Quantum Chemical Simulations for Astrochemistry

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The tunnel effect is a quantum mechanical phenomenon which allows quantum objects to pass potential energy barriers bigger than the total energy of the object. Following Newton's classical equations of motion the object is forbidden to pass the barrier but following the wave nature of quantum mechanics, the particle can tunnel through this barrier. The tunneling of atoms in molecules leads to surprising observations. In symmetric reactions, tunneling causes a splitting of the vibrational energy levels. In asymmetric reactions, the tunnel effect can increase the reaction rates and also enable chemical reactions which would not be observed classically. This is especially true when the temperature is very low as it is the case in the interstellar medium. Therefore, in astrochemistry in particular this quantum effect can play a significant role.

1 Atom Tunneling

On the microscopic scale of quantum physics, objects can be described either as particles or as waves. This is called wave-particle dualism and is one of the fundamental quantum mechanical principles. The wave nature of an object is mathematically described by a wave function Ψ which follows the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\,\Psi \tag{1}$$

Here, $\hbar$ is the so-called reduced Planck's constant and $\hat{H}$ is the Hamilton operator corresponding to the total energy – the sum of kinetic energy T and potential energy V – of a system:

$$\hat{H}\,\Psi = \left(\hat{T} + \hat{V}\right)\Psi = E\,\Psi \tag{2}$$

The wave function Ψ describes the physical quantum state of a system and the square of the absolute value can be interpreted as the probability density $\rho(x,t)$ to find the quantum object at the position x at the time t.

$$\rho(x,t) = |\Psi(x,t)|^2 \tag{3}$$

In classical physics, the total energy of a particle needs to be at least as high as the potential energy to overcome the barrier. In quantum mechanics, the wave function – and thus the

probability of finding a particle – on the other side of a barrier is not zero when the potential energy is bigger than the kinetic energy of the quantum object. For a rectangular barrier, as shown in figure 1, the wave function can be easily analyzed. In the classically forbidden region, the amplitude of the wave function decays exponentially. The analytical solution shows that exponential decay of the wave amplitude depends on the mass of the particle m, on the energy barrier E_A, and on the width of the barrier x.

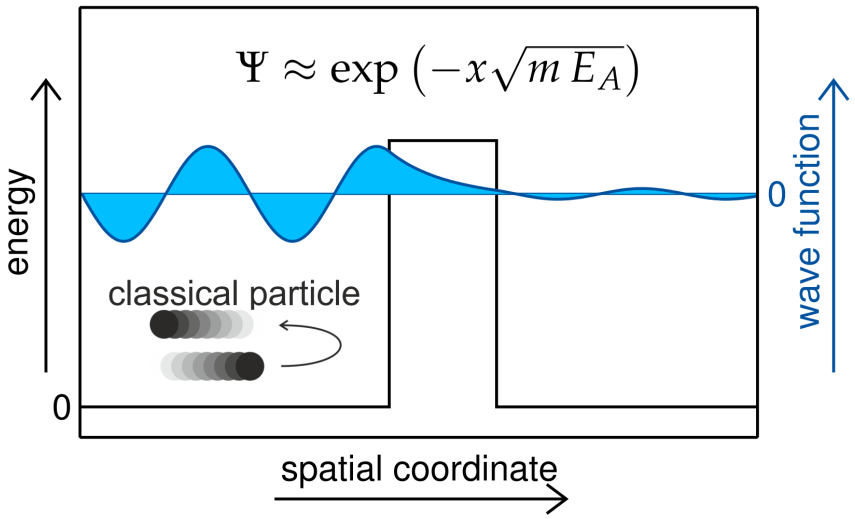

Figure 1: Wave function during the tunneling through a rectangular barrier. The equation above the barrier shows the analytical behaviour of the wave function within a rectangular barrier. The picture is taken and modified from reference [1].

Atoms and molecules are small enough to be labelled as quantum objects and activation barriers of chemical reactions can be tunnelled though if

- the atoms mainly involved in the motion are light, i.e. first or second period elements like hydrogen,
- the distances the atoms have to cover during the reaction is small, and
- the energy barrier is not extremely high.

At room temperature atom tunneling is nearly restricted to hydrogen atoms. Because of the mass dependence of the tunnel effect, deuterium (heavy hydrogen) atoms are less likely to undergo tunneling through the barrier. This leads to high kinetic isotope effects (KIEs) which are defined as the ratio of the reaction rate constant of the light system k_H and the reaction rate constant of the heavy system k_D:

$$KIE = \frac{k_H}{k_D} \tag{4}$$

The KIE is a suitable probe to examine the atom tunneling experimentally because it can be directly measured.

At lower temperatures atom tunneling enables chemical reactions, which would otherwise be impossible, and heavier atoms such as carbon or oxygen contribute to the tunneling motion. As the field of atom tunneling in chemical reactions is of increasing scientific interest and can not be covered in full detail, here we want to refer to a review which shows the progresses of the last years [1].

2 Astrochemistry

There are more than 170 different molecules observed in the interstellar medium. Astrochemistry describes the distribution, formation, destruction, and all other interactions of chemical species. The most important differences to the familiar reaction conditions in a lab are a low particle density, a particularly high photon density, and low temperatures. Hydrogen atoms and molecular hydrogen are comparably abundant species, thus, tunneling is a suitable mechanism for most reactions involving potential energy barriers.

Apart from the small gaseous molecules, there are also dust particles coated with water ice. These can work as catalysts *e.g.* in the hydrogen addition reaction to CO, which is a key step in the formation of formaldehyde and methanol in space [2, 3]. In general, there are different possible reaction mechanisms on a surface. Two of them, the Eley-Rideal mechanism and the Langmuir-Hinshelwood mechanism are discussed here, see Figure 2. In the former case, one atom or molecule is adsorbed on the surface and another one approaches from the gas phase and they directly form a transition state which then reacts to the products. In the Langmuir-Hinshelwood mechanism, both reactants are adsorbed prior to the reaction. After that, both of them can diffuse on the surface which proceeds either thermally or through atom tunneling. When both particles meet, they can form a transition state and react to the products.

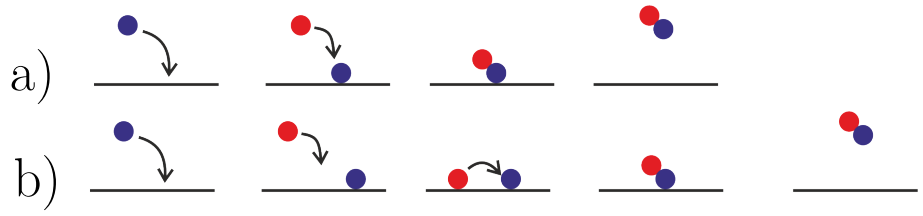

Figure 2: a) Eley-Rideal reaction mechanism. One particle is first adsorbed on a surface and a second one meets it directly forming the products. b) Langmuir-Hinshelwood mechanism. Both particles are adsorbed separately. Diffusion allows reaction to the products.

3 Results

Different chemical reactions which possess potential energy barriers were investigated [4, 5, 6, 7, 8]. A few of them are shown in Table 1. All of them are neutral-radical reactions with a potential energy barrier of a small to medium height. The potential is obtained by means of density functional theory (DFT) or, if possible, highly correlated wave function methods.

3.1 H_2 + OH

One prototype reaction for four-atomic systems is the reaction

$$H_2 + OH \rightarrow H_2O + H. \tag{5}$$

This reaction is assumed to be one of the main routes of H_2O formation in the interstellar medium and is therefore of high interest. The potential energy barrier and the imaginary frequency at the transition structure are calculated at CCSD(T)-F12 level to be 22.5 kJ/mol and 1199i cm^{-1}. For the low temperatures occurring in the interstellar medium this barrier would be too high to overcome. Nevertheless, the barrier is particularly thin as can be seen by the high imaginary

Reaction			Lit.
$H_2 + OH$	$\rightarrow$	$H_2O + H$	[4]
$H_2 + NH_3^+$	$\rightarrow$	$NH_4^+ + H$	[5]
$H_2O_2 + H$	$\rightarrow$	$H_2 + HO_2$	[6]
$H_2O_2 + H$	$\rightarrow$	$H_2O + OH$	[6]
$HNCO + H$	$\rightarrow$	H_2NCO	[7]
$CH_4 + OH$	$\rightarrow$	$CH_3 + H_2O$	[8]
$H_2CO + H$	$\rightarrow$	$H_2 + HCO$	
$H_2CO + H$	$\rightarrow$	H_3CO	
$H_2CO + H$	$\rightarrow$	H_2COH	
$H_2 + O$	$\rightarrow$	$H + OH$	

Table 1: Reactions studied in our group.

frequency and therefore, the tunneling effect is assumed to be distinct. We calculated reaction rate constants in the gas phase using the semiclassical instanton theory [4]. The reaction rates of all possible isotopologues were also calculated, see Figure 3. The strong impact of atom tunneling leads to high KIEs of 100-500 for the deuteration of the transferred hydrogen atom. The other two hydrogen atoms do not contribute significantly to the tunneling motion as is shown by the comparably low KIE of 1-10 for deuteration of these atoms.

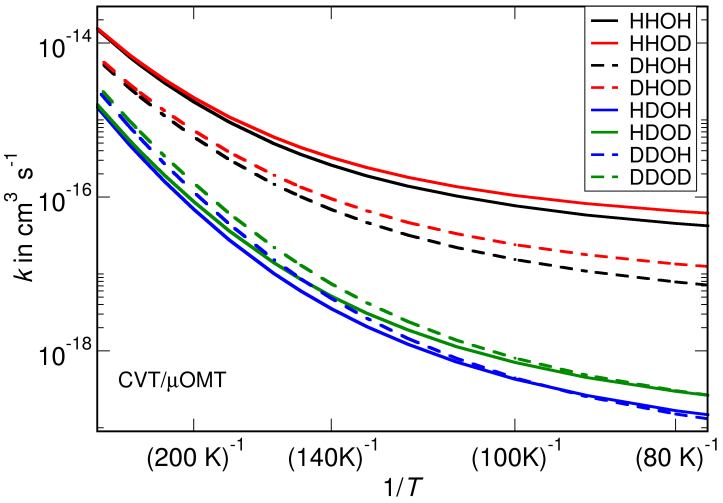

Figure 3: Temperature dependence of the reaction rate constants of all possible isotopologues (so called Arrhenius plots). Here, *e.g.* DHOD denotes the reaction of DH and OD to a D atom and HOD, as it is shown by the order of the letters. The picture is taken from reference [4] with kind permission of the American Institute of Physics (AIP).

We also simulated the reaction on a water ice surface as shown in figure 4 by means of a QM/MM framework. In this case, the four atoms directly involved in the reaction and 19 water molecules of the crystalline surface were included in the QM part and the MM part simulates an ice surface of 50 x 50 Å.

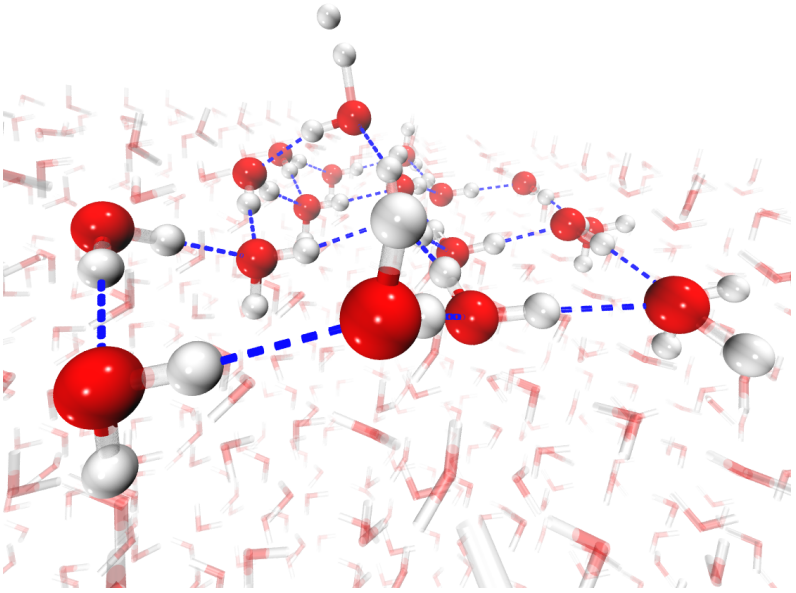

Figure 4: Transition state structure of the reaction of H_2 + OH on a crystalline ice surface. The water ice molecules in the QM part are shown as transparent ball and stick model while the MM molecules are shown as thin lines.

4 Conclusion

The study of the tunnel effect of atoms is an evolving field in experimental and theoretical chemistry. In particular at cryogenic temperatures atom tunneling leads to surprising results and can change stability and chemical reactivity qualitatively. Due to the large mass-dependence, high KIEs arise what makes atom tunneling detectable experimentally. Atom tunneling is found to occur in organic chemistry, biochemistry, as well as inorganic chemistry and it determines the reactivity at the cryogenic temperatures prevalent in e.g. the interstellar medium. Therefore, it is necessary to include atom tunneling in considerations and calculations of astrochemical reactions where potential energy barriers can only be passed if tunneling plays a dominant role.

In the case of the reaction of molecular hydrogen with OH radicals, the Arrhenius plot is curved because of the atoms – mainly the transferred hydrogen – tunneling through the potential energy barrier. This increases the reaction rate at the prevalent temperatures significantly and affirms that this reaction is a possible step in the formation of water in the interstellar medium.

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