

Experiments with Trapped Ions and Nanoparticles

By *D. Gerlich, J. Illemaann, and S. Schlemmer*

Faculty of Natural Science, Technical University of Chemnitz, 09107 Chemnitz, Germany

This contribution summarizes experimental work which has been performed predominantly in our laboratory using ion guides and specific traps for studying ions, molecules and dust particles under astrophysical conditions. After a short reminder of the basics of the technique and a brief discussion of our newest device, the nanoparticle trap, we shall review experimental results for low temperature gas phase collisions with H₂. In the last part we will summarize our present activities related to chemistry involving cold H atoms.

1. Introduction

Despite the fact that our knowledge on the role of hydrogen in space has significantly increased in recent years due to a combination of extensive new observations and astrophysical model calculations with fundamental theory and detailed innovative experiments, there are still many unsolved problems related to the interaction of H or H₂ with ions, radicals, surfaces and also photons. The most obvious example is the formation of H₂ itself; other examples include specific state to state cross sections, ortho-para transitions in H₂, H-D isotopic scrambling, formation and destruction of the H₃⁺ molecule, or the role hydrogen clusters and anions. In addition to gas phase reactions we will discuss in this paper our most ambitious goal, the detection of catalytic formation of H₂ molecules on a interstellar dust analogue localized in a cold trap.

2. Experimental: Ion guides and particle traps

2.1. Inhomogeneous RF or AC fields

From the point of view of experimental techniques, our research is predominantly based on the use of specific inhomogeneous, time-dependent, electrical fields, $\mathbf{E}_0(\mathbf{r}, t) = \mathbf{E}_0(\mathbf{r}) \cos(\Omega t)$. The method to trap or guide ions and many applications in ion physics and chemistry has been documented thoroughly in [Gerlich 1992]. For practical applications, there are two very important facts to remember. (i) In good approximation the main influence of the oscillatory force can be described by the so called effective potential $V^* = q^2 \mathbf{E}_0(\mathbf{r})^2 / 4m\Omega^2$, where m and q is the particles mass and charge, respectively. (ii) In order to stay within the range of validity of this approximation, one has to operate under conditions such that $\eta < 0.3$, where η is the adiabaticity parameter defined by $\eta = 2q |\nabla \mathbf{E}_0(\mathbf{r})| / m\Omega^2$.

This basic principle is quite general and the effective potential can be used for confining electrons (Ω must be in the GHz range), ions (radio frequency range), clusters or charged microscopic particles (audio frequency, AC voltages). Typical applications include strong focusing lenses in accelerator physics, the well-known Paul trap invented in the 1950's or the Guided Ion Beam technique developed in the 1970's. For a detailed review of the historical development and of specific applications see [Gerlich 1992]. This and other confinement techniques in combination with laser cooling and detection schemes have been the foundation for a number of precision measurements [Schneider 1999].

2.2. Temperature variable ion traps

Very important for studying gas phase reactions at temperatures and densities of interstellar interest are special traps with wide field free regions where the ions are cooled to the temperature of the cold electrodes or surrounding walls. Examples include the temperature variable 22pole trap and the ring electrode trap, which both have been described in detail [Gerlich 1994, Gerlich 1995]. These innovative devices have been utilized for experimental investigations of a variety of ion-molecule reactions. A proof of the unique sensitivity of these traps are the systematic studies performed on radiative association, a reaction mechanism of astrochemical importance [Gerlich and Horning 1992, Gerlich 1994]. In recent years, more versatile experimental setups, based on this technique, have been constructed by applying laser methods for ion preparation or detection [Schlemmer 1999 and 2000] or by integrating atomic beams [Haufler 2000]. This latter apparatus is now being used for studying reactions between stored ions and a cold effusive beam of H atoms.

2.3 The NPMS technique

Based on the fact that the effective potential can be tailored for many purposes we have designed a special trap for observing and characterizing one *single* nanoparticles over long times. Whereas in the above mentioned case of a cold ion cloud a wide field-free region is required, here the precise localization of the object determines the field geometry. This is best achieved with a Paul trap, i.e., with a quadrupolar field the effective potential of which is harmonic. In practice we have used a rather complicated electrode arrangement in order to fulfill a variety of boundary conditions [Schlemmer 1999a, 99b]. Briefly, the trap consists of two cones opposing each other at a distance of 6.6 mm. These two electrodes are surrounded by eight rods which approximate the usual ring electrode of a Paul trap. This open design has been chosen in order to obtain either a large solid angle for optical detection or to measure angular distribution of scattered light. Moreover the trap volume can be accessed through several ports with additional tools such as the particle source, the laser beam and an electron gun. The benefit of this new techniques lies in the combination of the following features: long time trapping of a single particle, isolation of the particle with respect to disturbing surfaces and gases, i.e., UHV- and low temperature conditions, very good localization of the particle (sub- μm). This makes it perfectly suited to sensitive optical detection (scattering, fluorescence, absorption, etc.)

One of the first obvious applications of this trapping technique is based on its mass resolving power in a mass range which is otherwise not accessible (NPMS: nanoparticle mass spectrometry). For this purpose, the oscillatory macro-motion of the particle is monitored using a collimated beam from a diode laser ($\sim 2.5 \text{ mW/mm}^2$) which is directed near the center of the trap. The light scattered from the particle is collected by a lens, transferred outside the vacuum and transmitted to an avalanche photo diode. The eigen-frequencies are determined by Fourier transforming the detected signal. It is important to note that the particles trajectory has to remain close enough to the center of the quadrupolar field, where both the electrostatic and the effective potential are harmonic. In this case the derived eigen-frequencies, which are proportional to the particles q/m ratio, are independent on the amplitudes. Controlled charging/discharging of the particle in steps of single elementary charges leads to the absolute charge and mass. Thanks to the long term stability of our experimental setup the particles q/m ratio can be followed over days.

First test measurements have been performed with 500 nm diameter SiO_2 spheres (nominal mass $m \sim 10^{-16} \text{ kg}$, $\sim 10^9$ SiO_2 molecules, $\sim 10^{11} u$). For these particles a mass resolution $\Delta m/m \sim 10^{-4}$ has been achieved in a single ten second measurement. Recording the modulated signal over minutes improves the resolution to the ppm regime (for details see Schlemmer *et al.* 1999]. Since the mass determination is based on a frequency measurement there are several possibilities to further improve the resolution significantly. Presently we extend the method to smaller particles by replacing the light scattering detection scheme with a LIF based method. For particles with a diameter of a few nm the secular frequencies are increasing from the few Hz- towards the kHz-regime reducing the time to determine q/m by FFT method. In addition low frequency noise which is hard to be rejected will no longer play a

role. Also gravitational compensation is no longer necessary. In total we are confident that single molecule mass resolution will become feasible. Planned applications of this method in combination with hydrogen atoms and molecules will be discussed below.

Another result which is also important for understanding catalytic properties of interstellar dust particles, is the precise registration of the actual charge of the particle and its distribution on the surface. In general, photons, electrons, ions or suitable neutrals can be used to change the charge of a stored nanoparticle in a controlled way. In a recent experiment [Schlemmer 1999b] one single SiO₂ sphere ($d = 500$ nm) has been bombarded with fast electrons. The individual events of charge jumps have been followed online step by step. From a series of such data quantitative values for the secondary electron emission yield have been derived.

Summarizing this experimental section we want to point out that confinement of charges in a fast oscillating field is a very versatile tool. Devices such as octopole beam guides, 22-pole ion traps, or nanoparticle traps open up a wide range of experiments which are important to understand the physical and chemical behavior of interstellar matter. In the following we summarize earlier applications of these methods to interactions of ions with the hydrogen molecule. In the last part we describe our present activities for determining sticking coefficients of H₂ and H on grain surfaces and for - finally - observing the formation of hydrogen molecules on dust grain equivalents.

3. H₃⁺, H⁺+H₂ collisions, and deuterated variants

The H₃⁺ molecular ion and the simple collision system H⁺+H₂ and isotopic variants play a specific role both in the chemistry of interstellar space and in our fundamental understanding of simple chemical reactions. Using the ion guiding and trapping technique, various aspects of this system have been studied over the last decades. Results include state-to-state differential cross sections [Gerlich 1977, Teloy 1978], integral cross sections and thermal rate coefficients for isotopic scrambling [Gerlich 1982] radiative and ternary association [Gerlich 1992b], rate coefficients for the growth of clusters [Paul 1995], and many specific results such as rate coefficients for ortho to para conversion [Gerlich 1990]. A variety of specific results from trapping experiments and from a merged beam arrangement can be found in [Gerlich 1992a].

Some of this experimental information already has been used in modeling certain aspects of the energy balance of the ISM; however it may be necessary that more detailed information has to be incorporated in modern models, for example, in order to understand the intensities of the H₂ ro-vibrational and pure rotational lines detected recently by ISO, or for predicting the correct branching ratios in reactions where D atoms compete with H atoms. Useful for such tasks are the numerical predictions which can be calculated from a dynamically biased statistical theory [Gerlich 1982]. This theory which has been developed some time ago [Gerlich 1977], describes in great detail the above mentioned experimental results. A few details concerning the inclusion of dynamical constraints which have been derived from trajectory calculations, have been published in [Gerlich 1980]. The statistical model also accounts in good approximation for the long range attraction and for restrictions imposed by the conservation of nuclear spin and parity. This is especially important for predicting correctly ortho to para transitions in the highly symmetric system H⁺ + H₂ [Gerlich 1990]. One also should be aware that isotopic fractionation, e.g. in D⁺ + H₂ collisions is strongly influenced by simple symmetry selection rules. From an experimental point of view, a renaissance of this simple statistical theory will become interesting for describing the results, we plan to measure for the H₂⁺ + H collision system.

The molecular H₃⁺ ion plays an important role in the subsequent ion - molecule chemistry. Since formation via radiative association of H⁺ + H₂ is negligible, the gas phase reaction of H₂⁺ with H₂ leading to H₃⁺ + H is an important step in the H - H₂ balance. This reaction has been studied using the

merged beams technique and also in a single beam arrangement using REMPI preparation of rotational states of H_2^+ [Glenwinkel-Meyer and Gerlich 1997].

4. Collisions of H_2 with other important ions

There are a variety of other basic reactions involving hydrogen molecules which may or may not influence its thermal or chemical balance or which are important for forming molecules of special interest. Examples we briefly refer to include the hydrogen anion H^- , the first step in the formation sequence of hydrocarbons and the reactions leading to ammonia.

For the anionic system $\text{H}^- + \text{D}_2$ and $\text{D}^- + \text{H}_2$ the importance of tunneling has been shown experimentally by measuring in a guided ion beam experiment the absolute integral and differential cross sections for reactive scattering at energies below the barrier [Haufler 1997]. Comparison of the integral cross sections for the two isotopic variants reveals a significant isotope effect. The measured barrier heights of 350 ± 60 meV for $\text{H}^- + \text{D}_2$ and 330 ± 60 meV for $\text{D}^- + \text{H}_2$ indicate that, at low temperatures, scrambling via this reaction is as inefficient as via the neutral analogue, $\text{H} + \text{D}_2$.

The endothermic reaction $\text{C}^+ + \text{H}_2(j) \rightarrow \text{CH}^+ + \text{H}$ has been studied experimentally and theoretically in the threshold region and an interesting effect of reagent rotation has been resolved in the experiment which is consistent with the *frozen nuclear spin* (FNS) approximation [Gerlich *et al.* 1987]. The large endothermicity of this reaction makes it extremely inefficient at low temperatures, as can be seen from the thermal rate coefficients published in this paper. Therefore, radiative association, i.e. direct formation of CH_2^+ via emission of a photon, becomes an important process in the formation of hydrocarbons [Gerlich & Horning 1992]. Precise values have been measured in the 22pole trap at low temperatures for p- H_2 , n- H_2 and n- D_2 . The results can be found in [Gerlich 1994].

The gas phase formation of ammonia starts by the reaction $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$, followed by a chain of hydrogen abstraction reactions. This system is of special interest since it is almost thermoneutral and one does not yet know, whether an activation barrier hinders the NH^+ formation or whether it is actually endothermic by about 12 meV. The reverse reaction $\text{NH}^+ + \text{H}$ and the fine structure dependence will significantly increase our knowledge on this simple reaction which plays a key role in the interstellar formation of ammonia. Ion beam and ion trap results have been reported for $\text{N}^+ + \text{D}_2 \rightarrow \text{ND}^+ + \text{D}$ in [Tosi 1994].

5. Collisions involving H atoms

Despite the fact that H is the simplest atom, experiments with a well prepared ensemble of these radicals are still a challenge. In the following we report briefly on two related activities, going on in our laboratory. These activities are based on the development of an intense temperature variable H or D atom beam source. Combining this source with a special 22pole trap device [Haufler *et al.* 2000] allows us to study a variety of important and interesting gas phase processes under conditions of the ISM. The integration of the H atom beam into the nanoparticle trap will allow to study surface mediated processes such as sticking and desorption or catalytic activities.

In the gas phase we will begin to study the interaction between H atoms and ions such as H_2^+ , NH^+ , CH^+ , C_2H_3^+ , C_3H_2^+ , etc. For sufficiently large molecular ions it is expected that an H atom just "sticks", i.e., the collision complex gets stabilized via radiative emission very efficiently [Herbst 1999]. A recent related issue is whether such charged or neutral molecules can be the missing link between atomic and molecular hydrogen. The catalytic cycle proposed is $\text{XY}^+ + \text{H} \rightarrow \text{XYH}^+$ followed by $\text{XYH}^+ + \text{H} \rightarrow \text{XY}^+ + \text{H}_2$.

A typical example which already may fulfill these assumption is the interaction of H atoms with $C_2H_3^+$ and $C_3H_2^+$. The reverse channel, i.e., collisions of $C_2H_2^+$ with H_2 have been extensively investigated [Gerlich 1993]. Very recently the rotational dependence of $C_2H_3^+$ formation has been measured by infrared excitation of the acetylene ion [Schlemmer 2000]. Despite all these activities the details of the asymptotic potential surface are unknown and one does not yet know whether under interstellar conditions the chemical equilibrium $C_2H_2^+ + H_2 \leftrightarrow C_2H_3^+ + H$ is determined by the asymptotic energies or by some small barriers. The next more complicated system concerns the $C_3H_3^+$ complex. Low temperature studies of radiative association vs. hydrogen abstraction have revealed a very interesting temperature dependence in $C_3H^+ + H_2$ collision [Sorgenfrei 1994].

6. H atoms and NPMS

The overall importance of grain surfaces for processing interstellar matter is generally accepted. Nonetheless one has to admit that not much quantitative knowledge exists on the actual role, these nanometer or micrometer large particles play in the chemical balance, e.g. in the catalytic formation of H_2 . For learning more about this fundamental process, interesting new experimental activities have been started in recent years some of which are discussed in this book. In the following we point out that, in comparison to these surface science activities, our NPMS technique follows a different approach which accounts more for the special properties of dust grains. One important difference between macroscopic surfaces and nanoparticles is that quantum confinement affects the band structure, optical properties and also the chemical behavior. Other differences are caused by finite size effects and the large surface to volume ratio. Another important aspects is that in most cases interstellar dust particles are charged.

As reported above the mass resolving power we have achieved so far is already suited to study in average processes such as adsorption and desorption of H and H_2 on nano-surfaces. In this way, coefficients for sticking and desorption or parameters describing mobility, diffusion, reaction, and tunneling can be determined quantitatively. Based on our present precision, the adsorption of one single hydrogen atom can be monitored simply as a 10^{-5} increase in mass. This corresponds to a jump in the secular frequency of the particles motion a factor of ten larger than the resolution. The ultimate goal of this NPMS technique is the direct observation of the catalytic activity of the grain by recording step by step the adsorption of individual H atoms and the desorption of hydrogen atoms or molecules.

Interesting questions are related to the finite size of the particle. For example the temperature of a structure consisting of 1000 atoms is raised by 15 K if the H-H recombination energy is distributed statistically among all degrees of freedom of the particle. If energy transfer is slow local heating will lead to even higher temperatures followed by evaporation or may be also chain reactions. Significant jumps in temperature can also be induced by absorbing a single photon or cosmic ray. Due to the small heat capacity it can be questioned in general, whether the nanoparticles "temperature" is in equilibrium with the "ambient temperature".

There are various laboratory approaches to find realistic analogues to interstellar dust grains. In our trapping experiment the 500 nm SiO_2 particles will be replaced by smaller particles and other nanoparticles containing Si and C and other ingredients. Using molecular beam techniques the particles may also be coated with realistic icy mantles which have been identified on interstellar grains by μm observations.

In conclusion we hope that the combination of an H-atom beam with our new NPMS technique will provide quantitative data needed to explain the abundance of molecular hydrogen in the interstellar matter. However, we also will continue to search for efficient low temperature catalytic gas phase cycles, producing H_2 as well.

Acknowledgement

Most of this work has been funded by the Deutsche Forschungsgemeinschaft via the *INK Methods and material systems for the nanometer scale* and in the *SPP Star formation*.

References

- Gerlich, D. (1977) Ph.D. Thesis, University Freiburg, Germany
- Gerlich D., Nowotny U., Schlier Ch., and Teloy E., (1980) *Complex Formation in Proton - D₂ Collisions*, Chem. Phys. **47**, 245.
- Gerlich, D. (1982) Calculations of reactive cross sections and rate coefficients for isotopic variants of the H⁺ + H₂ - system in the energy range 2 meV - 1.8 eV, in: Symposium on Atomic and Surface Physics, Eds. W. Lindinger, F. Howorka, T.D. Märk, and F. Egger, pp. 304 -309
- Gerlich D., Disch R., and Scherbarth S., (1987) *C⁺+H₂(j) @CH⁺+H. The effect of reagent rotation on the integral cross section in the threshold region* J. Chem. Phys. **87**, 350.
- Gerlich D., (1989) *Reactive scattering of N⁺+H₂ and deuterated analogs: Statistical calculations of cross sections and rate coefficients* J. Chem. Phys. **90**, 3574
- Gerlich D., (1990) *Ortho - para transitions in reactive H⁺+H₂ collisions* J. Chem. Phys. **92**, 2377.
- Gerlich D., (1992) *Inhomogeneous Electrical Radio Frequency Fields: A Versatile Tool for the Study of Processes with Slow Ions*. Adv. in Chem. Phys., **LXXXII**, 1.
- Gerlich D. and Horning S., (1992) *Experimental Investigations of Radiative Association Processes as related to Interstellar Chemistry*, Chem. Rev., **92**, 1509.
- Gerlich D., (1993) *Experimental Investigations of Ion-Molecule Reactions Relevant to Interstellar Chemistry*, J. Chem. Soc., Faraday Trans. **89**, 2199.
- Gerlich D., (1994) *Recent Progress in Experimental Studies of Ion-Molecule Reactions Relevant to Interstellar Chemistry* in: "Molecules and Grains in Space", I. Nenner (ed.), AIP Press, New York, 489.
- Gerlich D., (1995) *Ion-Neutral Collisions in a 22-pole trap at very low energies* Physica Scripta, **T59**, 256.
- Glenewinkel-Meyer T., Gerlich D., (1997) *Single and Merged Beam Studies of the Reaction H₂⁺ + H₂ @ H₃⁺ + H*, Israel J. of Chem., **37**, 343.
- Haufler E., Schlemmer S., and Gerlich D., (1997) *Absolute Integral and Differential Cross Sections for the Reactive Scattering of H + D₂ and D + H₂*, J. Phys. Chem., **101**, 6441.
- Haufler E., Schlemmer S., and Gerlich D., (2000) *The Transverse Ion Trap Apparatus: Combination of an 22pole Ion Trap with a molecular beam*, to be submitted to Rev. Sci. Instrum.
- Herbst, E., Le Page, V., (1999) *Do H atoms stick to PAH cations in the interstellar medium?*, Astron. Astrophys. **344** 310.
- Paul, W., Lücke B., Schlemmer S., and Gerlich D., (1995) *On the Dynamics of the Reaction of Positive Hydrogen Cluster Ions (H₅⁺ to H₂₃⁺) with Para and Normal Hydrogen at 10 K* Int. J. Mass Spectrom. Ion Proc., **150**, 373
- Schlemmer S., Illemann J., Wellert S., and Gerlich D., (1999a) *Non-destructive, Absolute Mass Determination of Sub-micrometer Sized Particles in a Paul-type Trap*, in: Trapped Charged Particles and Fundamental Physics, D. Schneider (ed.), AIP press, New York.
- Schlemmer S., Illemann J., Wellert S., and Gerlich D., (1999b) *Laboratory Experiments for the Investigation of Interstellar Dust Analogues*, in: The Physics and Chemistry of the Interstellar Medium, V. Ossenkopf (ed.), Shaker Publ.Co., Aachen.
- Schlemmer S., Kuhn T., Lescop E., and Gerlich D. (1999c), *Laser excited N₂⁺ in a 22-Pole trap, Experimental Studies of Rotational Relaxation processes*, Int. J. Mass Spectrom. Ion Proc. **185**, 589
- Schlemmer S., Illemann J., Wellert S., and Gerlich D. (2000a), *High Resolution Mass Determination of a single Femtogram particle*, submitted to Science.
- Schlemmer S., Lescop E., v.Richthofen J., and Gerlich D. (2000b) *Rotational dependence of the endothermic reaction C₂H₂⁺ + H₂ @ C₂H₃⁺ + H studied by infrared excitation of the acetylene ion*. submitted to J. Chem. Phys.
- Schneider D. (ed.) (1999) *Trapped Charged Particles and Fundamental Physics*, AIP press, New York.
- Sorgenfrei A., Gerlich D., (1994) *Ion-Trap Experiments on C₃H⁺+H₂: Radiative Association vs. Hydrogen Abstraction* in: "Molecules and Grains in Space", I. Nenner (ed.), AIP Press, New York, 505.
- Teloy, E. (1978) in *Electronic and Atomic Collisions*, ed. by G. Watel, North-Holland, Amsterdam, 591
- Tosi P., Dmitrijev O, Bassi D., Wick O., Gerlich D., (1994) *Experimental Observation of the Energy Treshold in the Ion-Molecule Reaction N⁺+D₂@ND⁺+D*, J. Chem. Phys. **100**, 4300.