Spectroscopy and Chemical Dynamics

John P. Maier* and Stefan Willitsch*

Abstract: Chemical physics and molecular spectroscopy are topics with a traditionally strong emphasis in the department. Current research focuses on the spectroscopic characterization of transient molecules present in interstellar space and the preparation, control and chemistry of ultracold molecules and ions in the gas phase.

Keywords: Astrophysics · Cold chemistry · Cold molecules · Interstellar molecules · Laser spectroscopy

Spectroscopy of Interstellar Molecules

John P. Maier

In order to learn about the structure of transient species, both neutral and ionic, so that they can be identified by spectroscopy, a number of approaches have been developed to detect and identify their electronic transitions for the first time. This is fundamental research but the results have important applications in terrestrial and astronomical environments.

Of particular interest to the research group of ***John P. Maier***[1] have been carbon-containing chains and rings. These are of relevance to regions of interstellar space- diffuse clouds, circumstellar shells, comets and atmospheres of planets. On earth they are intermediates in chemical reactions, flames and discharges. Once the electronic spectra of these species are known, they can be monitored there, and the details of the transitions provide information on the physical conditions of the media, such as temperature, pressure. There are three main obstacles to the detection and identification of the electronic spectra; their production in copious amount from precursors, the availability of sensitive methods for detection and the knowledge of the expected wavelength range of the transition. Because of the transient nature of the species, the most efficient means to generate them has proven to be the use of supersonic expansions coupled with discharges or laser vaporization. This enables a variety of exotic radicals to be formed under controlled conditions – collision free, at very low temperatures as is pertinent for interstellar space <100 K, and in a molecular beam. The concentrations thus formed (10^8 cm^{-3}) are sufficient for their detection by sensitive laser-based techniques. A number of approaches are used, ranging from the use of resonance enhanced two photon-ionisation (REMPI) for the neutrals to degenerate four-wave mixing (D4WM) and cavity ring-down (CRD) for both neutrals and ions, as well as radiofrequency (RF) traps for cations. Prior to the gas phase experiments, it is an advantage to locate the electronic transitions in 6 K neon matrices. This is based on the implantation of mass-selected species in the inert surroundings of the neon atoms.

The following illustrates the methodology and information forthcoming. A method has been developed and used with great success to locate the electronic transitions of mass-selected species in neon matrices. This is a combination of mass spectrometry and matrix isolation techniques. The instrument built is hitherto unique worldwide (Fig 1). Specially designed sources produce the cations or anions of interest with currents around nA. Following mass selection a neon matrix is grown, a 100–200 µm thin film on 1 cm^2 sapphire surface at 6 K. The concentration of the mass selected ions, or the corresponding neutrals produced by subsequent neutralization, is adequate to measure the absorption spectrum by passing light through the thin wedge of the matrix and propagating the light over 1 cm in a waveguide manner. Detection is *via* a CCD camera.

Correspondence: Prof. J. P. Maier*
Department of Chemistry
University of Basel
Klingelbergstrasse 80
CH-4056 Basel
E-mail: j.p.maier@unibas.ch
Prof. S. Willitsch*
Department of Chemistry
University of Basel
Klingelbergstrasse 80
CH-4056 Basel
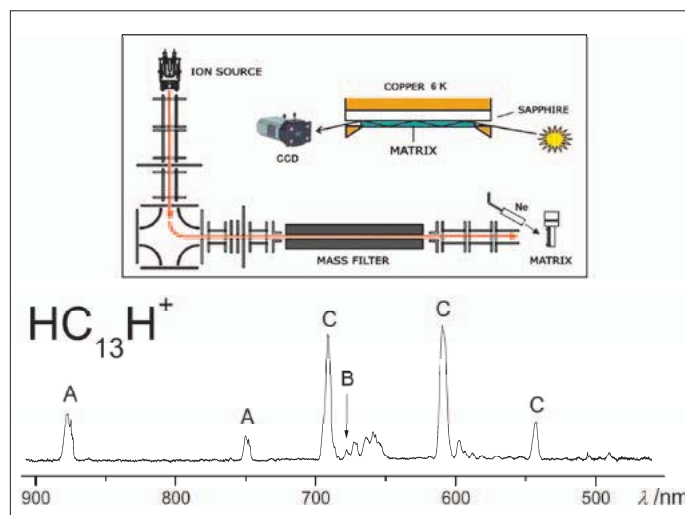E-mail: stefan.willitsch@unibas.ch

Fig. 1. Experimental set-up for the measurement of the electronic absorption spectra of mass-selected molecules in 6 K neon matrices. The inset shows the observed spectrum of HC$_{13}$H obtained by codeposition of HC$_{13}$H$^+$ cations, generated from acetylene, with excess of neon, followed by neutralization of the ions in the matrix.
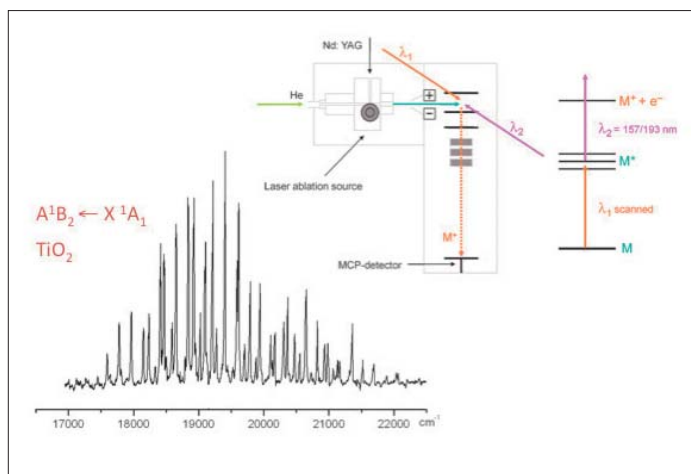
Fig. 2. Measurement of the electronic spectra of mass-selected neutral radicals using resonance enhanced ionisation technique. The spectrum shown is the $A^1B_2 \leftarrow X^1A_1$ transition of TiO_2, bent molecule with C_{2v} symmetry, with a complex vibrational pattern. TiO_2 was 'synthesized' within a supersonic molecular beam at 50 K by laser ablation of Ti over which oxygen seeded in helium is passed.

Fig. 3. Degenerate four wave mixing is a means to measure the electron spectra of transient species. The example shown is for HC_2S, produced at low temperatures in a supersonic slit jet expansion of CS_2/H_2 seeded in helium, through which a discharge runs. A two colour variant of the method is used in a double resonance mode to assign the rotational lines unambiguously.

In Fig. 1 the set-up is outlined. Acetylene gas in such ion sources provides numerous species of interest; for example the polyacetylene chains, 'synthesized' *in situ* by radical and ion-molecule reactions. Such chains are predicted to occur in the atmosphere of Titan, a moon of Saturn with physical conditions as on early earth, in pre-oxygen days. Knowledge of their electronic spectra is a means to identify them remotely by telescopes. The absorption spectrum shown in Fig. 1 is that of neutral $HC_{13}H$. It is produced from the mass-selected cation trapped by releasing electrons in the neon matrix. The species is linear according to the spectroscopic pattern observed and is assigned to the $A\ ^2\Pi\text{-}X\ ^2\Pi$ transition. One characteristic is the linear dependence of the transition wavelength versus length of the molecule. The surrounding neon atoms eliminate rotation of the molecule and the 6 K temperature ensures that whole population is in the lowest vibrational level in the ground state. The vibrational patterns observed correspond to levels in the excited electronic state accessible by selection rules and intensities governed by Franck-Condon factors. Apart from the solvation shift the pattern mimics the absorption expected in diffuse interstellar clouds at such low temperatures. The wavelength position of the observed bands will lie within 100 cm^{-1} or so of their gas phase values. This alleviates the gas phase search and $HC_{13}H$ has in fact been observed in the gas phase using a REMPI method outlined next. In this the polyacetylenes are produced in a pulsed supersonic beam of acetylene seeded in helium through which a discharge runs. A tuneable laser excites the transition and a second laser at 157 nm ionises the species.

The ions are selected according to their mass and counted. Fig. 2 shows the experimental arrangement and application to obtain an electronic transition of TiO_2. This molecule was studied because of its importance in terrestrial processes, catalysis, and presence in certain stars.

The species was produced in this case by laser vaporization of a titanium rod over which oxygen flows. The transition is between the ground and first excited electronic states, assigned to $A\ ^1B_2 \leftarrow X\ ^1A_1$ symmetry for the inferred C_{2v} structure. Under the experimental conditions used the internal temperature is around 50 K. The spectrum shows a complex vibrational pattern, indicative of a significant geometry change in the OTiO bond angle. Increasing the resolution with a continuous wave laser enables the rotational structure to be discernible revealing a bent OTiO configuration. Hence, the combination of mass selection and spectroscopy unambiguously identifies the molecule as TiO_2 and yields information on its geometry.

This is illustrated in Fig. 3 where the astrophysically interesting radical HC_2S has been probed both by CRD and D4WM methods. A slit jet expansion/discharge is used and thus the interrogating laser beam samples the radicals along a few cm. The concentrations of radicals down to 10^8 cm^{-3} can be detected. D4WM, being a non-linear technique, can be used advantageously to discriminate against overlapping absorptions and using it in a two photon colour mode as a double resonance technique to confirm assignments, as the insets of Fig. 3 indicate. The ns time resolution is better than that of CRD (µs range) and thus more sensitive to production rates of the species being synthesized in the discharge.

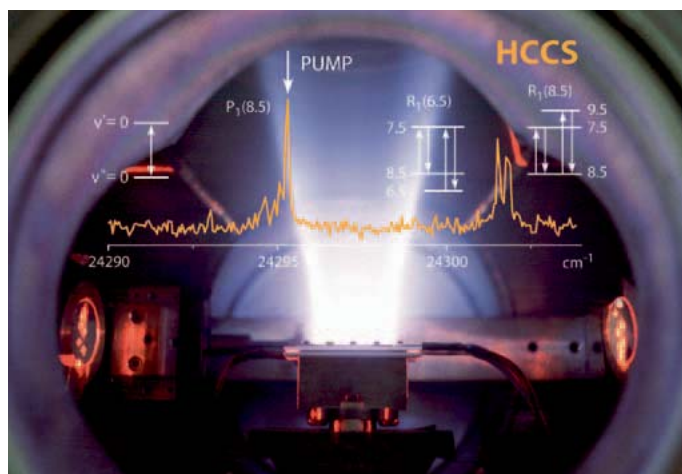A new development has been the use of RF traps to measure the electronic spectra of mass-selected cations. Fig. 4 shows how this is done in the case of cyanogen cation. The latter is present in Titan's ionosphere and thus the ability to monitor it by optical spectroscopy is of relevance. The cation is produced in a conventional electron impact source and is then led *via* a hexapole guide and a mass-selecting quadrupole into a 22-pole ion trap. There 10^4 ions are stored by a RF field. The vibrational and rotational degrees of freedom are relaxed to low temperatures by collisions with cryogenically cooled helium atoms. Detection of the electronic transition is accomplished by a two colour two photon process, analogous to the REMPI scheme used for neutrals. A tuneable laser induces the sought-after absorption whereas a second, higher energy, photon induces fragmentation, CN^+ in the case of $NCCN^+$. The trap is subsequently opened, CN^+ is mass-selected by the further quadrupole, sent to a particle detector and counted as function of the tuneable laser wavelength.

A distinct electronic absorption system is detected (Fig. 4). The spectrum can be directly compared with astronomical observations; the temperature of the ions is around 20 K and the transitions observed are from the v = 0 level of the electronic ground state, $X\ ^2\Pi$, to the accessible vibrational levels in the upper state, $B\ ^2\Sigma^+$. The rotational lines are not resolved because of lifetime shortening in the upper electronic state as result of intramolecular processes. This is an often encountered feature with polyatomic radicals and ions and is of significance to astronomical observations. A number of ionic systems have thus been studied, including the long linear polyacetylene cations up to $HC_{18}H^+$.
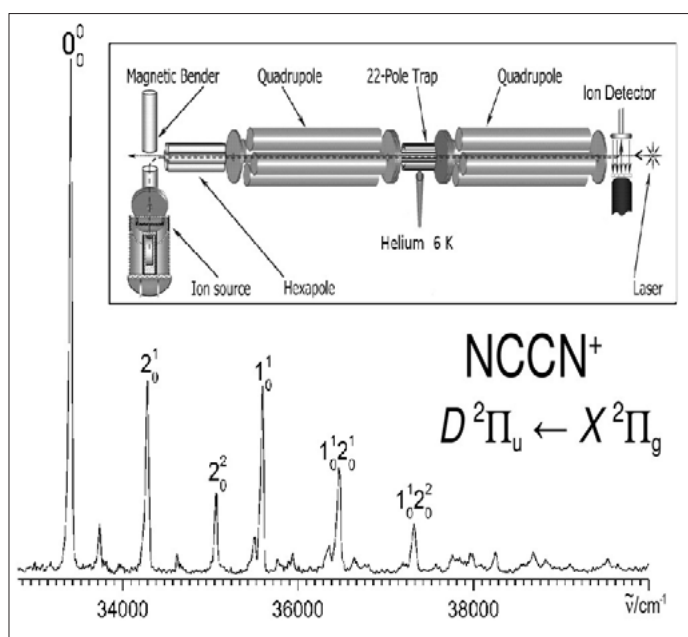
Fig. 4. Apparatus used to measure the electronic absorption of mass-selected cations at low temperatures. The spectrum shown is of cyanogen cation, formed in the ion source, mass-selected and stored in a 22-pole RF trap. The internal degrees of freedom are equilibrated to 20 K by collisions with cryogenically cooled helium. The transition of interest is located and induced by a tuneable laser while a second fixed frequency laser produces the CN$^+$ fragment. After opening of the trap the CN$^+$ ions are mass-selected and monitored. The spectrum shows the vibrationally resolved B $^2\Sigma^+\leftarrow$X $^2\Pi$ electronic transition.

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Chemical Dynamics at Sub-Kelvin Temperatures

Stefan Willitsch

Over the past 15 years a range of methods have been developed to manipulate and cool the translational motion of molecules and molecular ions in the gas phase.[1] 'Cold' molecules at translational temperatures T <1 K offer a range of intriguing scientific perspectives: Temperatures as low as a few hundred nanokelvin have been reached in diatomic molecules synthesized from ultracold atoms,[2] cold molecules have been prepared in well-defined rotational-vibrational and even hyperfine quantum states,[3] fully energy-controlled collisional studies have been performed with velocity-controlled molecular beams[4] and chemical reactions with single localized ions have been realized.[1a,b] The experimental technologies developed in this context are of considerable interest for an emerging field of research often referred to as 'cold chemistry' which is concerned with the study of chemical processes in this new physical regime.

Many chemical reactions 'freeze out' at low temperatures. However, for an important class of chemical reactions, namely the ones without activation barriers, the rate increases with decreasing temperature.[5] These include a variety of fundamental reactions with molecular ions and free radicals in the gas phase. At very low temperatures, these types of processes are dominated by dynamical (centrifugal) barriers which depend on the angular momentum of the collision between the reactands.[5,6] In many cases, the reaction rate shows a sensitive dependence on the rotational-vibrational and even hyperfine quantum state of the reaction partners[2,7] and resonance phenomena can strongly affect the chemical dynamics.[8] These effects also play a role at room temperature, but are usually obscured by thermal averaging over a broad distribution of collision energies and quantum-state populations. Consequently, cold-chemistry studies offer unique opportunities to characterize the dynamical details of chemical reactions which are not only of relevance at low temperature, but also for the understanding of chemical reactivity in general. Moreover, the tools developed for the manipulation of the motion and quantum state of molecules pave the way for schemes to accurately control chemical processes on a quantum-mechanical level.[6]

Over the past years, the research group of *Stefan Willitsch* has developed new approaches to study ion-molecule reactions at sub-Kelvin temperatures by combining for the first time techniques to prepare cold ions and cold neutral molecules in the same apparatus.[9] Atomic ions such as Ca$^+$ can be cooled down to millikelvin temperatures using laser cooling.[1a] When confined in an ion trap, cold ions localize in space as a consequence of the balance between their mutual Coulomb repulsion and the electrical forces of the trap. The resulting regular structures of ions which are conventionally termed 'Coulomb crystals' can be observed by imaging the fluorescence of the ions generated during laser cooling (Fig. 1). By coupling a Coulomb-crystal apparatus with a velocity selector to prepare continuous beams of translationally cold neutral molecules, it became possible to study ion-molecule reactions in the cold regime with extremely high sensitivity.[1a,b] Performing experiments with single localized ions enabled the study of reactive processes on the single-particle level and to accurately control the collision energies of the reaction partners.[9a] For prototypical ion-molecule reactions such as Ca$^+$ + CH$_3$F, these studies demonstrated the importance of shallow submerged barriers for the chemical dynamics at very low temperatures.[9b]

For over a decade, a persistent problem in the field was the preparation of translationally cold molecular ions in a well-defined internal, *i.e.* rovibrational, quantum state. Molecular ions are conventionally cooled 'sympathetically', *i.e.* by exchanging kinetic energy with simultaneously trapped laser-cooled atomic ions *via* the Coulomb interaction. Sympathetic cooling, however, does not affect the internal molecular degrees of freedom. As a consequence translationally cold, but internally 'warm' samples of ions are obtained. Fully quantum-state selected ensembles of ions, however, are essential for a range of different experiments, not only for studying the influence of the quantum state on the chemical reactivity, but also for applications in a completely different context, *e.g.* single-ion precision spectroscopy[10] or quantum-information processing.[11]
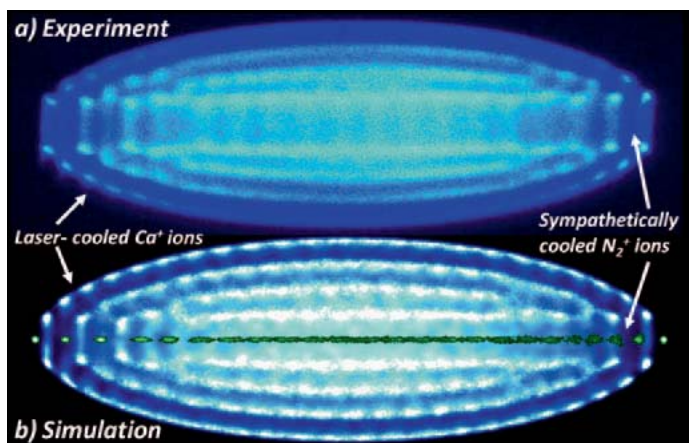
Fig. 1. Experimental (a) and simulated (b) false-colour fluorescence images of a Coulomb crystal containing 925 laser-cooled Ca^+ ions and 24 N_2^+ ions at a temperature of 15 mK. The molecular ions do not fluoresce and have been artificially made visible in the simulated image (see text).

Fig. 2. A cold-chemistry 'lab-on-a-chip': Surface-electrode ion trap for the sympathetic cooling of molecular ions.

Very recently, optical-pumping experiments achieved a partial accumulation of the population in the rotational ground state in systems such as MgH^+ and HD^+.[12] However, the efficiency of optical population-redistribution schemes is limited by the large number of levels which need to be accessed. This problem is exacerbated with increasing complexity of the molecule. Recently the Willitsch group has developed an alternative method which does not suffer from these restrictions and is applicable to a wide range of systems.[13] This approach is based on the selective generation of the molecular ions in a well-defined rotational-vibrational quantum state using threshold photoionization[14] immediately followed by sympathetic cooling. As an example, Fig. 1a shows a false-colour fluorescence image of Coulomb crystal of about 925 laser-cooled Ca^+ ions containing 24 sympathetically-cooled N_2^+ ions prepared in the rotational ground state. Because only the laser-cooled atomic ions fluoresce, the molecular ions appear as dark core in the centre of the image. For clarity, the N_2^+ ions have been made artificially visible in a molecular-dynamics (MD) simulation of the experimental image shown in Fig. 1b. At a translational temperature of 10 mK, the molecular ions arrange in a string-like configuration which is surrounded by shells of laser-cooled atomic ions. The N_2^+ ions have been prepared in the rotational ground state with a selectivity of 93±11% as measured by charge-transfer spectroscopy. The originally prepared rotational state is preserved on a timescale of 15 minutes that is long enough for a wide range of applications including studies of fully state- and energy-controlled chemical reactions.

Another line of current research focuses on the development of 'hybrid' traps for ions and neutral species[15] in order to study ion-molecule reactions down to millikelvin temperatures; three orders of magnitude lower than in previous studies. In combination with the recently established capability to prepare state-selected and translationally cold molecular ions, the Willitsch group aims to perform ion-molecule reactive-collision experiments affording unprecedented control over both the collision energy and the quantum states of the reactands. As a first step an ion trap for the sympathetic cooling of molecular ions is combined with a magneto-optical trap (MOT) for the laser-cooling of neutral atoms to study electron-transfer processes in the cold regime. Subsequently, a generalization of this approach is envisaged by merging ion traps with neutral-molecule traps.

Further, new ion-trap architectures are developed in the Willitsch group that provide increased flexibility as compared to the conventionally used linear Paul traps.[1a,b] In surface-electrode (SE) ion traps,[16] all electrodes are projected onto a plane so that the ions are trapped above a surface. SE traps have thus far mainly been used for the laser-cooling of atomic ions in quantum-information experiments.[16] However they also offer considerable advantages for chemical experiments with molecular ions. One advantage of this type of traps is the open geometry enabling improved access the trapping region and facilitating the introduction of molecular and laser beams as well as the combination with traps for neutral species.[15] Moreover, by miniaturizing the assembly on a microchip ion-trap networks can be realized in which several connected trapping regions are implemented on a single surface.[16] One can envisage a SE trap network in which consecutive chemical transformations and analytical tasks such as spectroscopy and mass spectrometry are performed in different trapping regions thus forming a cold-chemistry 'lab on a chip'.

Fig. 2 shows a photograph of prototype SE trap for the sympathetic cooling of molecular ions. Theoretical modelling of the trapping potentials and MD simulations of the Coulomb crystals show that sympathetically-cooled ions in such a device can be expected to exhibit significantly different thermal and structural properties compared to linear Paul traps. These properties can be adjusted by applying static voltages to control electrodes around the trapping region.[17]
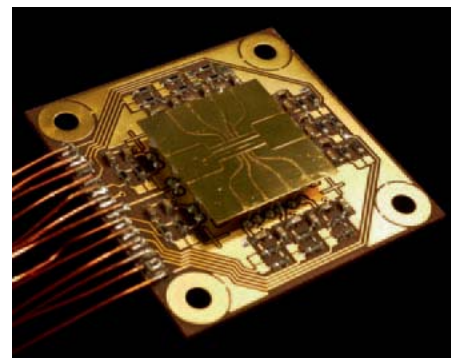
Experiments in this direction are currently in progress.

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