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.

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Spectroscopy of Interstellar Molecules

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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 (10^9 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 neutals 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 cm² 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.

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\textsubscript{13}H obtained by codeposition of HC\textsubscript{12}H\textsuperscript{+} cations, generated from acetylene, with excess of neon, followed by neutralization of the ions in the matrix.
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 $A^1B_2 \leftarrow X^1A_1$ 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.

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$_5$S 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 $10^6$ 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 ($\mu$s 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$^6$ 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 tunable 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 tunable 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$_{15}$H$^+$. 

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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$_5$S, 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.
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. These methods have been applied to the study of chemical processes at very low temperatures.

Many chemical reactions 'freeze out' at low temperatures. However, for an important class of chemical reactions, namely those involving activation barriers, the rate increases with decreasing temperature. These include a variety of fundamental reactions with molecular ions and free radicals.

In many cases, the reaction rate shows a sensitive dependence on the rotational-vibrational and even hyperfine quantum state of the reaction partners and resonance phenomena can strongly affect the chemical dynamics. 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.

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 cold-chemistry techniques with collisional energy-controlled studies. 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.

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Very recently, optical-pumping experiments achieved a partial accumulation of the population in the rotational ground state in systems such as MgH⁺ and HD⁺. 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 wider range of systems. This approach is based on the selective generation of the molecular ions in a well-defined rotational-vibrational quantum state using threshold molecular ions in a well-defined rotational-isolated ion trap. For clarity, the N₂ ions are 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 N₂⁺ 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 N₂⁺ 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 for a timescale of 15 minutes which 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 in order to study ion-molecule reactive-collision experiments affording unprecedented control over both the collision energy and the quantum states of the reactants. 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. In surface-electrode (SE) ion traps, all electrodes are projected onto a plane so as to form a magneto-optical trap (MOT) for the laser-cooling of molecular ions is combined with a trap network in which consecutive chemical reactions 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. Experiments in this direction are currently in progress.

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