

Quantification of the Role of Chemical Desorption in Molecular Clouds

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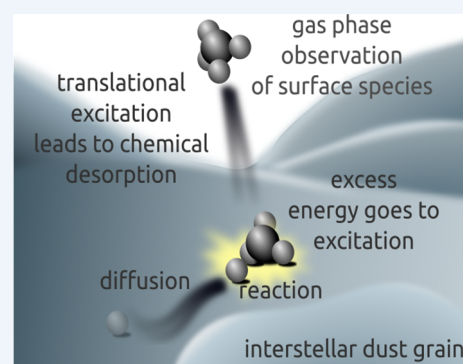


Supporting Information

CONSPECTUS: Dark molecular clouds have low temperatures of approximately 10 K and experience very little UV irradiation. These clouds are the birthplace of new stars and consist of gas and dust particles. The latter can act as a meeting place to facilitate surface chemistry to form saturated molecules such as formaldehyde, methyl formate, and dimethyl ether. These complex organic molecules or COMs become encapsulated in the ice that forms on the dust grains, and these ices are the precursor for cometary ices and other icy bodies. They likely played a role in bringing material to the early earth.

Although these COMs are likely formed on the surfaces of dust grains, several of them have been detected in the gas phase. This means that they have desorbed from the grain under these cold, dark conditions where thermal desorption and photodesorption are negligible. It has been speculated that reactive, or chemical, desorption is responsible for the high gas-phase abundance. After a surface reaction, its products might be vibrationally, translationally, and/or rotationally excited. Dissipation of the excess energy to translational energy can briefly increase the desorption rate, leading to chemical desorption. Astrochemical modellers have added terms to their rate equations to account for this effect. These terms, however, have had little experimental or theoretical verification.

In this Account, we use classical molecular dynamics (MD) simulations to give adsorbed molecules a fixed amount of energy as a proxy for excess energy and to record whether this leads to desorption. The excitation energy can be varied freely while keeping all other variables constant. This allows for the study of trends rather than being limited to a single reaction and a single system. The focus is on the dependence of the chemical desorption on the excitation energy, excitation type, and binding energy. Rotational and vibrational excitation was explicitly taken into account. An analytical expression for the chemical desorption probability was obtained in this way. It depends on the binding energy and reaction enthalpy. This expression was then implemented in a gas–grain astrochemical code to simulate the chemical evolution of a dark molecular cloud, and the results were compared against observational abundances of COMs in three different molecular clouds. The results with our new expression based on the MD simulations show good agreement for all species except H_2CO , which has both gas-phase and surface-formation routes. This is a significant improvement over models without chemical desorption or with other expressions for chemical desorption, as frequently used by other authors. It is encouraging to see that a general description with a firmer theoretical basis leads to a significant improvement. Understanding chemical desorption can help to explain the unexpectedly high gas-phase abundance of some COMs, and chemical desorption also provides a link between the gas phase and the ice mantle, and its understanding might help in creating a diagnostic tool to learn more about the ice composition.



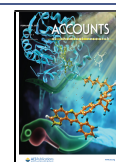
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1. INTRODUCTION

Dark molecular clouds are the birthplace of new stars. These clouds experience very little UV irradiation, have a low temperature of approximately 10 K, and consist of gas and dust particles. The dust particles are made of carbonaceous or silicaceous material and can act as a meeting place to facilitate surface chemistry as well as act as a third body to take up any excess reaction energy. Laboratory experiments on grain surface analogs have shown that saturated molecules such as formaldehyde, methyl formate, and dimethyl ether,^{5–9} often referred to as complex organic molecules or COMs, can indeed be formed under these conditions, and this is backed up by several quantum chemical studies.^{10–12} Gas-phase routes are much less efficient at forming saturated species, and hence COMs are generally considered to be formed on the surfaces of dust grains.

In recent years, however, several of these COMs have been detected in dark molecular clouds by radio telescopes.^{13–16} Since these COMs are observed in the gas phase but are likely formed on the grain, there still remains the problem of desorption. Thermal desorption is negligible for most species at 10 K, and photodesorption by UV irradiation is inefficient because of the low radiation field. Moreover, photodesorption is typically dissociative and can therefore not explain how these large COMs desorb intact. In this Account, we will focus on reactive, or chemical, desorption.¹⁷ After a surface reaction, its products might be vibrationally, translationally, and/or rotationally excited. Dissipation of the excess energy to translational energy can briefly increase the desorption rate, leading to chemical desorption. This appears to be a likely mechanism to explain the observed presence of COMs in the gas phase of cold, dense regions, and several gas–grain astrochemistry models have added a term to their rate equations to account for this in some way.^{18–23} An alternative mechanism that has been proposed is desorption by mantle explosion where chemical energy between radicals causes a run-away effect above a certain critical temperature, which leads to the explosion of the mantle.^{24–26}

The treatment of chemical desorption in astrochemical models ranges from a standard overall desorption probability for all reactions to more sophisticated treatments that include the reaction enthalpy, the binding energy and the number of internal degrees of freedom. The formalisms in all treatments are poorly or not constrained by experimental evidence. Garrod et al.^{17,18} applied Rice–Ramsperger–Kassel–Marcus theory to arrive at an expression for the desorption probability, and Minissale et al.²⁷ obtained an expression based on a collisional model that was in reasonable agreement with their experimental data for rigid surfaces such as graphite, whereas it

showed poorer agreement for flexible surfaces such as water ice.

Experimental verification is hard for several reasons: the systematic variation of parameters is challenging since a change in the reactive system leads to change in all relevant parameters, and as explained by Oba et al.,²⁸ it is difficult to obtain a desorption probability per reactive event as required in the models instead of per reactive species which is typically measured in experiments. We take a different approach by using classical molecular dynamics (MD) studies and giving adsorbed molecules a fixed amount of energy, as a proxy for excess energy and following their fate. The excitation energy can be varied freely while keeping all other variables constant. This allows for the study of trends rather than being limited to a single reaction and a single system. We have already done this for translational excitation on amorphous or crystalline ice surfaces.^{1,2} The desorption probability was found to depend on the amount of translational excitation given to a molecule and the binding energy to the surface.

The present account adds results on how chemical desorption depends on the excitation energy, excitation type, and binding energy. Rotational and vibrational excitation will explicitly be taken into account. The aim is to arrive at an analytical expression depending on the binding energy and reaction enthalpy for this probability. This expression is then implemented in a gas–grain astrochemical code to examine whether chemical desorption can indeed explain that the observed gas-phase abundance is in dark molecular clouds. Understanding chemical desorption can help to explain the unexpectedly high gas-phase abundance of some COMs. Also, chemical desorption also provides a link between the gas phase and the ice mantle, and its understanding might help in creating a diagnostic tool to learn more about ice composition. Interstellar ices rely on infrared observations which are much less sensitive than radio observations of the gas phase, for several reasons. These ices are, however, a precursor for cometary ices and other icy bodies,^{29,30} and more information about their composition can help us to understand the evolution.

2. EFFECT OF VIBRATIONAL AND ROTATIONAL EXCITATION ON CHEMICAL DESORPTION

To simulate excitation by chemical reactions, ad molecules are placed on top of an amorphous solid water (ASW) surface and are given a distinct amount of translational, vibrational, and/or rotational excitation. These excitations are used as proxies for excess energy in, for instance, surface reactions or photodissociation events where the photoproducts can remain highly excited after UV photodissociation. MD simulations do not allow us to simulate the reaction itself, and assumptions are required for the energies involved. Pantaleone et al.³¹ have used an *ab initio* MD to study the relaxation of the HCO radical in detail. This study is complementary to our classical MD approach because it considered only one particular reaction and used a very homogeneous proton-ordered crystalline water surface. The simulations start from the transition state, which is rather well defined for a crystalline surface. Infrared observations of interstellar water ice show that it is not crystalline but rather amorphous. An ASW surface has many different transition states depending on the initial binding site of the reactants, and with our approach we take into account the diversity of the binding sites on the surface.

Figure 1 shows the desorption probability as a function of the total additional energy given to the admolecule. The yellow

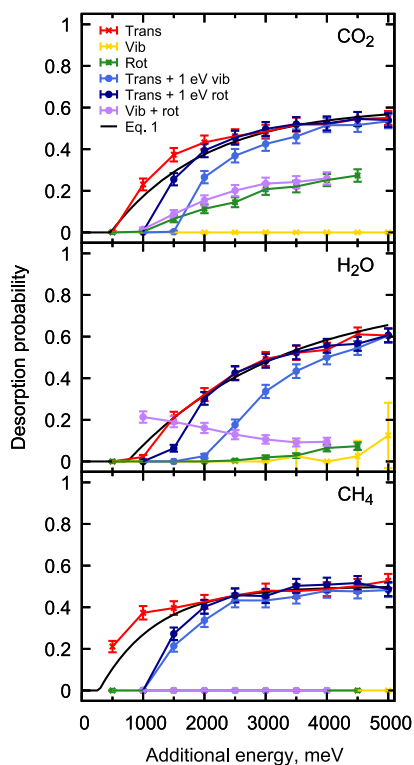


Figure 1. Desorption probability of the three admolecules (CO_2 , H_2O , and CH_4) as a function of the additional energy. Each curve represents a different set of simulations with a different type of energy contribution. The red, yellow, and green curves are for pure translational, rotational, or vibrational excitation, respectively. The two blue curves represent simulations of translational energy in combination with 1 eV of either vibrational or rotational energy that has been put into the molecule. The purple curve represents simulations where a total of 5 eV is given to the admolecule in a combination of rotational and vibrational excitation. Here the additional rotational energy is used on the x axis instead of the additional total energy to distinguish the simulations. The dashed line represents eq 1.

and green curves show purely vibrational and rotational excitations (up to 4.5 eV), respectively. This can be compared with our previous results on pure translational excitation in red.² As explained in the Methodology section, each individual point in this plot is the result of 2000 simulations, except for the yellow curves which result from 40 simulations per point. The red curves show clearly that translational excitation leads to desorption, where the desorption probabilities of all admolecules increase with excitation. Pure rotational or vibrational excitation, in contrast, does not lead to any significant desorption, even at energies that are as high as 4 eV. The only exception is the rotational excitation of CO_2 or H_2O at very high excitation energies.

Detailed analysis of the vibrational excitation revealed that vibrational excitation of a single bond quickly redistributes over all internal vibrational degrees of freedom. Subsequently, the admolecule–surface bond becomes excited, facilitating dissipation of the energy into the mantle rather than desorption.

The light- and dark-blue curves in Figure 1 represent simulations with a combination of excitation types: an increasing amount of translational excitation and 1 eV of vibrational or rotational energy for the light and dark curves, respectively. We chose 1 eV since this corresponds to a typical exothermicity, and the force field is still able to describe this bond energy with reasonable accuracy. The light-blue curves are simply shifted by 1 eV with respect to the red curves, which means that the additional vibrational energy does not have an effect on the desorption probability. The dark-blue curves, on the other hand, show a different trend. The combination of translational and rotational excitation enhances the desorption efficiency at low energy. The two contributions to the desorption probability are not simply additive since 1 eV of pure rotational excitation does not lead to desorption and the enhancement is visible only at low translational excitation.

Another noticeable result is that rotational excitations do not affect the three admolecules in the same way and that they are much more efficient in desorbing CO_2 and H_2O from the surface than CH_4 . This can be explained by the shape of the admolecules and their dipolar interaction. CO_2 has an anisotropic shape, whereas CH_4 is a nearly spherical molecule with no dipole, which makes the rotation almost imperceptible for the ice atoms. The rotation of CO_2 often leads to steric effects, whereas the rotation of H_2O has direct consequences for the hydrogen bonding structure.

The Supporting Information includes three movies of a H_2O molecule, which is given either 1 eV of rotational energy, 1 eV of translational energy, or a combination of both. In the latter case, the direction of translation and the axis of rotation are the same as in the pure translational and rotational simulations, respectively. The pure translational simulation shows that the H_2O rolls a short distance over surface but cannot escape since at least one of the hydrogen bonds (in green) stays intact during this rolling movement. Additional rotational energy facilitates the breaking of the final hydrogen bond. Pure rotational excitation occurs in place. The axis of rotation changes until it coincides with one of the hydrogen bonds. This hydrogen bond will stay intact, and additional rotational energy will not lead to desorption.

The purple curves in Figure 1 represent a series of simulations with a combination of rotational and vibrational excitation. Here, unlike for the other curves, the total additional excitation energy is 5 eV for all simulations in the series, but the relative contribution between vibrational and rotational excitation changes. The additional rotational energy is now used on the x axis instead, and the corresponding amount of vibrational energy is then $E_{\text{vib}} = 5 - E_{\text{rot}}$ (e.g., 1.5 eV means 1.5 eV of rotational energy and $5 - 1.5 = 3.5$ eV of vibrational energy). The purple curve is expected to follow the green curve of the pure rotational excitation, in which case vibrational excitation does not play a role. This can indeed be observed for CO_2 and CH_4 . The unexpected result comes with H_2O , where the combination of both excitation types leads to a high desorption rate and the individual components are rather ineffective. We again see that rotations can lead to desorption in combination with another type of excitation. The translation or vibration can temporarily weaken the hydrogen bond, at which time rotation can move the water molecule out of its preferred binding position, enabling desorption. This is also in line with the observation that the desorption probability is smaller at high rotational energy than at high vibrational energy since a substantial vibrational energy is required to

weaken a hydrogen bond whereas only a small amount of rotational energy is needed to take a water molecule out of its preferred orientation once the hydrogen bond is weak.

The “kick-out” desorption mechanism,^{32–34} where water substrate molecules are kicked out by excited molecules, was observed only for simulations with at least some translational excitation. It follows the same results that are reported in ref 2. A maximum kick-out desorption (9%) was obtained for CH₄ with a translational energy of 4.5 eV.

3. IMPLEMENTATION IN ASTROCHEMICAL SIMULATIONS

The previous section showed that desorption through excitation is a subtle interplay among various types of excitation. In general, we can conclude that translational excitation is the most important dissipation channel leading to chemical desorption and that additional rotational excitation can enhance the desorption further in a very similar way. In astrochemical gas–grain simulations, a large network of thousands of reactions, consisting of several hundreds of surface reactions, is simulated using coupled ordinary differential equations (ODEs) to obtain the evolution of the abundance of chemical species. Modellers hence use general descriptions to construct their ODEs and to obtain the corresponding rate constants. On the basis of the results presented in this Account and our earlier results, we recommend the following approach to describe the desorption probability of product *i*

$$P_{\text{CD}}^i = f \left(1 - \exp \left(- \frac{\chi^i \Delta H_{\text{react}} - |E_{\text{bind}}^i|}{3|E_{\text{bind}}^i|} \right) \right) \quad (1)$$

where ΔH_{react} is the reaction enthalpy, χ^i is the fraction of the reaction enthalpy that goes into the translational excitation of product *i*, E_{bind}^i is the binding energy of product *i* to the surface, and *f* is an empirical factor. The dashed line in Figure 1 represents this expression using *f* = 0.6, 0.8, and 0.5 for CO₂, H₂O, and CH₄, respectively. The MD simulations showed that the *f* factor can be directly linked to where the ad molecule is adsorbed on the surface (e.g., on top of the surface with *f* > 0.6 or in a pore with *f* = 0.5).² The deposition of H₂O and CO₂ results in ad molecules that are positioned mostly on top of the surface and not in a nanopore. These have a higher desorption probability than, for instance, CH₄. Methane can, because of its small interaction energy, diffuse over the surface and find a binding site that lies deeper in the surface, a nanopore, before it becomes completely adsorbed. Desorption from such a nanopore is harder, not only because of the stronger binding energy but also because of the geometrical barrier. In astrochemical simulations, species are typically not deposited on the mantle but are formed there from lighter, less-interacting species. We hence expect a value of *f* = 0.5 to be more representative.

Equation 1 was obtained from the MD simulations by applying

$$E^{\text{trans,exc}} \equiv \chi^i \Delta H_{\text{react}} \quad (2)$$

where $E^{\text{trans,exc}}$ is the translational excitation given to the molecule. For astrochemical simulations, another approach is required, which means that we need an estimate for χ^i . From the lack of any other information, often equipartition is assumed, where the energy released in reactions is equally distributed among all degrees of freedom²⁷ or all vibrational

degrees of freedom including binding to the surface.¹⁸ For bond-forming reactions, the formed bond is, however, more likely to be excited, and in dissociation reactions, rotational excitation and translational excitation likely dominate. We hence propose different strategies for one- and two-product reactions since one-product reactions are typically bond-forming reactions whereas in a two-product reaction a bond is likely dissociated as well. We introduce two different values for χ_i depending on the type of reaction, χ_1 or χ_2

$$\chi_i = \begin{cases} \chi_1, & \text{one-product reaction} \\ \chi_2 \frac{m_j}{m_i + m_j}, & \text{two-product reaction} \end{cases} \quad (3)$$

with m_i being the mass of product *i* and m_j being the mass of the other product in the case of a two-product reaction. The latter accounts for conservation of momentum. There are probably no universal χ_1 and χ_2 values but we use these as a first improvement over equipartition, and these universal values still allow for the treatment of chemical desorption in astrochemical models.

Garrod et al.¹⁸ and Wakelam et al.²¹ assume χ_2 to be negligible since the energy is shared between two products. However, for products with very different masses the translational energy going to the lighter species can still be substantial. Moreover, these typically have lower binding energies as well. Minissale et al.²⁷ report, for instance, a $40 \pm 10\%$ desorption efficiency for the HCO + H → CO + H₂ reaction. Unfortunately, very little information on reasonable values for χ is available. Quantum mechanical simulations that allow the treatment of reactions on ice surfaces typically do not report this type of information, and experimental data is limited as well, as discussed earlier.

An analysis of our trajectories shows that the transfer of energy among the different types of kinetic energy is slow with respect to dissipation to the surface or desorption of the product. Equipartition is hence not likely. We use χ_1 and χ_2 as free input parameters in the astrochemical model which we hope to further constrain by comparison with observations.

We currently limit this treatment to surface reactions. At a later stage, we will also adjust this for photodissociation reactions, but since this also has consequences for the treatment of photodesorption, it is beyond the scope of this Account.

4. CHEMICAL DESORPTION OF COMS IN DARK MOLECULAR CLOUDS

The effect of chemical desorption was tested by simulating a quiescent dark cloud. The radiation and temperature in this cloud is too low to expect any species formed on the grain surface to be in the gas phase on the basis of thermal desorption alone. These regions are hence an ideal test case for the importance of chemical desorption. The simulation results are compared against observational abundances for a selection of species and against a model with no chemical desorption, 1% desorption for all single-product reactions independent of the reaction enthalpy or binding energy, and applying the Minissale formulation.²⁷ In total, 28 different simulations were performed: the 3 reference models and a grid of 25 models with χ_1 and χ_2 , both varying between 0.05 and 0.5. The data obtained from the simulations was analyzed and compared to observational data from L1544, L1689b, and B1-b molecular

Table 1. Observed and Modeled Fractional Abundances of Organic Species Detected in Cold Interstellar Clouds

species	no CD	1% CD	Minissale	$\chi_1 = 0.05$	$\chi_1 = 0.1$	$\chi_1 = 0.2$	L1544	L1689b	B1-b
H ₂ CO	2.09(-09)	5.11(-09)	2.42(-09)	6.89(-09)	2.76(-08)	9.55(-08)		1.3(-09) ¹³	4.0(-10) ³⁵
CH ₂ CO	2.31(-11)	9.24(-11)	2.87(-11)	8.11(-11)	2.71(-10)	1.55(-09)	1(-9) ³⁷	1.9(-10) ¹³	
CH ₃ OH	2.12(-11)	4.80(-10)	2.28(-11)	1.95(-11)	2.32(-10)	8.38(-09)	6.0(-9) ³⁷		3.1(-09) ³⁸
CH ₃ CHO	1.09(-11)	1.03(-10)	7.14(-12)	9.76(-12)	7.93(-11)	1.41(-09)	2.1(-10) ¹⁶	1.7(-10) ¹³	1.0(-11) ¹⁵
CH ₃ OCH ₃	1.51(-11)	6.02(-11)	6.98(-12)	3.45(-12)	4.71(-11)	2.58(-10)	5.1(-11) ¹⁶	1.3(-10) ¹³	2.0(-11) ¹⁵
HCOOCH ₃	2.29(-12)	6.95(-11)	4.15(-12)	3.50(-12)	3.11(-10)	3.87(-09)	1.5(-10) ¹⁶	7.4(-10) ¹³	2.0(-11) ¹⁵

^a $a(-b)$ stands for $a \times 10^{-b}$. Quoted model abundances are at 10^5 years in phase 2 and with $\chi_2 = 0.2$.

clouds.^{13–16,35} Table 1 reports the model abundances after 2×10^5 years in phase 2 (total simulation time of 1.2×10^6 years, see Table 2) for a selection of these 25 models. The outcome

Table 2. Dark Cloud Physical Parameters

	phase 1	phase 2
n_{H} (cm ⁻³)	100	2×10^5
T_{dust} (K)	20	10
T_{gas} (K)	20	10
A_{v} (mag)	2	10
ζ (s ⁻¹)	1.3×10^{-17}	1.3×10^{-17}
duration (years)	10^6	10^8

was found to be rather insensitive to the exact value of χ_2 ; only for values of $\chi_2 = 0.5$ can a clear increase in gas-phase species be observed. The χ_2 value affects mostly the desorption of H and H₂, which will lead to a different hydrogenation chemistry on the grain, but does not directly lead to more COMs in the gas phase. The χ_2 parameter would likely have been more important if photodissociation reactions were included in the treatment as well. The results in Table 1 are all for $\chi_2 = 0.2$. The table clearly shows an increase in the gas-phase abundance for all species with increasing importance of chemical desorption. Good agreement is obtained for $\chi_1 = 0.1$ by taking into account cloud-to-cloud variations. The only exception is H₂CO, which has both gas-phase and surface-formation routes. This is a significant improvement over the three reference models. It is encouraging to see that a general description with a firmer theoretical basis leads to significant improvement.

Figure 2 shows the time evolution of the species in Table 1 in both the gas phase and on the grain. The ice build-up time increases with χ_1 . For $\chi_1 = 0.2$, some species are more abundant in the gas phase than on the grain, which points to very efficient desorption, possibly in combination with gas-phase formation. Under all conditions, the best agreement with the observations is obtained a few times in 10^5 years, in agreement with other modeling studies that included chemical desorption.^{16,20,36}

5. CONCLUDING REMARKS

Astronomers have a tendency to draw conclusions and extract general laws from a small set of observations. Part of this is pragmatism due to a limited availability of data and large uncertainties in the conditions under which they were taken. A clear example is the barrier to diffusion of surface species. This is assumed to be a universal, fixed fraction of the desorption energy. There is no fundamental physical argument for such a universal ratio to exist, and it is used solely due to the lack of data. The original ratio was estimated on the basis of a single experimental study, and in the astrochemical literature, it is still often referred to as “the” diffusion-to-binding energy ratio. As

chemists, we are often much more hesitant to draw such general conclusions and instead focus on individual systems.

Our results show that for chemical desorption the answer is probably somewhere in the middle. The MD simulations showed very similar desorption behavior for the three very different systems based on translational excitation regardless of the anisotropy of the molecule, its dipole moment, or its ability to form hydrogen bonds. Results are very different if we look at diffusion patterns for nondesorbing admolecules¹ or if rotational excitation is considered. In both cases, specific attractive and repulsive interactions are much more important. For the χ values, we made the strong assumption that a universal χ factor exists, again due to a lack of data. The fact that good agreement with observations is obtained for a single χ_1 value of 0.1 suggests that there are no very large variations between reactions. We compared only six species to observations, but these are formed through a large network of reactions and hence probe many reactions in this chain. This also explains the high sensitivity of the model results on χ_1 since the effect builds up over many reactions. We hope that quantum chemists will take up the challenge to quantify the kinetic energy distribution after reaction in terms of translational, vibrational, and rotational energy.

Photodesorption is considered to be an important process for releasing molecules into the gas phase in cold. For a few species such as CO and N₂, this occurs nondissociatively through the DIET process: desorption induced by electronic transitions.^{39,40} For most other species, the main channel is dissociative and surfaces photodissociate, after which the photoproducts can remain highly excited. Molecular dynamics simulations of H₂O photodissociation have indeed shown that the photoproducts can then desorb, depending on their excitation energy.^{33,41–43} The photoproducts can also react again and desorb in the form of water (reformation mechanism).

To date, the implementation of photodesorption in astrochemical codes has been fairly pragmatic. Either a universal desorption yield is applied, independently of the energetics involved or the binding energy, or only those molecules that have been measured in the laboratory are included. In both cases, this typically refers to species that desorb intact. We plan to further extend our chemical desorption treatment to photodissociation using very similar prescriptions. Currently, the reformation mechanism can already be treated by our formalism; we also aim to include dissociative photodesorption.

Finally, understanding chemical desorption is not only critical to explaining gas-phase observations in dark molecular clouds but might help to create a diagnostic tool for learning more about ice composition through gas-phase observations. Obtaining universal prescriptions, whenever possible, will aid in this effort.

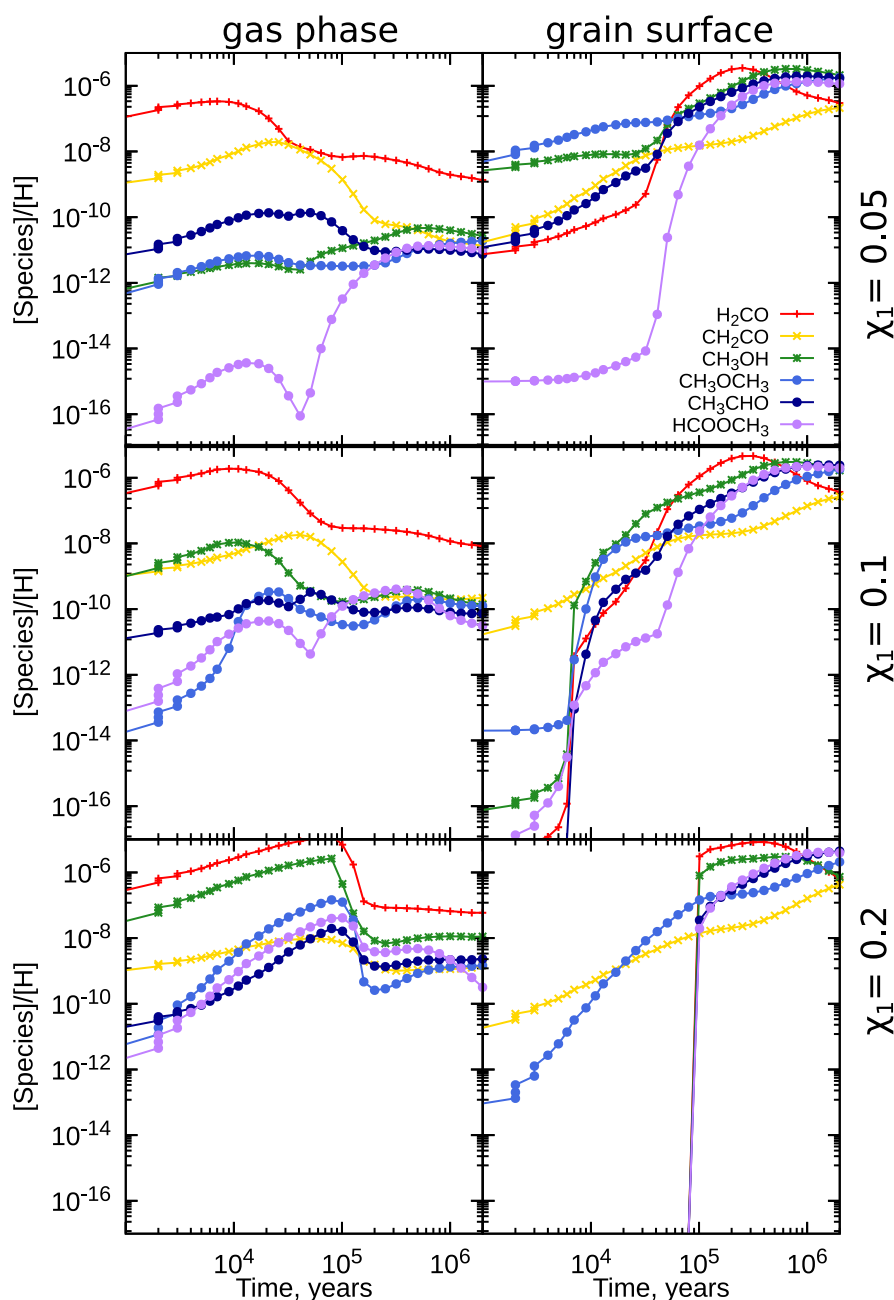


Figure 2. Time evolution of the abundances of selected species in the gas phase (left panels) and on the grain surface (right panels) for three simulations with $\chi_1 = 0.05, 0.1,$ and 0.2 . The value for χ_2 is set to 0.2 for all simulations, and only phase 2 is shown.

6. METHODOLOGY

6.1. Molecular Dynamics Simulations

6.1.1. Interaction Potentials. The H_2O intermolecular interactions were described using the q-TIP4P/f potential,⁴⁴ which is a flexible version of the TIP4P/2005 potential⁴⁵ to prevent the dissociation of O–H upon the introduction of the vibrational energy. The intramolecular interactions for CO_2 and CH_4 have been taken from refs 46 and 47, respectively. The intermolecular H_2O – CO_2 interaction is taken from Karssemeijer et al.⁴⁸ For H_2O , the charge model of the q-TIP4P/f potential is used. For the H_2O – CH_4 interactions, we refitted the H_2O – CH_4 PES_{2b}–CSM potential by Qu et al.⁴⁹ with a Beck potential. The dispersion contribution is cut off at 11.0 \AA , and the Coulombic part of the potential is computed

using a particle–particle particle-mesh solver with a relative RMS error in the per atom force of 10^{-6} .

6.1.2. Simulation Procedure. All MD simulations were performed using the LAMMPS package (version 16/02/16).⁵⁰ The same procedure was followed for three different admolecules on top of an ASW surface. An amorphous sample of 360 H_2O molecules is used. The production of the ice is detailed in our previous paper.² To trace the variations in binding sites, 1000 NVT equilibration simulations are performed for each of the three admolecules. For each run, the initial position of the molecule is randomly chosen in the x and y directions and $\Delta z = 7 \text{ \AA}$ above the surface. The orientation of the admolecule with respect to the surface is also chosen randomly. To promote binding to the surface, the

molecule is given a low initial velocity toward the surface. The Nosé–Hoover thermostat was used at a temperature of 10 K.

After equilibration, the admolecule was given an additional amount of translational, rotational, and/or vibrational energy. In each of the energy dissipation simulations, the admolecule is excited at the start of the simulation with a preset amount of energy. This energy is given either as translational kinetic energy, vibrational potential energy, rotational kinetic energy, or a combination of these. How this is achieved is detailed in the [Supporting Information](#). Energy transfer in this out-of-equilibrium system was then followed. To obtain statistics on this process, thousands of independent simulations were performed, except for pure vibrational excitation which has limited statistics of 40 simulations per energy value and per admolecule. The equations of motion are integrated over time using the standard velocity Verlet integrator. A time step of 0.5 fs was chosen to sample eight points per the fastest oscillation in the system. Per excitation type and excitation energy, 2000 simulations are performed, and for each of these simulations, the outcome (desorption of the admolecule, adsorption of the admolecule, absorption of the admolecule in the ice, etc) is recorded. The selection criteria for these outcomes can be found in the [Supporting Information](#).

6.2. Gas–Grain Chemical Model

Chemical desorption probabilities were implemented in a time-dependent gas–grain chemical model to simulate the chemical evolution of a homogeneous dark cloud with constant physical conditions. This is a rate-equation based kinetics model, which follows the abundances of species in both the gas and solid phases but without using location information of ice species within the ice mantle. The model therefore does not differentiate between reactions of species located on the ice surface and in the bulk mantle; however, grain–surface reactions are limited to occur within two monolayers worth of material in the ice mantle only. Here we give a brief explanation of the model. For more details, we refer to ref [51](#) and the references therein. The gas-phase network is the UDfA Database for Astrochemistry,⁵² known as Rate12. The solid-phase chemistry is based on the Ohio State University (OSU) network.⁵³ The total network includes gas–grain interactions such as desorption and adsorption processes and is updated with additional nitrogen chemistry reactions⁴ and CO hydrogenation reactions.^{3,10} A two-phase approach is used in which the abundances obtained by simulations under physical conditions related to diffuse cloud conditions (phase 1) serve as input for the simulations of a dense core (phase 2). The initial elemental abundances are from EA1 in ref [54](#), which follows Graedel et al.⁵⁵ [Table 2](#) summarizes the assumed physical parameters for both phases.

The chemical model that is used is based on the code developed by Drozdovskaya and Walsh.^{23,56} The changes made to their model are the following as detailed in the [Supporting Information](#).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.accounts.0c00636>.

Excitation of a H₂O admolecule with 1 eV of translational energy (MP4)

Excitation of a H₂O admolecule with 1 eV of rotational energy (MP4)

Excitation of a H₂O admolecule with 1 eV of translational energy and with 1 eV of rotational energy (MP4)

Additional details on the used methodology: termination criteria for the Molecular Dynamics simulations, vibrational and translational excitation approach, and changes made to the astrochemical model (PDF)

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Notes

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