Molecular modeling of heterogeneous processes in connection with atmospheric and interstellar chemistry

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Introduction
Both in atmospheric and interstellar chemistry, a comprehensive view of the elementary processes can be brought from computer simulations. The ice is actually present in both environments and its surface can activate reactions between adsorbed species normally forbidden in gas phase. In this poster, this will be illustrated by two examples. On the one hand, quantum and classical simulations have been carried out to characterize the photodissociation properties of a given pollutant at the ice. On the other hand, by means quantum chemistry calculations, the formation of organic molecules in space has been investigated and compared to the observations.

Atmospheric chemistry
The interaction between ice and halogenated species has received much attention in the past few years in the context of atmospheric chemistry and ozone depletion. Much theoretical and experimental work has been carried out in order to understand HOCl behavior adsorption and ionization at the ice interface, HOCl being a "reservoir" species for the production of Cl radicals, potentially destructive for the stratospheric ozone.

Methodology
Upon a Franck-Condon excitation, the HX molecule is promoted the first excited state. Time-dependent quantum wave packets and classical trajectories are propagated on this dissociative potential energy surface, the ice-HX interaction being described with a semi-empirical force field.

Photodissociation of HCl adsorbed on ice

Interstellar chemistry
It is believed that Formaldehyde, a primitive molecule, is formed on dust grains coated with water ice within Molecular Clouds through the reaction scheme

\[ H + CO \rightarrow HCO + H_2 \]

However, it is equally plausible that the second hydrogen may add to the oxygen of the Formyl radical to generate Hydroxymethylene (HCOH). Does the presence of water influence the energetics of this isomerisation (unfavorable in gas phase)?

Methodology:
Quantum chemistry calculations are performed using DFT (B97D functional) and ab initio MP2 have been used in conjunction with the aug-cc-pVTZ basis set to investigate how the sequential hydrogenation of CO is changed in clusters consisting water molecules.

Isomerisation of HCOH to H2CO

The concerted hydrogen atom exchange leads to a further reduction in the activation energy in the range 0 to 3 kcal/mol. This range is significantly lower than the isolated gas phase and the agreement between the B3LYP/MP2 and aug-cc-pVTZ is well within the errors associated with these methods and below 1 kcal/mol. This is within the range which is considered to be favourable in our working environment (T<100K).

With two water molecules present in the reaction ring a concerted hydrogen atom transfer mechanism is also observed. However, if we consider the trend in the activation energies as a function of the number of water molecules we see that the addition of the third water molecule does not further reduce the activation energy suggesting the reaction is optimum in the presence of two water molecules.

Effect of increasing the number of water molecules present in the reaction complex on the tunnelling rate of reaction

Using an Eckart model and a Boltzmann population distribution the rate was calculated as a function of temperature. This was done using the activation energies for the cases with N=3, 1, and 2. We see that the timescale goes from a matter of hours in the N=0 to the nanosecond timescale when one water molecule is involved in the reaction. The implication of this is that even if HCOH is efficiently formed on the dust grains it is isomerised too rapidly to be detected when water is present.