

ISOTOPIC EFFECTS IN ATOMIC AND MOLECULAR REACTIONS

RONALD McCARROLL

*Laboratoire de Chimie-Physique-Matière et Rayonnement (UMR 7614 CNRS),
Université Pierre et Marie Curie, 75231- Paris Cedex 05*

Abstract. Reactions between atoms and molecules at thermal and low collision energies can be strongly influenced by the isotopic mass of the reactants. Isotopic effects arise in several different ways. Whenever the collision process is only controlled by the adiabatic stationary states of the collision complex of the reactants, the isotopic dependence is fairly easy to account for since the adiabatic potential surface (PES) does not depend on the isotopic mass. But, as is often the case, the reaction proceeds because of the strong non-adiabatic coupling which occurs in the vicinity of avoided crossings (or conical intersections) of the PES. Then it becomes quite difficult to disentangle the isotopic mass dependence on the collision rates even for relatively simple ion-atom or atom-atom systems. As a general rule, the isotopic dependence changes in character around collision energies of a few eV. At energies exceeding a few eV, where small angle scattering is dominant, the cross sections scale with the velocity and isotopic effects are simple to predict. However, at energies lower than a few eV, there is no simple way of predicting isotopic effect other than by a detailed calculation. The situation becomes even more complex when resonance effects occur.

Another complication occurs when one or both of the reactant are molecules. Then, the collision rates may also depend strongly on the ro-vibrational internal energy of the reactants. The effect is particularly important for H₂ molecule and other hydrides, when one of the H nuclei is replaced by D or T. For example, the ground ro-vibrational state of HD is about 33 meV lower than the ground state of H₂. The vibration and rotation structure of a molecule depends strongly on the isotopic mass. For example, the ground state energy of HD is 33 meV lower than that of H₂. For this reason, the isotope exchange $D^+ + H_2 \rightarrow H^+ + HD$ is exothermic and has very large rate constants at low temperatures. This formation of HD is more abundant than might from natural abundance of D isotope. Similar effects are found for a wide variety of hydrides. These considerations are important for our understanding of interstellar molecule formation.

There is also another interesting problem associated with symmetrical molecules, such as H₂, O₂, N₂... in the case of isotopic substitution.. Not only does the rotational constant change, but the loss of nuclear symmetry can have a large effect. Typically these are important, for example, for problems such as conversion of ortho-H₂ to para-H₂. The case of O₂ is also of great interest in view of the over-abundance of isotopes of O₃ on the terrestrial atmosphere.

But there are still some unresolved problems. One concerns the determination of non-adiabatic coupling between adiabatic states. The problem arises because of the inadequacy

of an adiabatic representation in the asymptotic limit. This problem has been recognized for a long time. Many solutions have been proposed and some of these are successful. However, none are completely satisfactory as they all involve a modification of the adiabatic basis set. Some aspects of the problem both simple ion-atom charge exchange reaction and for non adiabatic *gerade ungerade* symmetry breaking in HD will be briefly discussed.