphous ice models, via classical molecular dynamics (MD) simulations. They ran thousands of simulations using approximate interaction potentials where the admolecules were given large (0.5–5 eV, equal to 50–500 kJ mol⁻¹) translational energies in random directions. Therefore, in these studies, all the chemical reaction energy is assumed to be canalized into translational motion of the admolecules and, for this reason, a statistical analysis was necessary to understand the fate of the energy for different injected trajectories. Thus, each simulation follows the evolution of the energy of the species, recording whether the molecule is desorbed, penetrates in the surface, or is adsorbed on the surface. Based on their large number of simulations, Fredon et al. (2017) and Fredon & Cuppen (2018) found that the desorption probability depends on the injected kinetic energy and binding energy of the species. Additionally, they provided a formula to estimate the CD probability, which depends on those two quantities. Despite careful and exhaustive statistical analysis on the simulations, there are some weaknesses to be pointed out: (i) the limits of force-field-based methods in dealing with chemical reactions; (ii) the injected energy of the admolecule which is only translational, while, after a reaction occurs, the energy should be partitioned also into vibrational and rotational levels; (iii) the relatively small size of the used water clusters, whose temperature may rise for high energy injections (~5 eV), thus resulting in an overestimation of the admolecule mobility.

Korchagina et al. (2017) studied the energy dissipation of the hydrogenation reaction of CO (producing HCO⁻) under the Eley–Rideal model at temperatures of 70 K. They used MD simulations at the self-consistent-charge density functional tight binding theory level, which is an approximation of classical density functional theory, based on parameterized integrals and charges. They used small molecular clusters, 1–10 water molecules, to simulate the ice surfaces and showed that the energy released after HCO⁻ formation can be dissipated (i.e., the reaction gives a stable HCO⁻) on clusters with $N \geq 1$ water molecules, and that the product remains adsorbed on the clusters (i.e., no CD) for clusters with $N \geq 3$. Such behavior is linked to the capacity of water to redistribute the reaction energy excess into vibrational excitation. However, such small clusters cannot represent the ice mantle when dynamical effects are taken into account, because, although very small clusters can stabilize the product by absorbing efficiently the nascent energy, the mobility of the molecule is strongly overestimated. Indeed, the cluster’s temperature increase linearly depends on the number of water molecules on the surface model: it should be large enough to be able to harness the reaction energy while restraining the temperature increase.

Kayanuma et al. (2019) studied the reaction of H− with adsorbed HCO⁻ on a graphene surface by means of ab initio molecular dynamics (AIMD) simulations, showing that in the case of HCO⁻ chemisorption (i.e., a chemical bond between the adsorbate and the surface), the products H₂ + CO are desorbed, while in the case of HCO⁻ physisorption (the interaction with the surface is of a dispersive nature), formaldehyde is formed without chemical desorption.

Here we present new AIMD simulations of the reaction H− + CO on a large periodic crystalline water-ice surface assuming the Langmuir–Hinshelwood (LH) mechanism. This reaction is the first step toward the formation of methanol on the grain surfaces, frequently studied both theoretically and experimentally (e.g., Hiraoka et al. 2002; Watanabe & Kouchi 2002; Woon 2002; Watanabe et al. 2007; Andersson et al. 2011; Rimola et al. 2014); therefore, in this context, it can be considered as one of the most important reactions in astrochemical studies. In addition, it is representative of the class of reactions with a relatively low reaction energy (less than 2 eV) needed to dissipate. Our scope is to understand from an atomic point of view how the energy released by the HCO⁻ formation is transferred toward the water surface, without any a priori assumption on how the reaction energy is distributed over the system. We emphasize that our approach is substantially different from the one used by Fredon et al. (2017) and Fredon & Cuppen (2018), described above. In our case, we do not need to address a statistical behavior (depending on the species trajectory), because we simulate the reaction itself and how its energy is dissipated by the formed HCO⁻. This does not depend on the initial H− trajectory because the energy of the H atom is thermal (at 10 K, specifically) and, therefore, negligible with respect to the energy released by the reaction (about 1.4 eV). The result could, in principle, depend on the initial position of the CO on the crystalline ice, for which there are a few possibilities, and we will discuss this point in the article. In summary, our AIMD simulations allow us to quantify whether the newly formed species has enough energy to break its interactions with the water surface and, consequently, to be injected into the gas phase.

Finally, although it is well known that interstellar ice is often amorphous, we chose a crystalline model because tuning the computational setup is easier. Once the system is carefully tested, our future works will focus on amorphous ice models. It is important to notice, however, that crystalline water ice has been detected in the ISM (Molinari et al. 1999) and, particularly relevant for planet formation studies, in proto-planetary disks (Terada & Tokunaga 2012), so therefore our simulations will be directly applicable in those environments.

The article is organized as follows. In Section 2 we present the computational methodology, in Section 3 the results and in Section 4 we discuss these results in view of astrochemical implications. Finally, in Section 5, we summarize the most important conclusions.

## 2. Computational Details

### 2.1. Methods

All the calculations have been carried out with the CP2K package (Goedecker et al. 1996; Lippert et al. 1997; Hartwigsen et al. 1998; VandeVondele & Hutter 2003; VandeVondele et al. 2005; Hutter et al. 2014). The atoms have been treated as follows:
core electrons have been described with the Goedecker–Teter–Hutter pseudopotentials (Goedecker et al. 1996; Hartwigsen et al. 1998), while valence electrons with a mixed Gaussian and plane wave approach (Lippert et al. 1997). The Perdew–Burke–Ernzerhof (PBE) functional has been used for all the calculations (Perdew et al. 1996) combined with a triple-ζ basis set for valence electrons plus two polarization functions (TZV2P). The cutoff for plane waves has been set to 600 Ry. The a posteriori D3 Grimme correction has been applied to the PBE functional to account for dispersion forces (Grimme et al. 2010, 2011). During the optimization procedure, only the H, C, and O atoms (the ones belonging to the HCO-) were free to move, while the atoms belonging to the ice surface have been kept fixed to their thermalized positions. All calculations were carried out within the unrestricted formalism as we deal with open-shell systems. The spin density was checked for reactants, transition state (TS), and product and it always remains well localized either on a H atom (reactant) or on HCO- (product). No spread of spin density through the ice was detected (see Figures A2–A4). The binding energy (BE) of HCO- was calculated according to the following formula:

\[ BE_{\text{HCO}} = (E_{\text{ice}} + E_{\text{HCO}}) - E_{\text{CPLX}} \]  

where \( E_{\text{CPLX}} \) is the energy of the HCO-/ice system, \( E_{\text{ice}} \) that of the bare ice surface, and \( E_{\text{HCO}} \) the energy of the HCO- alone, each one optimized at its own minimum. The \( BE_{\text{HCO}} \) will be used later on for comparison with the residual kinetic energy of the HCO- formation.

In order to reproduce the ISM conditions, the reaction was carried out in the microcanonical ensemble (NVE), where the total energy (i.e., potential + kinetic) is conserved. Moreover, we run an equilibration AIMD in the NVT ensemble (using the canonical sampling through velocity rescaling, CSVR, thermostat, with a time constant of 20 fs) at 10 K for 1 ps (with a timestep of 1 fs) for the bare ice surface to obtain a thermally equilibrated ice. Accordingly, the equilibrated velocities of the ice surface were used as starting ones for the NVE production, while the H and C velocities of HCO- were manually set according to the H–C bond formation. The evolution of the system was followed for 20 ps, using a timestep of 1 fs.

In addition, in the Appendix, we present results obtained from a benchmark study on the reaction of HCO- formation on a small cluster of three H2O molecules (H- + CO/3H2O → HCO/-H2O, see Figure A1), similar to the work by Rimola et al. (2014). The results show that PBE overestimates the energetics of the reaction (132 kJ mol\(^{-1}\) versus 91 kJ mol\(^{-1}\), provided by the CCSD(T) method, see Table A1). By contrast, frequency calculations, which are responsible for the vibrational coupling of the water molecules with the HCO- and, accordingly, of the kinetic energy dissipation efficiency, are in good agreement to those calculated at a higher level of theory (see Table A2).

### 2.2. Ice Model

Ordinary ice is proton disordered and, accordingly, its crystal structure cannot be simply modeled by adopting relatively small unit cells. A possible alternative is to adopt P-ice, a proton-ordered ice already successfully used in the past to simulate ice features (Pisani et al. 1996). P-ice bulk belongs to the Pna2_1 space group, and from the bulk we cut out a slab to simulate the (100) surface, shown in Figure A5. The size of the surface was chosen according to the amount of energy to be dissipated. Given that the HCO- radical formation is strongly exothermic (132.5 kJ mol\(^{-1}\); see Figure 1(c)), a sufficiently large water-ice slab is needed to absorb most of the nascent energy (see more details in Section 3). Therefore, the periodic cell parameters have been set to \( a = 17.544 \) Å and \( b = 21.2475 \) Å with a slab thickness of \( \sim 13 \) Å (which corresponds to four water layers). The model consists of 192 water molecules in total. In the CP2K code, the electron density is described by plane waves, and, accordingly, the surface is replicated also along the nonperiodic direction. To avoid interactions between the fictitious slab replicas, the \( c \) parameter (i.e., the nonperiodic one) was set to 35 Å.

### 3. Results

To study the CO hydrogenation on the ice surface, we simulated the reaction adopting a LH surface mechanism, i.e., with both the reactants (H- and CO) adsorbed on the surface. Accordingly, we first optimized the geometries of the reactants (H- + CO), TS (H-···CO), and product (HCO-) in order to obtain the potential energy surface of the reaction. As reported in Figure 1, the activation barrier (5.2 kJ mol\(^{-1}\), 622.1 K) is quite high if we consider the sources of energy available in the ISM. Indeed, it is well known that this reaction proceeds mostly through H tunneling (Hiraoka et al. 2002; Andersson et al. 2011; Rimola et al. 2014). However, as AIMD operates within the Born–Oppenheimer approximation, i.e., the nuclei motion is driven by classical equations, the quantum phenomena of atoms (such as the tunneling effect) cannot be taken into account. Since our aim is not to simulate the reaction itself, but to understand where the liberated energy goes, we run the simulation starting from the TS structure (Figure 1(b)). In this way, we force the system to evolve in the direction of the product. Therefore, the total energy to be dissipated is the sum of the energy barrier and of the reaction energy (5.2 + 132.5) kJ mol\(^{-1}\) = 137.7 kJ mol\(^{-1}\). It is possible to estimate the
expected temperature increase of the whole system after the reaction by invoking the equipartition theorem:

\[ T = \frac{2 E_{\text{nasc}}}{3 RN_{\text{at}}}, \]

where \( E_{\text{nasc}} \) is the nascent energy due to the H–C bond formation (i.e., 137.7 kJ mol\(^{-1}\)), \( N_{\text{at}} \) is the number of atoms in the whole system (3 for HCO\(^{-}\) and \( 3 \times 192 \) for the ice), and \( R \) the gas constant. Thus, the energy dissipation through an ice slab containing 192 water molecules should produce a global temperature increase of about 19 K (which is in perfect agreement with the very first spike in \( T \) of Figure A6, reaching 29 K = (10 K + 19 K) where 10 K is the starting temperature).

Then, when the simulation equilibrates, the temperature oscillates around 20 K. This very simple calculation is useful so as to have an idea of the number of atoms needed to avoid the nascent energy artificially rising to the total temperature.

Figure 2 shows the most interesting geometrical parameters of the system during the AIMD simulation (other geometrical parameters are shown in Figure A7). Both the temperature and potential energy oscillate around a stable value and they reach the equilibrium within 1 ps (see also Figures A6 and A8). As one can see in Figure 2, the H–C bond forms in the first tens of femtoseconds of the simulation (keeping in mind that we are starting from the TS). This is confirmed by the spin density evolution. At the beginning of the simulation, the unpaired electron is localized on H; once the H–C bond is formed the spin density is spread on the HCO\(^{-}\), with a higher percentage on the C atom (see Figure A9). After the H–C bond formation, the HCO\(^{-}\) moves on the surface in the sense of maximizing the H-bond contacts with the surrounding water molecules (Figure 2) and it lies in its most stable position after 1 ps, which corresponds to the equilibration of both the potential energy and the temperature. After this period, HCO\(^{-}\) stays in this stable position, without diffusing anywhere.

In Figure 3, the kinetic energy dissipation due to the H–C bond formation is reported. As expected, the kinetic energy released from the H–C bond formation rapidly drops (in less than 100 fs) and it is, simultaneously, absorbed by the water molecules of the surface. As one can see, at the beginning of the simulation, before 200 fs, the red line (\( T_{\text{HCO}} \)) is complementary with the green line (\( V_{\text{TOT}} \)). As the AIMD was executed in the NVE ensemble, when the kinetic energy drops, the potential rises by the same amount. However, after 300 fs, when the HCO\(^{-}\) starts to exchange energy with the surface, the red (\( T_{\text{HCO}} \)) and blue (\( T_{\text{ice}} \)) lines become symmetric, i.e., the energy loss of HCO\(^{-}\) is equal to the energy gain of the surface, in terms of kinetic energy. The most important message from Figure 3 is that, within the first picosecond, HCO\(^{-}\) loses 90% of its initial kinetic energy, which is immediately
transferred to the ice. Later, further along the simulation, HCO- continues to transfer energy to the ice at a slower rate. After 20 ps, its kinetic energy is around 15 kJ mol\(^{-1}\), at least twice as low as its binding energy. Therefore, it is unlikely that the HCO- will desorb. This is corroborated by Figure 2, where the H-bonds linking HCO- to the surface lie in a rather steady fashion after its formation (they essentially vibrate around their equilibrium position).

In order to give a detailed analysis of the energy dissipation on the ice surface, we used the atomic simulation environment (ASE) python module (Bahn & Jacobsen 2002; Larsen et al. 2017). The energy dissipation was analyzed by dividing the slab of water molecules in concentric shells centered on the reaction center (i.e., the C atom). Note that HCO- has been excluded from this analysis because we are interested in the dissipation across the ice itself. The concentric shells were defined as follows: (i) the first one is a hemisphere of 4 Å radius containing the closest water molecules to the CO molecule; (ii) the other shells are equally spaced from each other by 2.8 Å (average closest O–O distance between water molecules), up to a distance of 18 Å in order to also include the farthest water molecules from the reaction center. We emphasize that only a single unit cell was used for this analysis, which means that no water molecules from periodic replicas are included in the energy dissipation analysis. The sketch showing the water shells is given in Figure A10.

The results of the energy dissipation analysis are shown in Figure 4. The kinetic energy was normalized per water molecule, in order to remove the dependence on the number of water molecules (as each shell contains a different number of water molecules). One can see from the two first shells (0.0–4.0 and 4.0–6.8 Å) that the energy is rapidly transferred from HCO- to the ice, which is later uniformly distributed to the outer shells: within ~2 ps all shells have the same kinetic energy (in Figure A11, each panel reports the evolution of the kinetic energy for each water shell).

4. Discussion

In the present work, the HCO- formation reaction on an ice surface model has been used as a test case in order to study the kinetic energy dissipation due to the formation of a chemical bond (in this specific case, the H–C bond). This is particularly important because the energy released by the formation of a chemical bond may be a hot spot that makes other processes possible, like the desorption of the newly formed molecule or other molecules nearby. A crucial parameter is the timescale of the process: the main question is whether the released energy is available (and if so, for how long) and whether it can be used by other adsorbed species, or, in contrast, whether it is immediately dissipated through the ice surface. From Figure 3, the answer is very clear: the slab of water molecules absorbs ~90% of the nascent energy, which is equally distributed among all the water molecules of the ice surface within the first picosecond after the bond formation, and it is no longer available to assist other processes. In particular, and most importantly, the residual HCO- kinetic energy after 1 ps is almost half of the HCO- binding energy, which implies that HCO- will remain stuck on the surface and will not desorb.

Our simulations are based on three assumptions: (i) the starting position of the CO adsorbed on the ice is the most energetically favorable one, (ii) the surface of the ice is crystalline, and (iii) the reaction follows a LH mechanism. In the following, we discuss the validity limits of each assumption.

(i) CO position: The first assumption is based on the fact that, as molecules in cold molecular clouds move at low thermal (~10 K) velocities, landing on grain surfaces is slow enough for them to feel the electrostatic potential generated by the surface. Consequently, they have sufficient time to accommodate on the icy mantle, maximizing their interactions with the ice surface itself. In other words, the main driving forces of the adsorption process in cold molecular clouds are long range forces. Nonetheless, a few other starting positions may exist with respect to the one that was chosen for this study. For this reason, we have explored two other starting configurations, namely Pos2 and Pos3, reported in Figure A12. Both of them, after either geometry optimization (Figures A12(a) and (b)) or AIMD simulation (Figures A12(c) and (d)), lead to HCO- in the same position that is reported in Figures 1(c) and 2. In other words, whether CO is in the position we chose for the full AIMD simulations or in the other two positions, HCO- ends up having the same position, which means the same bonds with the surface and, consequently, the evolution of the system is the same.

(ii) Crystalline ice: As already mentioned in the Introduction, the major reason for choosing the crystalline ice structure is a computational one. In this respect, we should be cautious about the role of crystalline versus amorphous ice, because of the possibility that the symmetric electrostatic potential of the crystalline case can hinder the escape of the formed species from the surface and, in crystalline systems, the vibrational coupling might be more efficient than in amorphous ones, thus allowing a faster dissipation of the energy and, consequently, underestimating the desorption rate. Further studies need to be carried out in order to understand if the crystalline nature of the ice affects how the formed species behave because of the crystal symmetry compared to the random nature of the amorphous ice. Having said that, our simulations are valid and applicable in the environments where crystalline ice has been detected (e.g., Molinari et al. 1999; Terada & Tokunaga 2012).

(iii) LH mechanism: It is possible, and even probable, that the H atom will not arrive directly from the gas but rather is an atom that randomly grazes the ice surface. In this case, since the velocity of hydrogen is even smaller than if it landed from the gas, the results of our simulations would
not change. So, this choice is, after all, irrelevant for the purposes of our study.

In summary, we conclude that chemical desorption is not efficient in the H + CO reaction on crystalline ice, and this is a robust result. Laboratory experiments have proven to be difficult to obtain for this specific reaction. To the best of our knowledge, no experiment simulates it on crystalline ices. Minissale et al. (2016) obtained a measure of the H + CO CD when the reaction occurs on oxidized graphite. They found a CD efficiency equal to 10% ± 8%. Chuang et al. (2018) studied the CO hydrogenation process using a gold substrate, over which CO was deposited forming a thick layer of solid CO, which was subsequently bombarded with H atoms. They found that the global CD efficiency of the whole process up to the formation of CH3OH is low, ≤0.07 per hydrogenation step, assuming an identical efficiency for each reaction in the hydrogenation process (Chuang et al. 2018). As already mentioned, the surface where the CO is adsorbed and the reaction occurs is certainly of paramount importance, so a direct comparison between our computations and the above experiments is not obviously made. Yet, it seems that the latter agree on a small CD efficiency, if any, like our computations predict.

Finally, it is possible that for more exothermic reactions (like for example the last step to CH3OH, which is much more exothermic than H + CO) and weakly bound systems (like H2), CD can take place. This could also be the case for reactions occurring on grain surfaces of a different nature, such as silicates or carbonaceous materials, as their heat capacities are very different from those of H2O-dominated ices. Dedicated simulations should be carried out to assess it in these systems.

5. Conclusions

We studied the first step of the hydrogenation of CO on the interstellar grain icy surfaces by means of AIMD simulation. We studied the H + CO reaction occurring on a crystalline ice. Our goal was to understand it from an atomistic point of view and to quantify the possibility that the energy released in the reaction is only partially dispersed on the crystalline substrate and the residual energy is used to desorb the product, HCO−.

The main conclusions of the present study are:

(i) The reaction energy dissipation through thermal excitation of water molecules is extremely fast: after the first picosecond most of the reaction energy (137.7 kJ mol−1) is dissipated away through the ice, leaving HCO− with a kinetic energy of 10−15 kJ mol−1, more than twice as small as its binding energy (30 kJ mol−1).

(ii) As a consequence, the HCO− product is doomed to remain attached to the crystalline ice and no desorption can occur.

The astrophysical implications are that, in the environments where crystalline ices are present, like for example some protoplanetary disks, chemical desorption does not occur for the reaction H + CO. We suspect that this may be a general behavior for reactions dealing with hydrogen bonds, as they are responsible for both the cohesive energy and the interaction with the crystalline ice. However, in order to assess whether this is true, ad hoc simulations similar to those presented here are mandatory.

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Appendix

A.1. Computational Details

Two sets of convergence criteria were used: (i) for geometry optimizations to energy minima the energy threshold of the self-consistent field (SCF) procedure was set to ΔE = 10−7 au, while the thresholds on gradients and displacements were set to their default values (4.5 × 10−4 Ha Bohr−1 and 3.0 × 10−3 Ha Bohr−1, respectively), and (ii) for the TS search tighter parameters were adopted (ΔE = 10−10 for the SCF and 4.5 × 10−5 Ha Bohr−1 and 3.0 × 10−4 for gradients and displacements, respectively). These choices ensured good starting geometries for the AIMD simulation.

A benchmark study was performed using the same reaction on a smaller surface model, formed of three water molecules, in order to check the reliability of our results. The structures are shown in Figure A1, while energetic values and harmonic frequencies are reported in Tables A1 and A2, respectively. It is clear that PBE energies are quite far from those calculated at higher levels of theory, in particular with respect to the B2PLYPD3 and CCSD(T) methods. Hence, PBE results overestimate the chemical desorption, which in any case is not observed in our simulations. Harmonic frequencies computed at the PBE level, on the other hand, show very good agreement with those calculated at the B2PLYPD3 level (~10% difference), which is the most accurate method used in

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the frequency-calculation benchmark (CCSD(T) is excluded here because frequency calculations are computationally too expensive and we cannot perform them). This means that the vibrational coupling of HCO· with the water molecules is correctly described, and hence, also the energy dissipation.

### A.2. XYZ Files

We report the PBE/TZV2P optimized geometries of reactant, TS and product adsorbed on the ice surface, and the starting velocities of the AIMD simulation as XYZ files. These are available in the data.tar.gz package.

### A.3. Tables

Tables A1 and A2 (reaction energy and vibrational frequencies, respectively) report the results on the benchmark calculations we performed on the cluster models.

#### Table A1

| Method         | 1    | 2    | 3    | 4    | 5    | 6    | 7    |
|----------------|------|------|------|------|------|------|------|
| Energy (kJ mol⁻¹) | -132.1 | -122.6 | -121.0 | -108.0 | -45.5 | -91.3 | -90.9 |

**Note.** 1: CP2K: PBE-D3/TZV2P, 2: Gaussian: PBE-D3/6-311++G(d,p), 3: Gaussian: BHLYPD3/6-311++G(d,p), 4: Gaussian: BHLYP/6-311++G(d,p), 5: Gaussian: MP2/aug-cc-pvtz, 6: Gaussian: B2PLYPD3/aug-cc-pvtz, 7: Gaussian: CCSD(T)/aug-cc-pvtz.

#### Table A2

| Method         | 1    | 2    | 3    | 4    | 5    | 6    | Diff% (1-2) | Diff% (1-3) | Diff% (1-4) | Diff% (1-5) | Diff% (1-6) |
|----------------|------|------|------|------|------|------|-------------|-------------|-------------|-------------|-------------|
| Frequencies (cm⁻¹) | 450  | 443  | 431  | 434  | 441  | 422  | -4         | -14         | -10         | -14         | -12         |
| 473            | 509  | 471  | 483  | 437  | 418  | -5   | -6         | -9          | -8          | -13         | -11         |
| 524            | 601  | 588  | 562  | 573  | 572  | -4   | -6         | -8          | -10         | -12         | -10         |
| 753            | 753  | 721  | 716  | 677  | 684  | 0    | -4         | -5          | -10         | -9          | -9          |
| 994            | 974  | 877  | 915  | 880  | 891  | -2   | -12        | -8          | -11         | -10         | -10         |
| 1115           | 1108 | 1183 | 1183 | 1137 | 1146 | -1   | 6          | 6           | 2           | 3           | 3           |
| 1611           | 1583 | 1667 | 1670 | 1635 | 1640 | -2   | 4          | 4           | 1           | 2           | 2           |
| 1627           | 1593 | 1683 | 1686 | 1648 | 1655 | -2   | 3          | 4           | 1           | 2           | 2           |
| 1641           | 1623 | 1718 | 1712 | 1668 | 1673 | -1   | 5          | 4           | 2           | 2           | 2           |
| 1841           | 1847 | 2011 | 2014 | 1904 | 1871 | 0    | 9          | 9           | 3           | 2           | 2           |
| 2690           | 2643 | 2897 | 2867 | 2858 | 2804 | -2   | 8          | 7           | 6           | 4           | 4           |
| 3196           | 3232 | 3707 | 3680 | 3509 | 3480 | 1    | 16         | 15          | 10          | 9           | 9           |
| 3425           | 3474 | 3843 | 3846 | 3658 | 3643 | 1    | 12         | 12          | 7           | 6           | 6           |
| 3465           | 3507 | 3876 | 3869 | 3698 | 3683 | 1    | 12         | 12          | 7           | 6           | 6           |
| 3676           | 3703 | 4011 | 3996 | 3846 | 3821 | 1    | 9          | 9           | 5           | 4           | 4           |
| 3762           | 3785 | 4060 | 4051 | 3899 | 3885 | 1    | 8          | 8           | 4           | 3           | 3           |
| 3772           | 3795 | 4065 | 4063 | 3906 | 3892 | 1    | 8          | 8           | 4           | 3           | 3           |

**Note.** 1: CP2K: PBE-D3/TZV2P, 2: Gaussian: PBE-D3/6-311++G(d,p), 3: Gaussian: BHLYPD3/6-311++G(d,p), 4: Gaussian: BHLYP/6-311++G(d,p), 5: Gaussian: MP2/aug-cc-pvtz, 6: Gaussian: B2PLYPD3/aug-cc-pvtz.

### A.4. Figures

Figures A2–A4 show the spin density of reactants (H· + CO), TS (H·-CO), and product (HCO·), respectively. Figure A1 shows the cluster model used in the benchmark calculations. Figure A5 shows the bulk structure of P-ice, and the surface model used for all the calculation in the present work. Figure A6 shows the evolution of the temperature during the AIMD simulation. Figure A7 shows the evolution of some geometrical parameters (namely, the C-O bond of HCO·, and the O-H bond of a neighbor water molecule). Figure A8 shows the evolution of the potential energy during the AIMD simulation. Figure A9 shows the spin density evolution on H, C, and O atoms of HCO· during the AIMD simulation. Figure A10 shows a schematic representation of the water shells used for calculating the kinetic energy spreading. Figure A11 shows the kinetic energy evolution of each water shell. Figure A12 shows other possible staring configurations for the HCO· formation.
**Figure A2.** Spin density of the two reactants adsorbed on the (100) P-ice surface.

**Figure A3.** Spin density of the TS adsorbed on the (100) P-ice surface.

**Figure A4.** Spin density of the product adsorbed on the (100) P-ice surface.
Figure A5. PBE-D3/TZV2P optimized structure of the hexagonal ice bulk. The blue lines correspond to the bulk cut along the (100) plane.

Figure A6. Evolution of the temperature during the AIMD simulation.
Figure A7. Evolution of CO and OH bonds along the MD simulation. Colored lines in the graphs correspond to the colored circles in the top view structure of the HCO-/ice system.
Figure A8. Evolution of the potential energy during the AIMD simulation.

Figure A9. Spin density evolution of H, C, and O atoms belonging to the HCO· during the AIMD simulation.

Figure A10. Graphic representation of the shell division of the water-ice structure, each one in a different color. This is the shell structure used in the energy dissipation analysis. The reaction center, defined as the C atom of HCO· at the first AIMD step, is highlighted in yellow. Note that the ice structure was cut in half for the sake of clarity.
Figure A11. Kinetic energy evolution (in kilojoules per mole) of the ice surface. The ranges in the legend refer to the shells the water molecules belong to. The energy was normalized per water molecule.
Figure A12. PBE-D3/TZV2P optimized structure of Pos2 reactant (a) and product (b) on the crystalline ice surface. PBE-D3/TZV2P optimized structure of the Pos3 reactant (c) and 2 ps AIMD snapshot (d) on the crystalline ice surface.

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