

# Ion-Neutral Collisions at Low Energies

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Binary collisions between ions and neutral particles, at low energies (below  $\approx 1$  eV), play a central role in the physics and chemistry of low density plasmas and ionized gases. Interstellar clouds, planetary ionospheres, laboratory and industrial plasmas and discharges are relevant examples of systems where ion-neutral collisions are particularly important. At low energies, possible collision processes include chemical reactions, charge transfer, excitation and quenching of internal energy states. Ion-neutral collision dynamics is generally dominated by strong attractive forces due to the presence of a charged particle. This leads to reactive cross-sections which are orders of magnitude larger than in the case of neutral-neutral collisions. A collection of recent papers on these topics can be found in Ref. [1].

Interstellar clouds are low density plasmas with temperatures ranging from about 10 to 80 K. After the observation in 1941 of the absorption bands of  $\text{CH}^+$  about seventy distinct molecules have been identified in these regions. Starting from the atomic constituents which are the end point of nuclear reactions in stellar atmospheres, three synthesis mechanisms have been considered: neutral-neutral reactions, ion-neutral reactions and heterogeneous catalysis on interstellar grains. At low temperatures, chemical reactions between neutral particles in the gas-phase are generally too slow and cannot explain the synthesis of interstellar molecules. On the contrary rate-coefficients of ion-neutral reactions remain generally large and often increase at low temperatures. Major advancements in understanding interstellar chemistry have been made possible by laboratory measurements demonstrating that ion-molecule reactions are a key step for molecular synthesis (see A. Dalgarno in Ref. [1]). A relevant example is the laboratory identification of the radiative association:



The study of the Earth's ionosphere has historically stimulated the investigation of ion-neutral reactions. This work was pioneered by Ferguson's

group at NOAA (National Oceanic Atmospheric Administration — Boulder, Co), where swarm techniques were first applied to this type of studies. Nowadays the main problems related to ionosphere composition are nearly fully understood and during the last decade experimental investigations have been extended to lower atmospheric regions. In particular, stratospheric measurements have shown that even when the relative ion concentration is small and ion-neutral reactions have a minor impact on the chemical equilibrium, ion distribution measurements can give important information about the composition of neutral species. It has been demonstrated that the ion mass distribution can be sensitive to ppbv (parts per billion-volume) concentrations of trace gases (see A. Arijs *et al.* in Ref. [1]).

Environmental studies have demonstrated in recent years the existence of tremendous problems due to the release into the atmosphere of combustion products and other industrial gases. This has stimulated the development of new analytical instruments suitable for the real-time control of gaseous emissions and the monitoring of pollutants in air. The ideal instrument should be reliable, flexible (*i.e.* capable of detecting different molecular species), easy to use and, possibly, cheap. Commercially available instruments include optical systems and mass spectrometers. Optical instruments are generally preferred in "field" applications while mass spectrometers find their main use for laboratory analyses. A major drawback of mass spectrometry is related to the ionization process of neutral species. Conventional electron-impact ionizers usually lead to extensive fragmentation of neutral molecules and produce an ion mass distribution which is often difficult to relate to the neutral sample composition. Moreover electrons do not allow selective ionization of specific molecular species. As a consequence, different neutral molecules can contribute to the same peak in the mass spectrum. A well known example is the electron impact ionization of carbon monoxide in air samples which leads to the simultaneous formation of  $\text{CO}^+$

and  $\text{N}_2^+$  ions, both having mass of about 28 a.m.u. In order to separate the two contributions, a high resolution magnetic mass spectrometer must be used.

The development of "smart" ionization methods can help to overcome the above problems, allowing extensive use of mass spectrometric methods, by means of simple, low resolution (and low cost) instruments. The use of ion-neutral reactions as a tool for chemical ionization of neutral gases is well known. Recently in Innsbruck, W. Lindinger extended this method to the ionization of pollutants in air by means of thermal energy ions. In contrast to standard electron-impact ionization, this method allows selective ionization and at the same time dramatically reduces fragmentation problems. As an example,  $\text{Kr}^+$  at thermal energies charge transfers only with CO and not with  $\text{N}_2$ . Thus the ionization of CO in air by means of low energy  $\text{Kr}^+$  ions does not produce a significant amount of  $\text{N}_2^+$ , allowing the detection of ppmv (part per million-volume) CO concentrations by means of a simple, low resolution quadrupole mass spectrometer.

As discussed above, ion-neutral collisions at low energies represent an important topic of molecular dynamics and their study finds relevant applications in different fields. Further advancements in both basic and applied research are related to the availability of accurate and detailed sets of data cross-sections and the branching ratios of reaction products. Moreover it is necessary to understand in detail the role of kinetic and ro-vibrational energies in collision processes.

## Experimental Methods

Over the past decade, different experiments have been designed for investigating the role of kinetic and ro-vibrational energies in ion-neutral collision processes. Experimental techniques can be grouped into three main categories: beam experiments, drift experiments and a third category which contains other methods such as ion traps, ion cyclotron resonance (ICR), thresh-

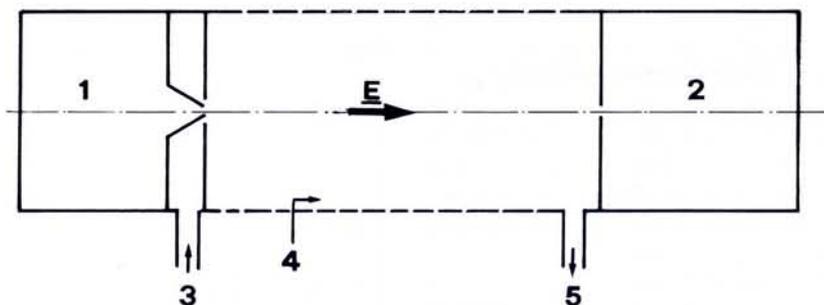


Fig. 1 — Schematic view of a flow drift tube apparatus: 1) ion source and mass selector, 2) mass analyser and ion detector, 3) buffer gas inlet, 4) neutral reactant inlet, 5) buffer gas outlet. A constant electric field  $E$  is applied to the drift region of the apparatus.

hold photo-electron photo-ion coincidence (TPEPICO) techniques and so on.

In principle, beams are ideal for studying reaction dynamics. The combination of an ion beam with a supersonic neutral beam [2] allows the measurement of differential cross-sections giving detailed information about the collision mechanism. Moreover crossed-beam methods can be used for preparing the initial internal state of the reactants and for analyzing the distribution of final states. In particular, apparatus providing simultaneous energy and angular analysis of product ions can be used for translational spectroscopy experiments. In these experiments, the final energy disposal is determined *via* energy conservation by measuring the translational energy of the product ions [3]. This method is particularly efficient in the case of reactions where product ions are distributed over a limited number of well spaced energy levels. Unfortunately the application of crossed-beam experiments at energies below a few eV is limited by severe experimental difficulties. A powerful approach for dealing with low-energy ion beams is based on the use of radio-frequency octopole guides. They consist of eight parallel rods connected to opposite phases of an RF oscillator. The effect of the RF field is to confine ions in the transverse direction [4]. Octopoles are ideal for integral cross-section measurements (see J.D. Burley *et al.* in Ref. [1]) because of the high efficiency in guiding low-energy primary ions and in collecting scattered ions.

From the experimental point of view the "easiest" approach to the study of low energy ion-neutral collisions is represented by drift-tube experiments. These methods belong to the general class of swarm techniques (a swarm is a large number of particles moving with a random velocity component in a buffer gas) [5]. In a typical experiment, ions are introduced into a tube filled with a non reactive neutral buffer gas to which some traces of the reactant gas

are added. Ions are carried downstream by the influence of an electric field  $E$  oriented along the tube axis (see Fig. 1). Because of collisions with the buffer gas, ions reach a drift velocity  $v$  which is proportional to the ion-mobility  $U$  and  $E$ . As a consequence, the laboratory ion velocity is randomly distributed with a component, equal to  $v$ , in the  $E$  direction and the kinetic energy is determined by both the drift velocity and the random thermal velocity. Wannier has shown that for an atomic ion, drifting through an atomic buffer gas, the mean kinetic energy  $KE_L$  measured in the laboratory frame is given by:

$$KE_L = 3 k_B T/2 + (m + M)v^2/2 \quad (2)$$

where  $k_B$  is the Boltzmann constant,  $T$  the buffer gas temperature,  $m$  the ion mass and  $M$  the buffer mass. Drift experiments are suited to work in the energy range going from thermal energies up to a few eV. This range can be extended at lower energies by cooling the tube. The approach has been developed by groups at Birmingham [6] and Heidelberg [7]. Alternative experimental methods useful for reaching very low-energies are based on low temperature ion-traps (see S.E. Barlow and G.H. Dunn in Ref. [1]) and supersonic jets (CRESU) (see B.R. Rowe and J.B. Marquette in Ref. [1]).

### Energy Dependence of Ion-Neutral Reactions

The simplest approach to ion-neutral collision theory is based on the Langevin model. At low energies the interaction is largely dominated by the long-range part of the potential. In first approximation this potential is given by the charge-induced dipole term:

$$V(R) = -\alpha q^2 / (2 R^4) \quad (3)$$

where  $q$  is the ion charge,  $\alpha$  is the isotropic polarizability of the neutral and  $R$  is the distance between the centres of mass of the interacting particles. The "collision" cross-section can be easily calculated if tunnelling effects are neglected and it is assumed that a collision occurs whenever the interaction

energy is sufficient to overcome the centrifugal barrier. The cross-section  $\sigma$  calculated in this way is inversely proportional to the relative velocity  $v_r$ . The corresponding Langevin rate-constant  $k_L$  is defined as:

$$k_L = \langle \sigma v_r \rangle \quad (4)$$

where  $\langle \rangle$  denotes the average.  $k_L$  is independent of the collision energy (see Fig. 2, curve b) and is given by:

$$k_L = 2 \pi q (\alpha/\mu)^{1/2} \quad (5)$$

where  $\mu$  is the reduced mass of the system. Typical values of the Langevin rate-constant range from  $10^{-10}$  to  $10^{-9}$   $\text{cm}^3 \text{s}^{-1}$ . These values are surprisingly close to experimental rate-constants for several reactions, for example exoergic proton-transfer reactions. This can be understood for exoergic reactions without activation energy because in this case the only condition for a reaction to occur is that particles are sufficiently close to each other. This condition is satisfied whenever reactants "hit" the repulsive core of the potential behind the centrifugal barrier.

Although the Langevin model has been used over years as a general tool for evaluating the order of magnitude of reaction rate-constants, several experiments in which rate-constants are measured as a function of kinetic or internal energies have shown strong deviations from Langevin predictions. This is not surprising because the Langevin model completely neglects the internal structure of the interacting particles and the details of the reaction mechanism. For many reactions which are slow at thermal energy, the kinetic energy dependence of the rate-constant goes through a pronounced minimum (see

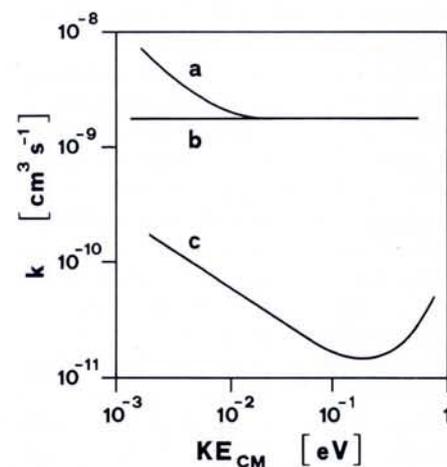


Fig. 2 — Three examples of the qualitative behaviour of the ion-neutral reaction rate-constant ( $k$ ) as a function of the centre-mass kinetic energy ( $KE_{cm}$ ): a) ions reacting with polar molecules, b) Langevin limit, c) reactions involving the formation of a complex.

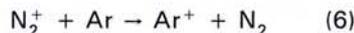
Fig. 2, curve c). This has been interpreted as evidence for a complex formation of the reactants. The minimum results because the complex lifetime which determines the reaction probability, is an inverse function of the relative velocity. At higher energies, the increase of the rate-constant is generally explained by the opening of endoergic channels.

Another class of ion-molecule reactions where the simple Langevin model cannot be applied involves polar molecules. At sub-thermal energies, a dramatic increase of the rate-constant is observed reaching values much higher than  $k_L$ . This has been explained by taking into account the fact that for polar molecule reactions, the collinear collision geometry is the most favourable. Rotational excitation will prevent this configuration. Thus an increase of rotational temperature will lead to a reduction of the reaction rate-constant. The finding has of course a strong impact on models explaining molecular synthesis in interstellar clouds.

#### Vibrational Effects

In the case of molecular ions it has been observed that drift experiments carried out with different buffer gases yield often different values of the reactive rate-constant. This fact has been related to the vibrational excitation (and quenching) of molecular ions by collision with the buffer gas (see W. Lindinger in Ref. [1]). The effect of vibrational energy on reactivity can be demonstrated in a direct and elegant way by coincidence photo-ionization techniques. In these experiments, detection of threshold electrons in coincidence with product ions enables an accurate determination of the quantum state of the reactant ions to be made [8].

Advances in the study of vibrational effects have made possible the development of the so-called "ion-monitor" technique [9]. This method has found wide application in drift experiments to analyze the vibrational energy distribution of ions. Recently in Orsay it has been applied also to ICR spectrometry for studying the radiative decay of vibrationally excited ions (see G. Mauclaire *et al.* in Ref. [1]). The method consists of using specific ion-neutral reactions which are strongly dependent on the vibrational state of the reactant ion. For these reactions the number of product ions is a measure of the number of vibrationally excited ions. As an example the fraction of molecular nitrogen ions with vibrational number  $v \geq 1$  can be measured by the charge-transfer reaction:



For the ground state  $\text{N}_2^+(X, v = 0)$  ions this reaction is endoergic by about 0.18 eV and does not proceed at a significant rate. A dramatic increase of the reaction rate-constant is observed when  $\text{N}_2^+$  ions are vibrationally excited: the  $\text{Ar}^+$  signal can then be used to estimate the fraction of  $\text{N}_2^+(X, v \geq 1)$ .

Chemical diagnostics of ion vibrational populations has made possible in the last few years the systematic study of vibrational quenching (and excitation) of diatomic ions in collision with neutrals. The large value of quenching rate-constants and its decrease with the increase of collision energy have been interpreted as due to the fact that collisions are driven by the long-range attractive tail of the potential and that transfer of vibrational energy occurs through the formation of a transient complex followed by vibrational pre-dissociation (see Fig. 3). This is an extension of the bound-free vibrational pre-dissociation of Van der Waals molecules to the free-free binary collision limit. In cases where a large attraction does not exist, vibrational relaxation is inefficient and its probability increases with relative collision energy. In this case the energy transfer arises from the short range repulsive forces. The criterion for whether the attractive or the repulsive potential will dominate quenching must relate to the ratio between the well depth  $\epsilon$  and the relative collision energy  $KE_{\text{cm}}$ . If  $KE_{\text{cm}} \ll \epsilon$ , attractive forces are expected to dominate the quenching process. On the contrary if  $KE_{\text{cm}} \gg \epsilon$ , vibrational relaxation will be driven by the repulsive potential. In experiments where  $KE_{\text{cm}}$  can be varied, one should observe a minimum in the quenching rate-constant as a function of  $KE_{\text{cm}}$ . So far such a minima have been reported for  $\text{O}_2^+$  in collision with Kr [10] and  $\text{NO}^+$  in collision with  $\text{CH}_4$ . Extensive studies in this field are currently in progress in several European laboratories (Orsay, Innsbruck, Aberystwyth and Trento).

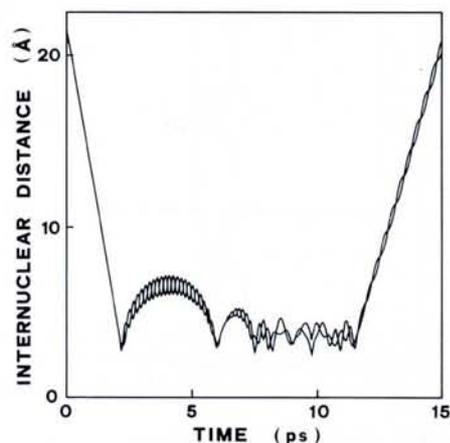


Fig. 3 — Example of a trajectory leading to vibrational relaxation of  $\text{O}_2^+$  in collision with Kr through the formation of a transient complex. Internuclear Kr-O distances are shown as a function of time. The intersection between the two lines is due to  $\text{O}_2^+$  rotation. Collision energy is 0.04 eV.

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