

# The problem of cooling ions in a low density ion trap.

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In recent years remarkable progress was achieved in the development of methods which allow one to measure cross sections or rate coefficients for ion-molecule reactions at very low energies or temperatures. In the majority of these experiments which have been reviewed recently<sup>1</sup> the reactant species are contained by a dense buffer gas which may be cooled cryogenically or by supersonic expansion. This high number density environment has the advantage of many thermalizing collisions but often leads to higher order kinetics. For example the process of radiative association is completely masked by three-body (termolecular) association and, particularly at low temperatures, the association reactions are often proceeding in the so-called "saturation regime".

This problem has been overcome by using ion trapping methods which have the unique feature that they can work at much lower number densities, since long interaction times lead to a significant increase in sensitivity. The first low temperature and low density collision studies have been performed in a Penning ion trap<sup>2</sup> and later in a ring electrode radio frequency (rf) ion trap.<sup>3</sup> The use of suitable inhomogeneous rf fields<sup>4</sup> has been further developed and systematic studies of radiative association processes became feasible.<sup>5</sup> Presently, experiments are performed in our laboratory in a 22-pole rf ion trap the nominal temperature of which can be varied between  $T_n=10$  K and 300 K.<sup>6</sup>

Various ion trap measurements have revealed that the presence of the buffer gas can significantly perturb the outcome of ion-molecule collisions and that it is sometimes misleading to extrapolate high pressure data to conditions such as prevailing in interstellar clouds. An example is the  $C_3H^++H_2$  system where, already at  $[He] > 10^{13}$  cm<sup>-3</sup>, hydrogen abstraction becomes suppressed by

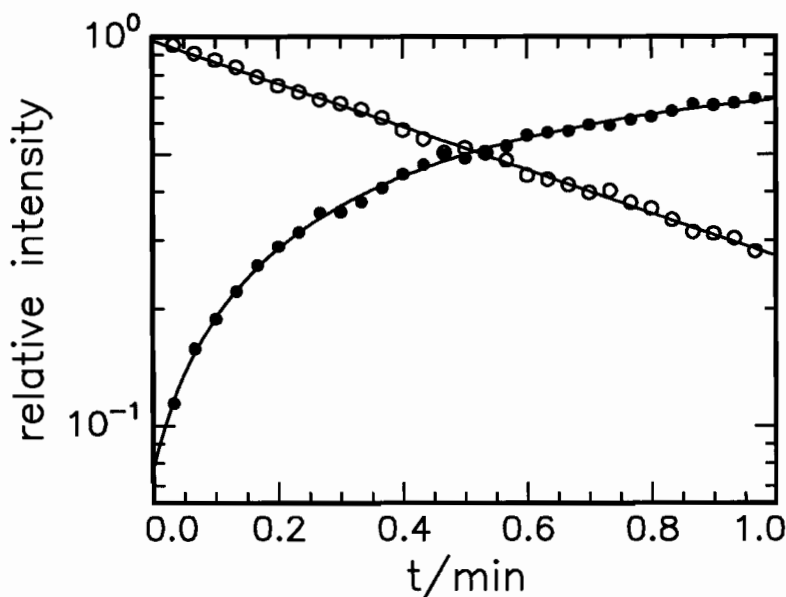


Fig. 1. Time evolution of  $C_2H_2^+$  ions stored in hydrogen target ( $[n-H_2]=1.6 \times 10^{10}$  cm<sup>-3</sup>) in the 22-pole ion trap at  $T_n=10$  K.<sup>9</sup> The exponential fits with a single time constant (solid lines) indicate complete thermalization of the ions. The by far dominant reaction is radiative association. Formation of mass 27 which is predominantly due to  $C_2HD^+$  is here out of scale since purified hydrogen ( $[HD]/[H_2]=4 \times 10^{-5}$ ) was used.

ternary association.<sup>7</sup> Another example is the association reaction of  $\text{CH}_3^+$  with CO where the long life-times of the collision complexes lead to saturation problems as discussed recently by Horning et al.<sup>8</sup> However, these experiments have also shown that measurements at very low total number densities suffer from the disadvantage that the ions may not experience sufficient collisions to be really thermalized to the cold ion-trap environment. This contribution will discuss briefly these difficulties and will indicate some solutions to overcome such problems.

In our ion trap experiments, reactions are studied by periodically filling the trap with ions from an external source and by extracting its content after various times for mass analysis. Depending on the reaction process, repetition periods between ms and many minutes are chosen. The initially hot ions are usually cooled by inelastic collisions with neutrals whose temperature is determined by that of the electrodes and surrounding walls. At very low collision rates and long storage times the coupling of the internal degrees of freedom to the low temperature black-body radiation field becomes also important. It is rather safe to assume that equilibrium conditions are reached if the rate for attenuating the primary ions and for forming products becomes independent on the storage time.

As a typical example, Fig. 1 shows the temporal change of acetylene ions stored at a temperature of 10 K in hydrogen. The  $\text{C}_2\text{H}_2^+ + \text{H}_2$  system has attracted a lot of interest in the last years and various experimental and theoretical studies have focused on the question whether the formation of the  $\text{C}_2\text{H}_3^+$  products is endothermic and/or hindered by a barrier (see Ref. 9 and references therein). Early ion trap measurements<sup>5</sup> were confused by  $\text{C}_2\text{H}_3^+$  background ions which were formed during the thermalization of the primary ions. This problem was significantly reduced by utilizing very low  $\text{H}_2$  number densities and by extending the storage time up to 1 min. It is obvious from the exponential functions which fit the data nicely that the ions are really in thermal equilibrium. Within the shown range the only products are  $\text{C}_2\text{H}_4^+$ . They are almost exclusively formed by radiative association since three-body collisions are negligible at the low  $[\text{H}_2]$ .

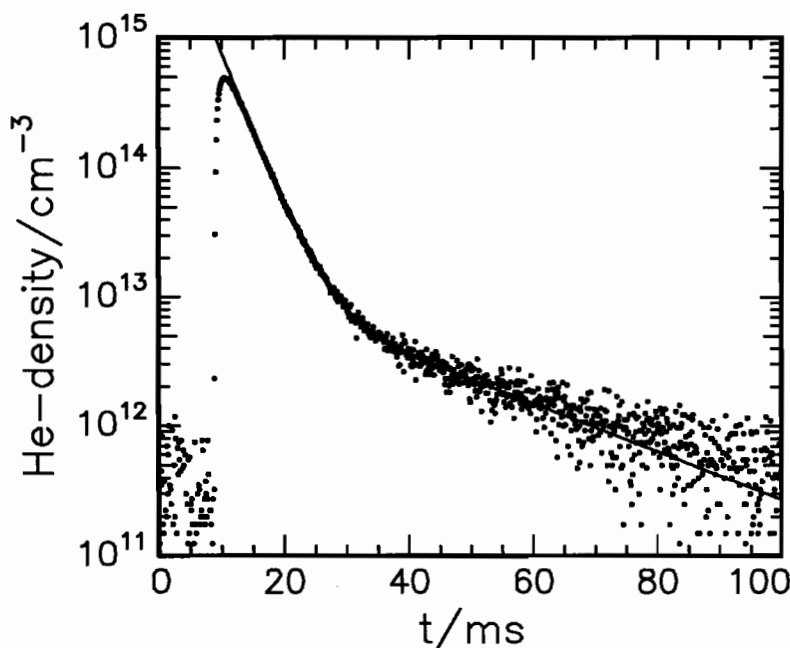


Fig. 2. Time dependence of the He-gas pulse injected into the ion trap for thermalizing the ions using a piezoelectric pulsed valve. The FWHM of the pulse is 5 ms. As can be seen from the fit, the decay of the number density after the pulse is described by two time constants, 3.5 ms and 23 ms. The first one is determined by the small volume ( $\sim 15 \text{ cm}^3$ ) of the box surrounding the trap electrodes and the conductance of the entrance and exit tube, the second one by the volume of the apparatus.

It is not always possible (or economical) to operate at very low number densities and to wait long enough for the trapped ions to be internally cooled by radiation. Problems arise especially if the ions undergo reactions with traces of the background gas. In such cases the ions can be thermalized by injecting them together with a very intense, short He pulse into the trap. For this purpose an additional piezo electric valve was included into the apparatus. As can be seen from Fig. 2 peak number densities up to  $10^{15} \text{ cm}^{-3}$  can be obtained. During the gas pulse (FWHM 5 ms) the ions make in the order of  $10^4$  collisions. Within 20 ms, the number density drops with a fast time constant of 3.5 ms by 2 orders of magnitude. The subsequent decay has a larger time constant of 23 ms; however, in most cases the rates of ternary processes involving the He buffer gas atoms are negligible after 100 ms. This measuring procedure is presently used to thermalize  $\text{CH}_3^+$  and  $\text{C}_2\text{H}_2^+$  ions for studying their radiative association with CO at low temperatures.

There remains finally the question: what is the actual temperature of the trapped ions? Long storage times or many collisions lead to equilibrium conditions but not necessarily to a temperature which is given by the black-body radiation field or the buffer gas. It is also well known from Paul-traps that ion-neutral collisions lead to a transfer of energy from the radio-frequency field to the ions. This heating process is significantly reduced in traps with a wide field free region (ring electrodes or 22-pole geometry) as shown by numerical simulations.<sup>4</sup> Also various experimental tests based on temperature-dependent rate coefficients (e.g. for the reaction  $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ , for the formation of  $\text{He}_2^+$ -dimer ions or the growth of  $\text{H}_n^+$  clusters) have lead to the conclusion that the coldest ion cloud (at a nominal temperature  $T_n = 10 \text{ K}$ ) is characterized by  $15 \pm 5 \text{ K}$ . In order to measure more directly the translational and internal temperature an experimental program has been started using high resolution laser methods. As a first result the translational temperature of  $\text{N}_2^+$  ions stored in Ar gas was derived from laser induced charge transfer.<sup>10</sup> In this study a single-mode diode laser (783–787 nm) excited the  $\text{N}_2^+$  ions into the  $A, v=2$  state. Between 300 K and 50 K the temperatures derived from the Doppler profile were in good overall accordance with the nominal values of  $T_n$ . To extend the accessible temperature range for these spectroscopic methods down to 10 K one must trap suitable ions in He or  $\text{H}_2$  buffer gas. One candidate is  $\text{He-N}_2^+$ , a weakly bound (14 meV) van-der-Waals-cluster which is known to undergo laser induced predissociation after X-A excitation of the slightly perturbed  $\text{N}_2^+$ .<sup>11</sup> Corresponding experiments are in preparation.

- 1 M. A. Smith in: *Current Topics in Ion Chemistry and Physics*, Vol. 2, C. Y. Ng, T. Baer, and I. Powis, eds., Wiley, New York (1993).
- 2 S. E. Barlow, G. H. Dunn, M. Schauer, *Phys. Rev. Lett.* **52**, 902 (1984) and J. Luine, G. Dunn, *Ap. J.* **299**, L67 (1985).
- 3 D. Gerlich, G. Kaefer, *Ap. J.* **347**, 849 (1989).
- 4 D. Gerlich, *Adv. in Chem. Phys.* **LXXXII**, 1 (1992).
- 5 D. Gerlich and S. Horning, *Chem. Rev.* **92**, 1509, (1992).
- 6 D. Gerlich, *J. Chem. Soc., Faraday Trans.* **89**, 2199 (1993).
- 7 A. Sorgenfrei and D. Gerlich in: *Physical Chemistry of Molecules and Grains in Space*, Book of Proceedings, C. Troyanowsky (ed.), AIP, New York, (1994).
- 8 S. Horning, D. Gerlich, D. Smith, *J. Chem. Phys.* subm. (1994)
- 9 D. Gerlich in: see Ref. 7.
- 10 W. Paul and D. Gerlich in: ICPEAC 1993, *Book of contributed papers*, eds. T. Anderson *et al.* 807, (1993).
- 11 E. J. Bieske, A. M. Soliva and J. P. Maier, *J. Chem. Phys.* **94**, 4749 (1991)