3.1 Bericht Teilprojekt 4

3.1.1 Titel / Title

Infrarot- und Ferninfrarot-Spektroskopie molekularer Ionen: Vom Hydronium-Ion (H_3O^+) über Cluster bis zum Eis.

Infra-red and far infra-red spectroscopy of molecular ions: from the hydronium ion (H_3O^+) via clusters to ice.

3.1.2 Berichtszeitraum / reported period

01.07.2003 - 31.12.2006

3.1.3 Projektleiter / principle investigator

Schlemmer, Stephan, Dr., Dipl.-Phys., Universitätsprofessor
I. Physikalisches Institut, Universität zu Köln

3.2 Zusammenfassung / Abstract

3.2.1 Wortlaut des Antrags / abstract of the proposal

Die meisten Moleküle zeigen ihre charakteristischen spektralen Fingerabdrücke im infraroten und submillimeter Wellenlängenbereich. Daher konzentrieren sich zukünftige Beobachtungsmissionen wie Herschel auf diesen Spektralbereich. In diesem Projekt wird die Kombination eines 22-Pol Ionenspeichers mit abstimmbarer IR Laserstrahlung dazu benutzt, um Spektren astrophysikalisch relevanter Moleküle zu bestimmen. Die Schwingungs-Rotationsanregung des Muttermoleküls führt zu einer Änderung der Anzahl von Produktionen in ausgewählten Ionen-Molekül Reaktionen (laserinduzierte Reaktion [LIR]). Der Nachweis der Produkte dient damit als sehr empfindlicher Nachweis für die IR bzw. FIR Anregung. Das Hydronium Ion und Wasser Cluster Ionen stehen im Mittelpunkt der Untersuchungen, da Wasser eine Schlüsselrolle in vielen astrophysikalischen Umgebungen zugeschrieben wird. Strukturelle Isomere können identifiziert werden und ihre thermische bzw. nicht-thermische Zusammensetzung im Speicher mittels LIR untersucht werden. Ebenso können Prozesse innerhalb des Clusters wie Isomerisierung oder chemische Reaktionen in Heteroclustern studiert werden. Diese Untersuchungen sollen helfen, den Übergang von Molekülen zu sehr kleinen Aggregaten zu verstehen.

Most molecules show their unmistakable chemical signature at infrared and sub-millimeter wavelengths, therefore future observational missions like Herschel will focus on this spectral range. In this project, the combination of a variable temperature 22pole ion trap (TV-22PT) and tunable IR-laser radiation is used to obtain laboratory spectra of molecular ions relevant to astrophysical chemistry. The ro-vibrational excitation alters the product abundance from selected ion-molecule reactions which serves as a very sensitive detector for IR or FIR absorption of the parent ion (laser induced reaction [LIR]). The hydronium ion and water cluster ions are the prime targets of this project because water is a key ingredient in many astrophysical environments. Structural isomers can be identified and their thermal or non-thermal composition in the trap can be investigated using LIR. Also intra-cluster processes such as isomerization or chemical reactions in heterogeneous clusters can be studied and help to understand the transition from molecular species towards very small grains.

3.2.2 Zusammenfassung des Berichts / abstract of the report

The objective of this project is the determination of IR and FIR spectra of molecular ions as well as the quantitative understanding of the dynamics of ion molecule reactions at temperatures relevant to the interstellar medium. In a 22-pole ion trap apparatus the rather specific and ultra-sensitive method of laser induced reactions (LIR) is applied to obtain spectra for small hydrocarbon ions as well as other small ions of astrophysical relevance. It was the original aim to focus on the possibility to record spectra of very cold water cluster ions as model systems for water ice. Unfortunately the proposed LIR mechanisms did not work out. Due to the moves to Leiden and later to Köln a substantial reconstruction of the 22-pole apparatus was not possible. Therefore the focus of the project has been directed towards spectroscopy of $C_2H_2^+$, CH_5^+ and H_2D^+ for which the main results were obtained. In all cases new vibrational modes were found and characterized. The detailed LIR studies revealed information on the break down of the separation of the motions of electrons and nuclei for the description of a molecule. For $C_2H_2^+$ the Renner-Teller coupling of electronic and nuclear motion was determined experimentally for the first time. For H_2D^+ the experiments show that non-Born Oppenheimer terms in the potential energy surface are relevant. For CH_5^+ first overview spectra from about 500 cm^{-1} up to 3200 cm^{-1}

could be recorded. Comparison to theoretical work confirmed the structural scheme for this very floppy molecule as a CH_3 tripod to which a H_2 moiety is attached by a three centre two electron (3c2e) bond.

3.3 Ausgangsfragen, neuster Stand der Forschung / Initial goals, current status of the field

This project is the continuation of TP4 of the first period of funding of the FGLA but with the aim to focus the method of laser induced reactions (LIR) to specific systems of interest in the astrophysical context. Water complexes have been chosen as templates for water ice systems in particular for ice layers on interstellar grains. Although isolated water complexes are not expected to exist in space in high enough concentrations to be observed by present telescopes, it was an important aim of this project to extend the methodology to more complex systems.

In order to evaluate the results of this project it is important to recall the boundary conditions which emerged due to the move of the PI and the apparatus from Chemnitz to Leiden in April 2003 and further to Köln in March 2006. Thanks to the generosity of Dieter Gerlich in supporting the move of the 22-pole ion trap apparatus it was possible to continue the work begun in Chemnitz. Funding of one graduate student (Edouard Hugo, hired in 2004) by DFG allowed to obtain part of the results presented here. In Leiden the group had access to two solid state ice experiments which were also used to record IR spectra of interstellar ice analogues and also to obtain temperature programmed desorption (TPD) spectra of these ices. This work was mostly funded by the Dutch science foundation (NWO). Nevertheless this work is also strongly related to the astrophysical questions of this project. After about one year in Leiden the PI was offered a C3 position in Köln in the astrophysics institute, which was accepted and started in late 2004. In Köln the group has access to a number of new experiments which focus on the high-resolution spectroscopy of molecules of astrophysical interest. In the meantime the 22-pole apparatus was bought from Chemnitz using startup money. In 2005/2006 a new all solid state spectrometer in the 2-3 mm wavelength range (100 GHz) has been build. In addition the OROTRON instrument, the most sensitive 100 GHz spectrometer available worldwide, has been used to obtain spectra of water dimers. As a result of these substantial changes the main direction of the project changed significantly.

In Leiden the main aim was to obtain a first funding of the laboratory group. In order to be successful in the highly competitive dutch system it was mandatory to make use of the free electron laser FELIX in Rijnhuizen/Utrecht as soon as possible. Our beamtime application was successful and the first beamtime was granted in January 2004. At that time we repeated LIR measurements of the C-H stretching vibration of $C_2H_2^+$, see below. Most importantly we obtained the first spectra of the ν_5 cis bending vibration of $C_2H_2^+$. This was a first low bending vibration spectrum taken with LIR.

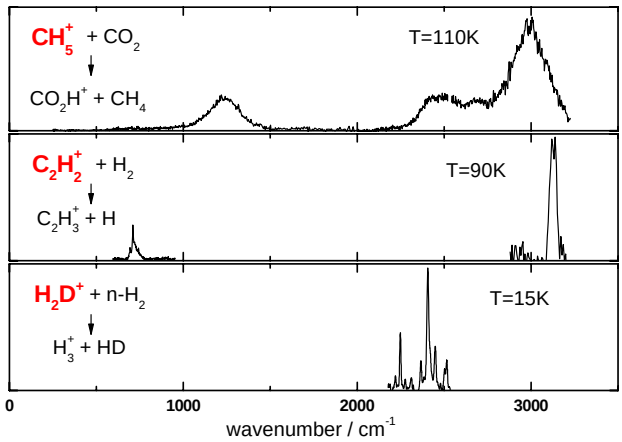


Fig. 1: Summary of the LIR spectra obtained during the funding period. Many details of the spectra are not observable in these broad, low resolution spectra. However the wide spectral range covered by combination of LIR and FELIX is demonstrated in this overview.

In 2003 we proposed two major routes for the application of LIR in order to obtain spectra of water cluster ions. The first route was to find favorable reactions to exchange e.g. a hydrogen for a deuterium in a water cluster ion in order to use isotopic labeling as a detection method. First experiments along these lines have been carried out already in Chemnitz in 2003. Since the reaction of H_3O^+ (m=19 u) with HD to form H_2DO^+ + H_2 did not proceed ($k < 10^{-15}$ cm^3/s) at the low temperatures aimed for, this route had to be discarded. The second route involved the formation of water cluster ions in an external source. A corona discharge nozzle for this approach was available from earlier cluster experiments in the Gerlich group. However, due to the lack of initial funding in Leiden it was impossible to set up a differential pumping stage including a turbo molecular

pump with pumping speeds larger than 1000 l/s. Therefore this route could not be followed. Instead, as the LIR experiments with other astrophysically interesting molecules were successful, we decided to continue LIR of those molecules, as was also suggested by the astronomers in Leiden, Köln and by the reviewers of our initial proposal.

As a result of these developments and the successes of LIR we focused on IR spectra of other astrophysically important ions like $C_2H_2^+$, CH_5^+ and H_2D^+. Fig. 1 shows an overview of all the spectra we obtained in the last three years relevant for this report. This project has been imported to the SFB494 in Köln and was positively evaluated. Therefore LIR spectroscopy and dynamics is also funded after the end of the FGLA.

3.4 Angewandte Methoden / Applied methods

Various methods have been used in the project. Storage of ions at variable temperatures in a 22-pole ion trap as described in detail before (e.g., Gerlich 1995) in combination with laser induced reactions (LIR) was the main experimental tool in this project. Further details can be found in earlier work (Schlemmer *et al.* 1999, 2002, 2005b).

Experimental: trapping

Traps have been used for many years to store ions and to study ion-molecule collisions in great detail. Thanks to the invention of higher order multipole traps, mainly developed in the group of Dieter Gerlich (1992), it became possible to study these collisions at energies comparable to those of cold environments in space, in particular dense molecular clouds. In recent years we combined the trapping technique with IR and FIR radiation sources (Schlemmer *et al.* 2002, Asvany *et al.* 2005a, 2005b). As it turns out many reactions of astrophysical interest are substantially enhanced due to internal excitation of the ion. This fact is used in the method of laser induced reactions to obtain (i) spectra of molecular ions and (ii) state specific knowledge of the ion molecule reaction. The method is so sensitive that only ~1000 parent ions are necessary.

Basic concept: LIR

The LIR technique has been developed in the group of Dieter Gerlich. First experiments have been conducted already in Freiburg. In Chemnitz the method was first used in the IR wavelength range. During this project the technique has been extended into the mid-IR and FIR wavelength range, especially thanks to the available of the free electron laser FELIX at FOM Rijnhuizen/Utrecht, which can be tuned from 40 cm^{-1} up to 3200 cm^{-1}.

In short, ions are generated and collected in a storage ion source, mass selected in a quadrupole mass filter and then pulsed into the 22-pole ion trap. On entrance the ions are cooled down to the ambient cryogenic temperature by a short intense helium pulse. During the storage period of several seconds, the ions are subject to reactant gases and tunable laser light entering one end of the apparatus through the axially transparent setup. The result of this interaction is measured by extracting the stored ion cloud into another mass filter and counting the reaction products in the detector. With this setup, a LIR spectrum of the ions is recorded by counting the products of a suitable ion-molecule reaction as a function of the laser frequency. Some results concerning spectroscopy have been summarized in the book of abstracts of the FGLA meeting in Pillnitz 2005 and have been published recently (Asvany *et al.* 2005a, 2005b, and Schlemmer *et al.* 2006, 2005a, 2005b).

UHV surface science apparatus: CRYOPAD

Thanks to the move to Leiden one UHV apparatus for studies of interstellar ice analogues was available. This machine has been reconstructed and finished during the PI's appointment and became operational in 2004. First results of this experiment have been published recently (van Broekhuizen *et al.* 2006, Öberg *et al.* 2006, Fuchs *et al.* 2006 and Bisschop *et al.* 2006) and will only be described briefly below.

Millimeter – wave spectrometers

In the Köln laboratory spectroscopy group a millimetre-wave intracavity spectrometer (OROTRON) is available for the investigation of pure rotational transitions and internal motions of weakly bound complexes. In this instrument a beam of molecules is intersected with the cavity of a backward wave oscillator (BWO). Due to the intracavity absorption the sensitivity of the instrument is exceptional and allows for the detection of extremely weak or forbidden lines. As a result, very detailed information on the intermolecular potential is available from this experiment.

Also very high-resolution THz spectrometers are used in collaboration with Frank Lewen to investigate low lying vibrations of complex molecules. With the OROTRON instrument particular tunnelling motions of the water dimer are accessible with very high sensitivity. Using some start up money a new all solid state millimetre spectrometer has been built.

3.5 Ergebnisse und ihre Bedeutung / Results and their importance

LIR of small molecules

Based on the successful experiments on $C_2H_2^+$ another beamtime was granted for January 2005. During this beamtime the most visible success of this project could be achieved, taking a global IR spectrum of protonated methane, CH_5^+. The spectrum is shown in Fig. 3. In addition to the high frequency wing of the C-H-stretching motion at 3000 cm^{-1} which has been observed previously by White *et al.* (1999), two lower frequency features extending down to 2300 cm^{-1} have been detected. Furthermore, there is a broad H-C-H bending band centering around 1200 cm^{-1}.

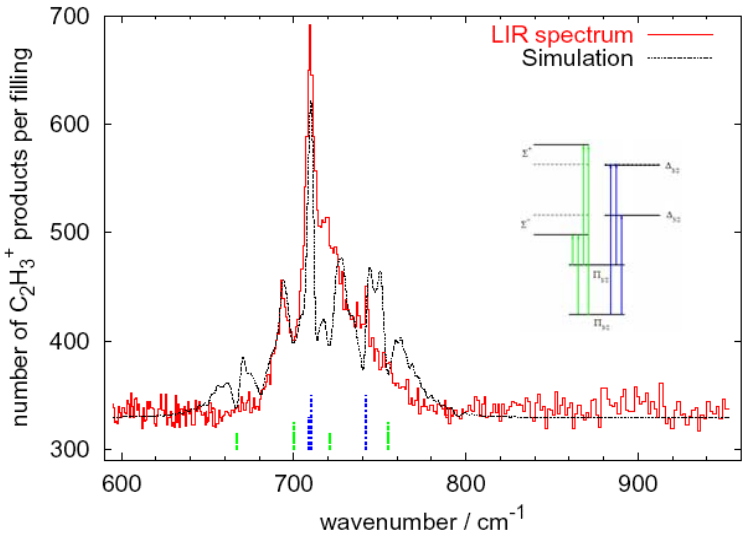


Fig. 2: Spectrum of the ν_5 cis bending vibration of $C_2H_2^+$

As mentioned above, FELIX has been used for recording the ν_5 cis bending vibration of $C_2H_2^+$ (Asvany *et al.* 2005a). The recorded spectrum of the number of $C_2H_3^+$ product ions is displayed in Fig. 2. Both electronic transitions Δ-Π and Σ-Π with their corresponding spin-orbit and Renner-Teller substructure have been observed and have been partly resolved. Using a perturbative analysis, the vibrational frequency and the Renner-Teller parameter have been determined to be ω_5=710 cm^{-1} and ε_5=0.032. This year a new REMPI work with full rotational resolution on $C_2H_2^+$ was published by Yang & Mo (2006). They determined ω_5=704.1 cm^{-1} and ε_5=0.019 which is in good agreement with our results. This example demonstrates that LIR is a competitive technique to REMPI for the study of primary ions provided a high-resolution IR source is available. In contrast REMPI does not work for secondary ions, which can only be formed in a sequence of ionization and reaction. Here LIR is a very sensitive tool for spectroscopy.

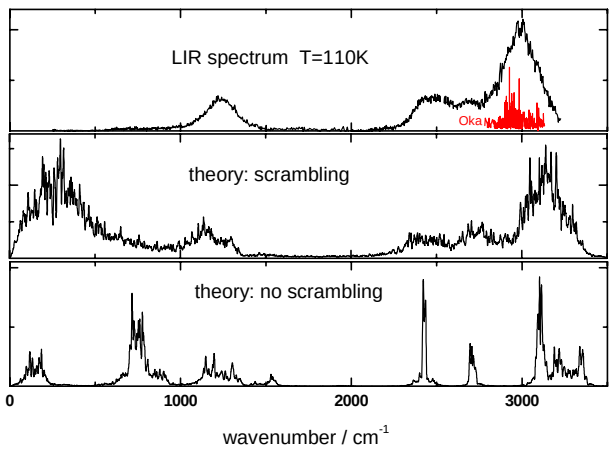
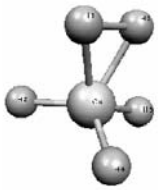


Fig. 3: *Upper panel:* Experimental LIR spectrum of CH_5^+. The endothermic proton transfer to CO_2, i.e. detection of HCO_2^+, is used to monitor the excitation of the CH_5^+ parent molecule. In red the high-resolution study of the Oka group in the C-H stretching region is reproduced for comparison. *Middle and lower panel:* theoretical spectrum calculated at different temperatures, simulating a scrambling and non-scrambling situation in CH_5^+.

By measuring the dependence of the LIR signal on the neutral number density (here H_2), lifetimes of the excited state have been determined. Fluorescence into the vibrational ground state can be a competitive channel compared to reaction when the radiative lifetime is of the same order of magnitude as the time between collisions. Careful analysis of the complex kinetics reveals the radiative lifetimes for the C-H stretching vibration, $\tau_3 = (3\pm1)$ ms, and for the ν_5 cis bending vibration of $C_2H_2^+$ $\tau_5 = (200\pm50)$ ms. Moreover, it turns out that excitation of the stretching vibration is about ten times as efficient to drive hydrogen abstraction as compared to the bending vibration. More details of this study are discussed in Schlemmer *et al.* (2005a). This example shows another time that LIR not only serves as a spectroscopic method, but also reveals characteristic times and rate coefficients of a given collision system. A summary of the current status of the experimental tool of LIR has been described recently (Schlemmer and Asvany 2005b).

Based on the successful experiments on $C_2H_2^+$, another beamtime was granted for January 2005. During this beamtime the most visible success of this project could be achieved, taking a global IR spectrum of protonated methane, CH_5^+. The spectrum is shown in Fig. 3. In addition to the high-frequency wing of the C-H-stretching motion at 3000 cm^{-1} which has been observed previously by White *et al.* (1999), two lower frequency features extending down to 2300 cm^{-1} have been detected. Furthermore, there is a broad H-C-H bending band centering around 1200 cm^{-1}.

The measurements were complemented by calculations of the IR spectrum at finite temperatures from the Fourier transform of the classical time-autocorrelation function of the total dipole moment. The underlying trajectories were generated by microcanonical *ab initio* molecular dynamics relying on a density functional treatment. As a result of this combined theoretical and experimental effort, CH_5^+ can be considered as a H_2 moiety attached to a CH_3 tripod.



These subunits give rise to different CH-stretching fingerprints. The broad feature around 3000 cm^{-1} is due to stretching within the tripod, while its two low-frequency 'bumps' are attributed to stretching involving the H_2 moiety. The broad H-C-H bending feature is predicted by the simulations and confirmed by the LIR measurements. The observed single broad peaks are indicative for the hydrogen scrambling of CH_5^+. This fluxionality is caused by a low-lying C_{2v} transition state for the scrambling motion, as well as the ease of rotation of the H_2 moiety. A more detailed description of the work in collaboration with the group of Prof. Marx (Bochum) can be found in Asvany *et al.* (2005b). First spectra of deuterated versions of CH_5^+ have been recorded. This study is not completed since during these experiments in January 2006 there was a fire at FELIX, which destroyed part of the free electron laser. Also our trap experiment was affected. Due to the fall out of smoke as a consequence of the fire all electronic devices needed to be cleaned which damaged a considerable fraction of the equipment. In practice it took three months to reconstruct the apparatus such that first experiments with a cold trap could be achieved in June 2006, when the FGLA finished. Despite these difficulties we are very grateful to the brave FELIX team which had to face a much bigger loss. Thanks to their enthusiasm FELIX came into operation again later this year. Our plans are to continue recording IR spectra of some of the deuterated versions of CH_5^+, see below.

A third example for IR spectroscopy deals with the astrophysically important H_2D^+ ion. Also during our 2005 beamtime at FELIX first spectra of the fundamental vibrations ν_2 and ν_3 have been recorded (see Fig. 1 lower panel). The endothermic reaction $H_2D^+ + H_2 \Rightarrow H_3^+ + HD$ could be substantially enhanced by the ro-vibrational excitation of the H_2D^+ parent ion. In order to record a spectrum the number of H_3^+ ions has been detected as a function of excitation wavelength. While for the fundamental frequencies high-resolution data are available, higher overtone transitions are sparse. The first overtone of ν_2 and combination bands have been studied recently by Farnik *et al.* (2002). In this work, diode lasers covering the range between 6200-7200 cm^{-1} have been used to record 19 transitions in H_2D^+ and several more transitions in D_2H^+. Thanks to the very high quality predictions of the transition frequencies by the Tennyson group in London, it was possible to find the transitions.

As has been described earlier (Farnik *et al.* 2002) several levels of H_2D^+ and D_2H^+ can be strongly perturbed by Coriolis and Fremi interactions. Therefore it is practically impossible to predict the line frequencies from effective Hamiltonian models. The *ab initio* methods of Tennyson and co-workers treat the problem more rigorously and therefore any interaction is treated implicitly. In addition the theory includes non-Born-Oppenheimer corrections of the potential energy surface. As a result theoretical predictions are accurate below

the 1 cm^{-1} level, i.e. spectroscopic accuracy is achieved. The spectroscopic accuracy of our experiments is below the 0.01 cm^{-1} level and serves therefore as a critical test for theoretical predictions.

Fig. 4 shows a comparison between experiment and theory. In all cases two quanta of the ν_2 bending vibration have been excited. In addition one quanta of each vibration (ν_1 symmetric stretch, ν_2 bending, ν_3 asymmetric stretch) are excited in these modes. Apparently the discrepancy between theory and experiment is largest for the bending vibration. This finding is not unexpected since the current state of the non-BO treatment is based on a diatomic model which comes much closer to a stretching vibration in a polyatomic molecule than a bending vibration. This example shows, that more extensive models have to be developed in order to achieve a better agreement between theory and experiment. While this is certainly possible the question is whether such a calculation would be valuable for any potential application, in particular in an astrophysical environment. Indeed, the calculation of highly excited molecular species is strongly needed in order to understand the emission curves of stars like our sun which can carry substantial atmospheres and which have surface temperatures which can vary a lot, e.g. due to sun spots (3000 K on the sun) where the temperature of the gas is substantially lower than for the rest of the surface (6000 K). Spectra of such objects are strongly determined by the spectra of highly excited species like H_3^+, water, methane etc. Because of this situation it is very valuable to test theory which predicts all these lines up to the dissociation level and above.

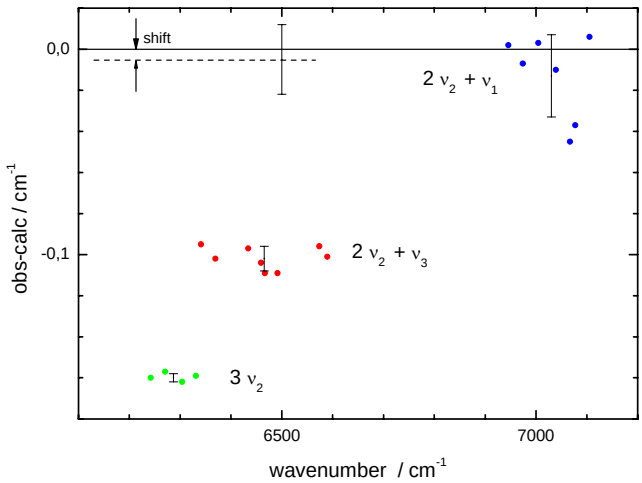


Fig. 4: Comparison of the observed to the calculated transition frequencies of second overtone vibrations for H_2D^+. Discrepancies between theory and experiment are below 0.15 cm^{-1}, which is exceptional for a polyatomic species. Significant differences are found with respect to the different vibrational motions. The observed tendency hints at limitations of the present day non-Born Oppenheimer treatment (see text).

It is gratifying to see that present day theory compares rather well with experiment. Including more sophisticated non-BO treatments for such light systems as mentioned above will help to reach similar accuracies for even higher levels of excitation. A joint publication with J. Tennyson is in preparation.

From an experimental point of view the LIR intensities from the H_2D^+ experiments can be used to determine the rotational state distribution of the cold H_2D^+. It will be described in section 3.6 how such measurements can be used to understand the deuterium fractionation in the most fundamental reaction: $H_3^+ + HD \Rightarrow H_2D^+ + H_2$. This work is continued within SFB494 project E4.

The role of deuterium fractionation of small molecular ions has been studied in this project without the use of laser excitation. Measurements on the temperature dependence of the proton transfer reaction $CH_5^+ + CO_2 \Rightarrow HCO_2^+ + CH_4$ have been carried out. Fig. 5 shows one example of a trap experiment at 294 K. From this measurement a rate coefficient of some $6x10^{-11}$ cm^3/s has been derived. This small value drops for lower temperatures in an Arrhenius type behaviour. From the slope of the Arrhenius curve an activation energy of (542±30) cm^{-1}, corresponding to (6.5±0.4) kJ/mol, has been determined. This value is more than a factor of two larger than the difference in proton affinities of methane (540.5 kJ/mol) and CO_2 (543.5 kJ/mol) as recommended by the NIST chemistry webbook.

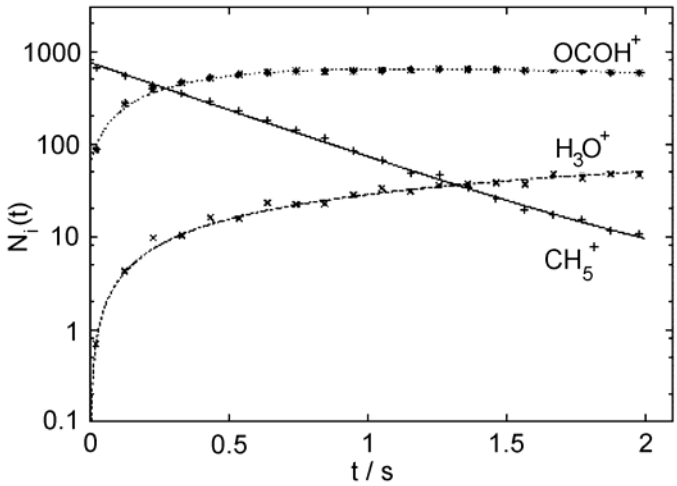


Fig. 5: Number of various ions, N_i, as a function of storage time t at T = 294 K. Determination of the rate coefficient for proton transfer from The injected CH_5^+ react with CO_2. In the simulation (solid lines) the exothermic proton transfer to the H_2O background is accounted for.

In Chemnitz the equilibrium rate coefficient has been determined rather carefully in a trap experiment where an equilibrium between CH_5^+ and HCO_2^+ has been established. Also these experiments have been carried out as a function of temperature. From the temperature dependence of the equilibrium rate coefficient the difference in proton affinity has been determined to be (7.1±0.5) kJ/mol. This value is in much better agreement with our value for the activation barrier than with the literature value for the PA difference. Therefore it might be safe to assume that the proton transfer reaction is endothermic but without an additional barrier.

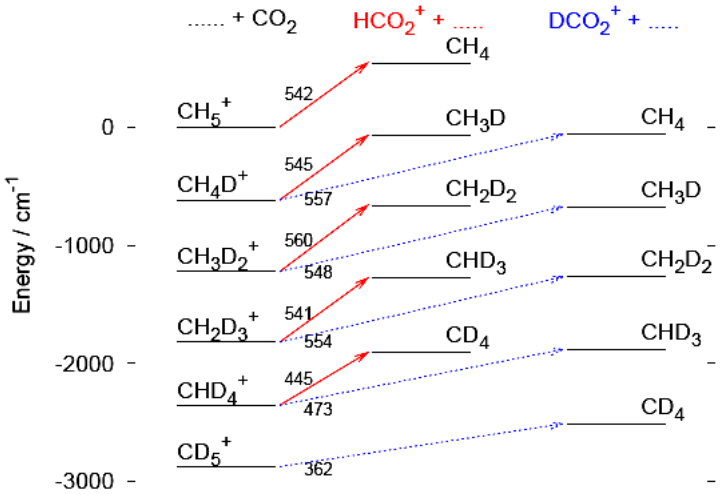


Fig. 6: Energetics for the proton / deuteron transfer from methane to CO_2 for different isotopologues. The activation energy for the fully hydrogenated case has been adopted from this work, 542 cm^{-1}. All ZPE differences are taken from spectroscopic data (methane in all isotopic forms) and theoretical predictions (HCO_2^+, DCO_2^+ and CH_5^+ in all isotopic forms).

More activation energies have been determined for the proton transfer reaction of CH_5^+, CD_4H^+ and CD_5^+ in collision with CO_2. Proton transfer becomes less endothermic for the deuterated versions of CH_5^+. According to the picture of a barrierless but endothermic reaction this behavior is due to the differences in zero point vibrational energies of the corresponding reactants and products (ZPE). Since the ZPE is rather well known for methane and its isotopologues the observed differences can be related to the differences in ZPE of protonated methane and protonated CO_2. Calculated values for the ZPEs are available for all species. The combined experimental (difference in PA) and theoretical (ZPEs) energetics of the reactions considered are displayed in Fig. 6. Differences between measured and calculated activation energies are found for the deuterated proton transfer reactions. Lower experimental values hint at smaller ZPE differences in CH_5^+, CD_4H^+ and CD_5^+ than predicted. As a result trap experiments can serve as a quantitative test for state-of-the-art theory predicting potential energy surfaces (PES) and ZPEs. A joint publication between the Chemnitz group (D. Gerlich, A. Luca, and H.-J. Deyerl) and the Köln group (O. Asvany, E. Hugo and S. Schlemmer) is in preparation.

Interstellar ices

In Leiden the focus of the laboratory work lies on experimental investigations of interstellar ices. A wide variety of IR spectra of ices of mixed and layered ices are available as a database (http://www.strw.leidenuniv.nl/~lab/databases/). The focus of these data lies on the main molecular species in interstellar ices.

In recent years the "match and mix" approach to reproduce the observed spectra from ISO and presently from the Spitzer satellite telescope is changed for more fundamental experiments, trying to understand the underlying mechanisms. For this purpose two surface science apparatus operating at UHV conditions have been built over the last six years. CRYOPAD, the CRYOgenic Photoproduct Analysis Device, became operational in 2004. The first work concentrated on the quantitative determination of binding energies of molecules in ice in order to understand the freeze out of important constituents like CO and N_2. In many astronomical sources CO has been observed to be frozen out while N_2, which is traced by N_2H^+, is not (e.g. Bergin & Langer 1997). Fig. 7 shows the possible scenarios of ice compositions. As molecules freeze out at different temperatures, layered ices are expected to play an important role. However, heating processes can lead to mixed ices. Both situations are associated with different desorption behaviors which have been studied in great detail in the last two years in the Leiden laboratory. Desorption rates and sticking coefficients for CO and N_2 interstellar ices have been determined by Öberg *et al.* (2005) and later in even greater detail by Bisschop *et al.* (2006). The relative difference between the CO and N_2 binding energies as derived from these experiments is significantly less than that currently adopted in astrochemical models. Detailed infrared spectroscopy studies of solid CO-CO2 mixtures and layers have been carried out by van Broekhuizen et al. (2006).

These studies of interstellar ice analogues are continued by the new head of the laboratory group in Leiden, Harold Linnartz. The ultimate goal is to understand the formation mechanisms of more complex molecules which cannot be formed in gas phase processes in large enough quantities to explain observations. One chemical route concerns hydrogenation of CO which is believed to be the main route to the formation of interstellar methanol. Due to the new Spitzer telescope, ices are studied via their main IR bands. Very detailed measurements reveal nowadays maps of solid ices. The Leiden observatory group lead by Ewine van Dishoeck is pushing the frontiers toward this direction, see for example: *Origin and evolution of ices in star forming regions: A VLT-ISAAC 3-5 micron spectroscopic survey* (van Dishoeck *et al.* 2003). Like for the gas phase molecules maps of the ices show the physical and chemical structure of star forming regions. The Köln spectroscopy group will also in the future concentrate on the detection of gas phase molecules, irrespective whether formed in gas phase processes, or on grains, or in icy mantles and desorbing, or even undergoing gas phase reactions after desorption from grains.

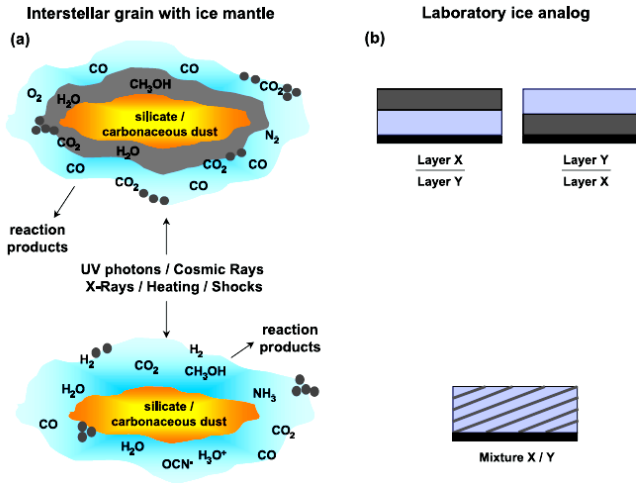


Fig. 7: (a) Two schematic models of the structure of an interstellar ice mantle, (top) formed due to the condensation of gases, thermal distillation or via surface reactions, and (bottom) formed as a result of thermally induced diffusion and chemical reactions induced in the bulk of the ice mantle. Reaction products that may desorb in the process of formation, or due to thermal warming of the ice are indicated. (b) Two schematics of a simulated interstellar ice mantle under laboratory conditions showing a layered (top) and a mixed (bottom) ice analogue composed of molecules X and Y. They are used as models for more complex situations potentially found in space.

3.6 Zusammenfassung und Ausblick / Summary and future

Zusammenfassung / Summary

Thanks to the funding within the FGLA it was possible to develop LIR into a mature technique for IR and FIR spectroscopy of molecular ions. $C_2H_2^+$, CH_5^+ and H_2D^+ have been explored quite intensively. In all three cases new spectral features or new ro-vibrational lines have been detected. Comparison to theoretical work on these important examples helped to improve our understanding on the molecular structure (CH_5^+) the intramolecular potential (H_2D^+) and couplings between the electronic and vibrational motion of a molecule ($C_2H_2^+$). Applying LIR to water cluster ions was unsuccessful. Alternative routes of LIR, e.g. unimolecular decomposition, have not yet been tried because of the lack of a differential pumping stage.

Ausblick / future

Based on the present LIR work several new directions are a natural extension of this interesting method:

- Combination of LIR with millimetre and submillimetre radiation should make it possible to record pure rotational spectra of molecular ions. Direct rotational excitation of H_2D^+ has been tested with the help of FELIX, which can be tuned from 40 cm^{-1} up to 3200 cm^{-1}. 100 cm^{-1} of extra rotational energy should be sufficient to drive the hydrogenation reaction in collisions with H_2. However, first tests at FELIX did not yield any LIR signal. This might be due to efficient rotationally inelastic collisions. Unfortunately these studies were interrupted by the fire at FELIX early in 2006. Another route towards this direction is to diminish the LIR signal of a particular IR transition by rotational pumping of the ground state. This method should work very well at low temperatures when only few states are populated. Therefore H_2D^+ is a very good candidate for this method. It is planned to use higher overtone transitions from a 1.4 µm laser for the probing and FELIX for a pure rotational excitation. High resolution sources in the THz range are available in Köln and could open this very interesting field. For H_2D^+ the rotational spectrum is rather well known. However, for the interesting CH_2D^+ molecule this is not the case. For a complex molecule like CH_5^+ such a scheme is probably much more difficult to apply due to the more crowded spectrum. Nevertheless this method appears as one of the promising methods to unravel the structure of CH_5^+ in greater detail.
- H_5^+ is the important intermediate molecule in collisions of H_3^+ with H_2. Understanding the structure of this molecule and in particular of its isotopologues poses a very critical test to state-of-the-art theory. Recently this system has attracted great attention by a number of theoretical groups (Bowman and McCoy, see e.g. Xie *et al.* 2005). Experiments along these lines are still missing except for the early low resolution study by Okumura *et al.* (1988).
  H_5^+ has to be formed in a high pressure discharge source as was missing for the current project. An alternative is to produce the cluster in the trap prior to LIR experiments. This approach would call for a non-destructive, *in-situ* mass separation. Several techniques can be considered. Mass selective excitation like in ICR apparatus is one option. Another method concerns the superposition of a quadrupolar field of a mass selector with the high order multipole field of a low temperature trap. A third choice is a split trap consisting of a mass selective and a trapping part which could be accessed alternatively by applying appropriate DC potentials. Much engineering development has to be put in the design of an operating trap.
- Other molecules of astrophysical interest can be explored using LIR. Among these belongs C_3H^+.
- LIR is an important method to reveal information on the efficiency of inelastic and reactive collisions as well as radiative processes. In order to exploit this in a more quantitative way, the LIR signal has to be analysed very carefully. For this it is essential that the LIR signals are reproducible to rather high levels of accuracy. This requires not only stable trapping conditions but also stable laser sources for the excitation. Current experiments with H_2D^+ show that reliable relative Einstein B-coefficients can be determined when LIR starts from the same ground state level. A full simulation of the LIR experiments finally allows the determination of reliable rotational state populations. In case of H_2D^+ the ratio of ortho to para hydrogen plays a crucial role for the rotational population. At laser powers above several mW many transitions can be saturated. As a consequence depletion sets in for the limited number of parent ions. This can be seen when comparing measurements to full simulations. As a result rate coefficients for inelastic processes (rotation, fine structure, hyperfine structure and nuclear spin) can be derived. First results for H_2D^+ show that rotationally inelastic processes in the vibrational ground state are much less efficient than anticipated. Very systematic studies along these lines will reveal a detailed insight into the possible fates of ion-molecule collisions.

Several of the discussed options for LIR are currently developed in the existing 22-pole trap apparatus in order to form the basis for new scientific aims.

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