Elementary processes in chemical dynamics

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Abstract - A review of recent work on molecular beam experiments performed
at the Chemistry Department of the University of Perugia is presented.
Measurements of intermolecular potentials for several systems and
preliminary results on reactive scattering of ^{1}D oxygen atoms are
discussed.

INTRODUCTION

The ability to model plasmas, lasers, flames and atmospheres is of fundamental importance
for modern applications of gaseous chemical kinetics. In order to develop such reliable
models one needs detailed information on the dynamics of the elementary processes involved.
The number and the variety of these processes are such that the values of the rate
parameters needed have to be obtained from several fields related to chemical kinetics; the
dynamical characterization of elementary processes is one of the major sources of this
information.

Our group in Perugia has been engaged for several years in the theoretical, computational
and experimental aspects of the dynamics of elementary chemical processes. For reason of
space I will limit these notes only to the aspects of the determination of intermolecular
potentials from experimental measurements by molecular beams, a problem which has been
pursued for several years, and to the reactions of ^{1}D oxygen atoms, which have been
undertaken only recently.

INTERMOLECULAR POTENTIALS

Intermolecular potentials, in spite of their weakness, are responsible of many macroscopic
properties of matter and play also an important role in chemical reactions since they
determine the asymptotic behaviour of the forces between the atoms and the molecules
involved.

Most information about these potentials comes from scattering studies and specifically from
the measurement of two main observables: the integral cross section and the differential
cross section. The two observables correspond to two basically different experimental
configurations. Integral cross sections are measured from the attenuation of a projectile
beam from a target, as a function of velocity, and differential cross sections from the
detection of the particles deflected at a given angle. Both types of experimental
configurations are operative in Perugia.

The theoretical approach to scattering has reached a high level of accuracy not only for
spherically symmetric systems, where the two body potential function depends only on the
distance, but also for more complex anisotropic systems, for which accurate approximations
have been developed. Particularly interesting is the interpretation of effects which can be
associated to quantum interferences between wave-like particles detected at a given angle
and coming from trajectories with different impact parameters. These effects show up in
both integral and differential cross section measurements and can be related to important
features of the potential. Thus the differential cross section, measured at suitable
values of collision energy as a function of the scattering angle, may show broad maxima
(called "rainbow" effect) and high frequency oscillations ("diffraction oscillations")
associated to the value of the potential well depth and to that of the finite distance
where the potential becomes equal to zero, respectively. The integral cross section,

measured as a function of the collision energy, may show the "glory" effect, an oscillatory feature related to the product between the depth of the potential well and the equilibrium distance. A trial-and-error fit with a flexible parametric expression of the experimental features described above and of the absolute value of the integral cross section, which fixes the long range behaviour of the interaction, allows us to reach a very accurate representation of the intermolecular potential.

The most recently investigated systems are reported in Table 1. These potentials are basic for understanding various gaseous properties, including transport phenomena. Particular care has been devoted to verifying the consistency between our accurate, microscopic measurements and the more averaged information coming from macroscopic measurements, when available.

TABLE 1. Systems recently investigated

System	Reference
Atom-atom (closed shell)	
He,Ne/Ne,Ar,Kr,Xe	(1,2,3)
Atom (closed shell)-molecule	(4)
N_2/He,Ne,Ar[a],Kr	(5,6,16)
O_2/He,Ne[a],Ar[a]	(5)
NO/He,Ne[a],Ar,Kr	(5,7)
Cl_2/He[a],Ne[a],Ar[a]	
CO_2/He	(8)
CH_4/Ne,Ar,Kr,Xe	(9)
Atom (open shell)-atom (closed shell) or molecule	(10)
$F(^2P)$/He,Ne,Ar,Kr,Xe,H_2[a],CH_4[a]	(11)
$O(^3P)$/He,Ne,Ar,Kr,Xe,H_2,CH_4	(12,13,14,15)
$N(^4S,^2D,^2P)$/Ar,Kr	(16)
$Cl(^2P)$/........[b]	

[a]To be published

[b]Work in progress

Complete information about the results can be found in the quoted literature, but I want to recall here our contribution for systems with open shell atoms and, in particular, for those where oxygen and fluorine atoms are involved. In these cases the interaction is more complicated since a manifold of potential energy curves is operative, due to the different states of the open shell atoms. The problem was disentangled by performing a magnetic analysis of the atomic beam. The selection of the atomic magnetic sublevels of the open shell atoms has allowed us to obtain unique information about these anisotropic interactions and to characterize the weak bonds of diatomic rare gas oxides and fluorides.

DYNAMICS OF ^{1}D OXYGEN ATOM REACTIONS

The study of chemical reactions of electronically excited oxygen atoms, $O(^1D)$, under single collision conditions is a very recent line of research in our laboratory and the results obtained appear to be very encouraging. The importance of these reactions appears clearly not only from a fundamental point of view but also for the role that $O(^1D)$ may play in the chemistry of stratosphere. Although rate constants have been measured for a number of reactions, very little is known about their dynamics.

The experiments were performed using the differential apparatus which was slightly modified for reactive scattering. The oxygen atom beam was produced in a high pressure radiofrequency discharge source in O_2/He and O_2/Ne mixtures; the presence of suitable amount of excited atoms has been tested through the well known reaction with H_2 giving OH + H. It is clear that reactions of excited oxygen atoms can be studied in presence of a large amount of ground state atoms only when the reaction rates of the latters are very low, so that their products can not be detected: this is the case of O + H_2.

The reactions investigated so far are those with HCl and HBr which fulfill the requirements described above. In both cases the halogen oxides produced in the reactions were detected and their angular and velocity distributions were measured. Both reactions show a predominant backward angular distribution in the center of mass but, while ClO shows also a significant forward scattering, BrO shows an equal amount of sideways and forward scattering. A large fraction of available energy is appearing in translation, 43% for ClO + H and
   60% for BrO + H. These results would suggest that these channels proceed mainly by direct abstraction of the halogen atom, with a possible contribution of an insertion mechanism, and that the differences between ClO and BrO distributions may be due to the different role of angular momentum. We have not be able to detect any product, halogen atoms or hydroxyl radicals, coming from the OH + X channels. The detection of these products is much harder than that of halogen oxides because OH is the lightest product of the reactions and therefore is likely spread all over the space, while the halogen atom signal is covered by the background arising from the fragmentation of elastically scattered hydrogen halides. A rough estimate, based on the failure to detect these products, would fix to one the upper limit of the ratio of cross sections for the channel leading to OH and that leading to XO. These estimates may still be consistent with the rate constant measured for $O(^1D)$ + HCl but not for that of $O(^1D)$ + HBr.

Acknowledgements

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