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Investigation of reactions and species dominating low temperature combustion

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Abstract

The focus of our proposal is to determine the enthalpies of radicals dominating ignition. The resulting thermo-chemical data will be discussed and verified in the following years with other groups especially those organized in the new COST action CM0901.

The preparation of relevant radicals in treatable quantities is a challenge. We approached the problem using pyrolytical and electric discharge driven radical sources. We developed pulsed sources suitable for laser based experiments as well as continuous sources that can be used in the synchrotron beamline environment. Beyond the typical working regime of these radical sources we will continue to investigate them under the aspect of a “micro-reactor”.

Spectroscopic techniques were applied to determine the internal energy states of the produced radicals. With fs- TCFW-mixing techniques the energy map of low-lying ro-vibrational states can be determined, data not available for many key radicals. Pump probe techniques are used to monitor the dissociation path of intermediate molecules. We started with the interpretation of spectrally dispersed TCFWM signals. Evaluation however is far from straight forward. Still, there is a great motivation to understand the mechanisms producing the dispersed signals: One measurement unveils everything one would like to know about the dynamics of the addressed molecular states.

Enthalpies of radicals can be worked out via a positive ion cycle with VUV-spectroscopies at SLS in a complementary way. In cooperation with external groups up to now thermochemical data of radicals appearing as fragments of Iodomethane, di-tert-butyl peroxide and isomers of phenyl-bromopropyne. In continuation of the current project work we are on the verge to start measurements on peroxy radicals.

Aims

The project “Investigation of reactions and species dominating low temperature combustion” aims at the characterisation of species that govern ignition. A base is to be established for the spectroscopic investigation of peroxy radicals, the educts for the most relevant molecules at the start of low temperature combustion. We intend to directly measure the formation and dissociation enthalpies that up to now were only indirectly inferred from kinetic experiments or from model calculations. The characterization of peroxy radicals is a very complex task and we anticipate problems that can only be solved with a careful investigation of accompanying species like alkyl radicals, olefins, aldehydes, hydroperoxyalkyl radicals and hydroperoxides.

The aim of this project was two fold:

Measurement of molecular features such as binding energies and dissociation patterns of well studied and spectroscopically accessible molecules and radicals (e.g. H_2CO, HO_2) that can be directly compared to theoretical predictions.

Application of the measurement techniques to alkyl peroxy radicals in order to improve the database of a class of molecules playing a dominant rôle in combustion and atmospheric chemistry.

Several experimental techniques have to be developed and concerted to achieve these aims. Many of the involved measurement techniques have to be developed and tested on spectroscopically well known or fairly accessible molecular systems.

Achievements

Introduction

In the frame of the project “Investigation of reactions and species dominating low temperature combustion” different approaches were undertaken to unveil energetics and dynamics of small molecules, radicals and intermediate species relevant in combustion and atmospheric chemistry. The molecules were prepared in different environments ranging from cold molecular beams to gas samples at high pressure and temperature. Frequency resolved [1-10] and fs-time resolved variants [11-16] of resonant four wave mixing spectroscopy have been applied to investigate the state specific dissociation mechanisms of formaldehyde excited to states near the dissociation threshold. The dynamics in the electronic ground state, including Coriolis interactions between different vibrations, could be well characterized by fs-coherent anti-Stokes Raman scattering (fs-CARS) [14].

A substantial part of our effort was spent to setting up a VUV beamline at Swiss Light Source (SLS). The beamline is dedicated to chemical dynamics. The different kinds of spectroscopic experiments including VUV- and photo-electron spectroscopy (PES) using tunable synchrotron radiation are optionally combined with time-of-flight mass spectrometry (TOF) [17-19]. TOF mass spectrometry is currently expanded with imaging concepts to achieve “complete” and accurate information on mass, energy and momentum of molecular fragments. Our work comprises the determination of thermodynamical data of intermediate species relevant in fields such as atmospheric chemistry, combustion and astrophysics with unprecedented accuracy [20-23].

Femtosecond non-linear spectroscopy

The methodology developed and applied to H_2CO [11, 12] at the begin of the project was carried on to TCFWM (Two colour four wave mixing) measurements on tert-buytl peroxy radicals. TCFWM signals are registered versus the delay between pump and probe pulses producing curves called transients. The transients reflect beatings of dipole transitions between energy levels addressed by the pump and probe pulses. A Fourier transform of the transients from time to frequency domain unveil the beating frequencies between those rovibrational Raman transitions that are excited within the bandwidth of the pump laser.

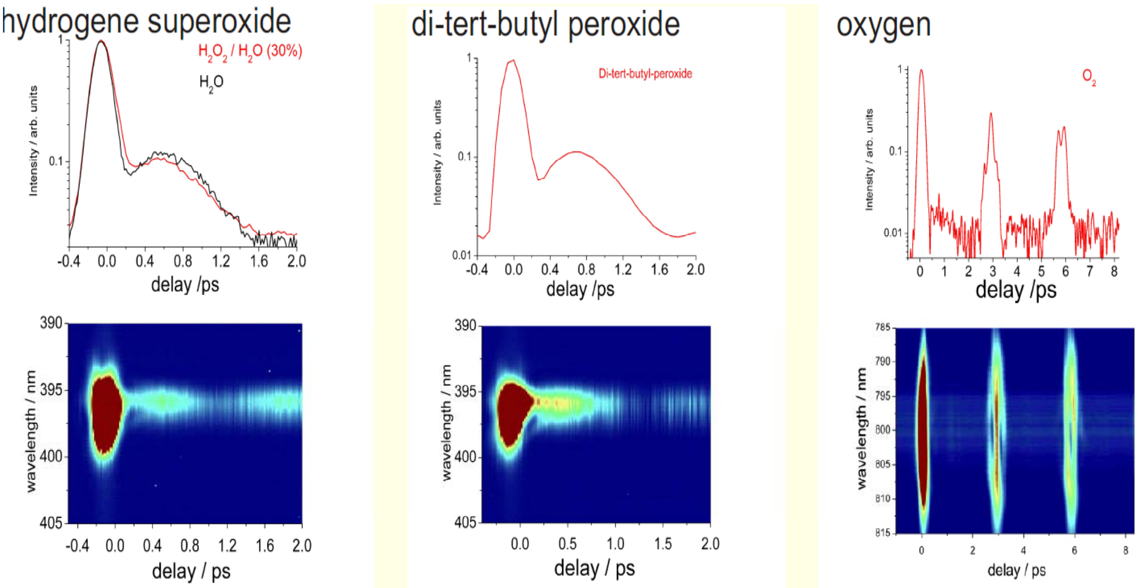

Fig 1. Integral and dispersed TCFWM signals for H_2O_2, $C_4H_{18}O_2$ and O_2. As is evident in the dispersed signal for O_2 (panel bottom right) the transient show variations depending on the wavelength. Due to a high S/N ratio small variations of the transients can be evaluated. These variations are also present, though less obvious, in the other panels of the bottom row.

The most prominent absorption in DTBOO (Di-Tert-Butyl-Peroxide) is in the UV spectral range between 340 nm and 230 nm. The photo excitation leaves the molecule in a non bonding orbital configuration. The molecule is then expected to break symmetrically at the RO-OR bond, producing vibrationally 'hot' TBO (Ter-Butoxy) radicals. The absorption of photons below ~ 230 nm wavelength correlates to a direct dissociation channel yielding $TBOO^{\bullet}$ radicals (Ter-Butyl-Peroxy) as products. However, independent of the used excitation frequency, our measurements indicate that an asymmetrical dissociation into TBOO prevails. We reported on these measurements performed with a spectrally integrated measurement of the signal in the last annual report.

More information can now be obtained by registering spectrally dispersed signals. Fig 1. shows three examples of dispersed spectra for H_2O_2, DTBOO and oxygen. The centre frequency of the probe is set near 396 nm for the H_2O_2-, DTBOO- and at 800 nm for the oxygen-experiment, respectively. In the panel for oxygen it can be readily seen, that a horizontal trace at the centre frequency yields another transient than a horizontal trace at a frequency off centre. While the centre trace shows a small maximum at the first recurrence around 3 ps and a "hole" at the second recurrence around 6 ps, two clear maxima are observed at the same locations for traces at frequencies off centre. Such differences are hidden in an integral measurement represented by the transients in the upper panel. Though not as obvious, similar variations can be observed in the measurements with H_2O_2 and DTBOO. The small variation can still be evaluated due to a high signal to noise ratio. A physical interpretation of the transients as a function of different wavelength, however, is very involved and the associated problems are not yet solved. Still, there is a great motivation to understand the mechanisms producing the dispersed signals: It can be shown that one measurement unveils everything one would like to know about the dynamics of the addressed molecular states (typically two rovibronic state ensembles in two different electronic states). Moreover, using fs-lasers, a measurement is typically finished after a scan of 20 minutes. If a fs-pump pulse is combined with a ps-probe pulse, a measurement could be done even in one single shot.

Dispersed signals generated in a fs-TCFWM process were registered with a 300 mm spectrograph equipped with a CCD camera. As input beams the fundamental at 800 nm or the second harmonic output of a Ti:Saph fs-laser (CPA 1000, Clark MXR, Dexter MI) was used. Fig. 2 shows three transients taken for DTBOO at different delay times τ_{12} between the two pump pulses. The transient is plotted against the delay time τ measured between the later pump pulse and the probe pulse (800/τ_{12}/800/τ/800/800). The parameter τ_{12} indicates the delay between the two initial pump pulses. With $\tau_{12} = 0$ the nonresonant contribution at zero delay is strong (panel bottom right). The non-resonant contribution is not specific for a molecule and not much information can be obtained from it. As soon as the probe pulse no longer overlaps with the two pump pulses, i.e., is delayed more than two times the pulse width (~100 fs) of the laser pulses, the non-resonant contribution ceases and the resonant contribution due to the induced polarization remains. Due to rotation and vibrations of different periodicity the polarization scrambles with increasing time and the signal fades off in an interval of about 2 ps. After some time

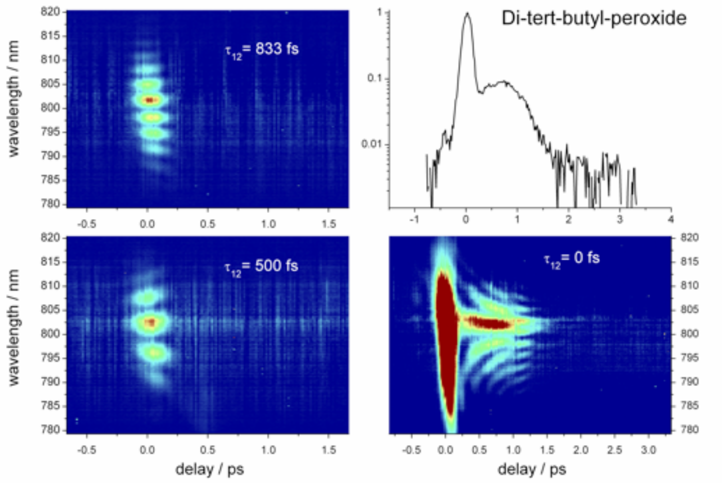

Fig. 2 Heterodyne signals with di-tert-butyl-peroxide taken at three different delays (parameter) between the two pump pulses. Right top a spectrally integrated transient is depicted.

corresponding to the common multiple of all involved rotational and vibrational periods the polarization would restore and the signal would recur. The time of recurrences is much longer than the 3 ps covered by the panels in Fig. 2.

The non-resonant contribution can be totally suppressed if the delay τ_{12} is set unequal zero, as gets obvious in the two other panels of Fig. 2 for τ_{12} = 500 fs and 833 fs, respectively. However, to restore the full information about a molecule the signal had to be acquired over a full ps-range of increasing τ_{12} delays. As the signal appears for $\tau_{12} \neq 0$ only close to coincidence of the second pump pulse and the probe pulse, the scan over the τ delay may be shortened.

The results are currently compared with spectra modelled with molecular data published in [24] and derived from own ab initio calculations (Gaussian). The transients at different wavelength (horizontal cut through the signal field at a specific ordinate) can be interpreted in terms of fundamental ro-vibrational modes and beat frequencies. Of special interest are torsion vibrations of di-alkyl-peroxides at low frequencies. When highly excited, these vibrations can go "overboard" i.e. become a rotation (as a pendulum that, if excited high enough, will "turn over"). It is difficult to establish the energy map of states near the transition from vibration to rotation (hindered rotator) theoretically. Our measurements are aware of low lying states and can thus be used to get experimental evidence of this ro-vibrational complication. A tentative interpretation of the measured transients is currently under way. Finalization of the findings could not yet be achieved and has to be subject to forthcoming work.

It is a most promising procedure to measure dispersed signals $E_{s,\omega}(t)$ mixed with a well-defined additional field $E_{LO,\omega}(t)$. This field can play the role of a local oscillator (called so in mathematical analogy to HF-technology). The coherent superposition results in

$$\left|E_{s,\omega}(t)+E_{LO,\omega}(t)\right|^2 = \left|E_{s,\omega}(t)\right|^2 + \left|E_{LO,\omega}(t)\right|^2 + 2\left|E_{s,\omega}(t)E_{LO,\omega}(t)\right| \qquad (1).$$

The last term in this equation indicates that part of the signal (heterodyne) is directly proportional to the term $E_{s,\omega}(t)$, as $E_{LO,\omega}(t)$ can be treated as a known quantity. It is easier to detect the linear signal than its smaller square. Moreover, if the phase of $E_{LO,\omega}(t)$ can be fixed also the signal can be detected phase sensitively. The measured beating pattern, corresponding to the last term in equation (1), unveils beating frequencies linearly as an amplitude modulation. Without a local oscillator, only the power (the square) of the signal field could be registered leaving room to more than one interpretation. The heterodyne experiment can be set up easily if the frequency of the local field is the same as the signal, as insinuated in equation 1. One of the input beams superposed to the signal fulfils the task.

The obvious interference pattern observable in all panels of figure 2 showing dispersed spectra is most probably due to such heterodyning with an additional field. The information content of the interference pattern in respect of the investigated molecules is still disputed. The extra field shows up spontaneously in our experiment. Similar effects were reported in other experiments. The interpretation of where this fifth field is derived from is still not yet conclusively proven [25, 26].

Two colour resonant four wave mixing (TC-RFWM) on C_2, C_2^-

The sensitivity of TC-RFWM (two colour resononant four wave mixing) for the detection of radical species in a molecular beam has been improved substantially. We applied our measurement techniques to the C_2 and C_2^- anion. C_2 plays a role in many chemical environments and can be detected in interstellar space as well as in many hydrocarbon-fuelled flames. In flame diagnostics C_2 became notorious as a disturber of the often applied CARS temperature measurements. In the common set up with Nd:YAG lasers the Swan band of C_2 interferes with the stimulated CARS spectrum from which temperature is inferred.

With application of a slit source comprising a discharge arrangement [6, 8] we could achieve a sensitivity down to a density of 10^9 cm^{-3}. In contrast to the widespread believe that FWM is only applicable to majority species, we could registered well defined spectra even of the C_2^- anion at “vanishing” densities: The C_2^- were prepared in our molecular beam set up with a density of less than 10^{10} cm^{-3}, i.e. the probed sample consisted of only 10^7 molecules. A density of 10^{10} cm^{-3} corresponds to the density of the rest gas in what is else called high vacuum (10^{-6} mbar). We showed that the complex one-photon spectra of C_2 which is caused by overlapping transitions are simplified dramatically by two-colour four-wave mixing and reveal weak spectral features like satellite transitions and perturbations of close lying electronic levels [1]. Due to strict selection rules, TC-RFWM measurements allow to address single transitions that appear blurred by nearby transitions when linear spectroscopic techniques are used. Choosing appropriate TC-RFWM excitation schemes, coincident or overlapping lines can be addressed one by one. Assignment of perturbed transitions is achieved by intermediate level labelling in the spectral Swan system. Several new and already reported lines could be reassigned and the molecular constants could be improved such that all measured spectral features can unambiguously be detailed out with common models.

The TC-RFWM set up is now ready for four-wave mixing experiments with peroxy radicals produced in the discharged slit-jet using a mixture of halogenated hydrocarbons and O_2 in analogy to the procedure documented in ref. [27]. Moreover, the discharge driven slit source, or its cylindrical equivalent, will be tested at SLS for general use in the VUV beamline set up.

The experimental facilities developed in our laboratory are generally well suited to take the investigations on peroxyl radicals one step further. Precursors and conditions for the slit-jet discharge can be optimized by fs-ionization monitoring. The Two-Colour Four-Wave-Mixing (TC-RFWM) spectroscopies we have developed so far will be applied for level labelling due to its potential to simplify congested spectra. The high temporal resolution of the available FWM techniques (100 fs to 10 ns) is capable of probing specific instances of the gas pulse, when there is an optimum between abundance and low temperature. The expected precise spectra unveil detailed rotational and fine structure parameters that can be used to benchmark ab initio computations.

Theses

In a co-operation with the group of Prof. F. Merkt, Laboratorium für Physikalische Chemie, ETH Zürich, their expertise on photo-electron spectroscopy could be combined with our experience on the electronic spectroscopy of formaldehyde. Detailed information about the $3p_x$ Rydberg states and the rovibrational energy level structure of the cation could be worked out. Specific vibrational states of the ion are accessible by exciting suitable Rydberg states in a two photon step with subsequent single photon ionization. With this scheme, information on the energy of the ground- and the 61- and 41- vibrational levels of the cation could be obtained [3, 8, 28]. The measurements on formaldehyde using FWM and photo-electron spectroscopy were compiled in the thesis of Margarete Meisinger [29] working in our group until May 2009. Apart from their importance for state-specific cation production, low-lying Rydberg states open ways to the study of additional unimolecular dissociation channels that occur in the VUV energy region around 68000 cm^{-1}. Such investigations are relevant as a benchmark to control and improve current ab initio calculations.

In parallel to the frequency domain investigation the dynamic of formaldehyde excited to the S_1 state manifold was investigated with ultrafast femtosecond (fs) laser spectroscopy. In 2009, Andreas Walser finished his thesis [30] on the topic: “Investigation of ultrafast molecular dynamics of combustion relevant species by time resolved non-linear Raman spectroscopy” [11, 14]. His approach of time resolved four wave mixing involves the coherent interaction of three deliberately delayed laser pulses with a molecular ensemble. The induced macroscopic polarization induced by two pump fields acts as a source for a fourth coherent signal field when interrogation by a third field at a delayed time τ. Information about the rovibrational manifold in the first excited state (S_1) are obtained when the pump pulses are in resonance. To reach this resonance the excitation laser has to be tuned to the UV domain around 300 nm. If resonances with electronic states are avoided information about the ground sate manifold (S_0) can be worked out.

Absoprtion measurements at the VUV beamline

The SLS/VUV beamline comprises a grating monochromator providing a resolution of ~ 1meV at 10 eV. In order to suppress higher harmonic radiation, (i. e. radiation at wavelengths 2λ, 3λ, …nλ, besides the wanted λ), we installed a gas filter upstream to the so-called PEPICO endstation. There is no solid filter that could be used as a window and that passes radiation at e.g. 15 eV cutting off radiation at 30 eV. Only rare gases can be used for this purpose. Our gas filter works with Kr, Ar, Ne and their mixtures at a pressure of a few 10 mbar. To maintain vacuum on both sides, upstream and downstream, there is differential pumping over several sections divided by small pupils with a passage just big enough to pass the light beam having a diameter of smaller 2 mm. Due to this differential pumping there is a constant gas flow from the gas filter towards the endstation. Therefore, hydrocarbon compounds can be introduced into the endstation vessel at pressure up to 40 mbar without any risk to contaminate beamline optics maintained in vacuum at 10^{-9} mbar in front of the gas filter.

As a first candidate for an absorption measurement we introduced DTBOO. The absorbance has been measured for photon energies from 5.4 - 9.8 eV with a spectral resolution of < 10 meV. The DTBOO vapour pressure in the chamber was 0.1 mbar and the absorption length was ~ 30 cm. The absorption cross section strongly increases below 220 nm (> 5.63 eV) by orders of magnitude and a relative maximum is reached at ~ 180 nm (6.8 eV), which is in the vicinity of the dissociating B $^2A''$ – state. The IP of DTBOO at 8.78 eV [31] is also clearly seen by the appearance of a second plateau in the absorption spectrum. The weak-modulation of the absorbance just below the Ionization threshold energies may indicate the presence of several Rydberg states. The absorption measurements can be compared with NIST data [31] tabled for wavelength in the visibel to UV domain in order to get an extrapolated calibration of the cross section.

These absorption measurements establish a valuable tool that can be applied to all molecules having a high enough vapour pressure at room temperature. Keeping in mind that many absorption tables, e.g., those published in the NIST chemistry webbook, contain rather old data in a limited energy range (typically < 7.5 eV), and with limited resolution, the easy to perform measurement at the VUV beamline are certainly a point of interest.

Using an appropriate source or very low pressures the PEPICO endstation allows not only to measure at what wavelength radiation is absorbed, but also what ion is produced or, in the case of dissociation, what fragments are produced. We are now going to develop measurement schemes allowing the detection of fragments emanating from the dissociation of DTBOO as a function of energy.

Imaging photoelectron photoion coincidence spectroscopy (iPEPICO)

In 2008 the VUV beamline arrived at its final status, open for internal and external users. Some of the pilot users in 2008 now continue their work as regular users. Among them, the groups of Ingo Fischer (University of Würzburg), of Balint Sztaray, (Univ. of the Pacific) and of Richard Tuckett (University of Birmingham) established as long term users. New users, Prof. Dr. Agust Kvaran, (Univ. of Iceland) and Christine Joblin, (Centre d'Etude Spatiale des Rayonnements, CESR) got an appointment to use the VUV beamline in the first half of 2010.

The iPEPICO (imaging Photoelectron-Photoion Coincidence) setup is installed and fully operational. The set up consists in essence of two acceleration regions for ions and electrons flying in opposite directions. The acceleration regions share the same axis and start at the interaction region where photons from the beamline interact with molecules injected as a molecular beam. The photoelectrons, are detected after a short travel whose duration (time-of-flight, TOF) is neglected and provide signals to start a time counter for the measurement

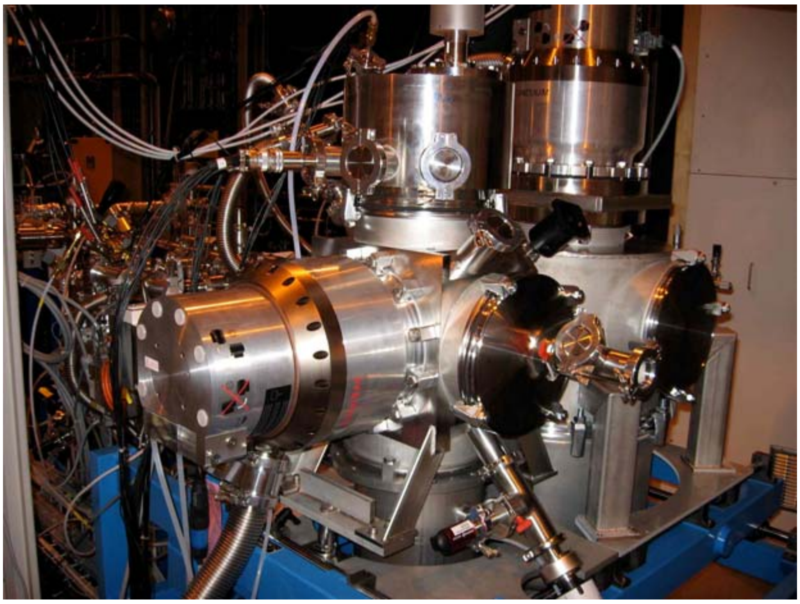

Fig.3. Interaction chamber of the PEPICO endstation. The vertical cylinder on top left contains the imaging electron detector. Ions fly vertically down. The light beam traverses the interaction chamber on the axis defined by the small thin tube protruding to the right.

of ions that will arrive later at a detector. The arrivals of the photoions are registered with the time counter. Ion times of flight (TOF) can be determined. From the ion-TOF the mass of an individual ion can be inferred. A special feature of the PEPICO set up is its “velocity imaging detector”, which allows the measurement of the kinetic energy of the photoelectrons with 1 meV accuracy. Electrons with a velocity component orthogonal to the acceleration axis will arrive at the detector a certain distance away from the axis. We use a position sensitive detector to measure this distance. Electrons with the same absolute momentum perpendicular to the flight axis arrive on the detector in concentric circles. After a convolution the kinetic electron energy can be retrieved allowing the study of dissociating ions with a defined internal energy. Of special interest are electrons with zero kinetic energies (ZEKE). Evaluating only ZEKE events alleviates substantially the evaluation of possibly reached internal energy states of the ion prior to dissociation. With the kinetic energy of electrons and the energy of the ionizing photons, a full energy balance of a dissociation process can be established if also the ionization threshold of the fragment ion is either known or can be derived from an additional measurement.

A new data acquisition program was developed, basing on a correlation between electron and ion counts [19]. The code comprises a graphical user interface and scripting possibilities for automated data acquisition and analysis. The electronics and the software are the first in this field to enable a triggerless multi-start/multi-stop setup for two-particle coincidence experiments.

Due to a major upgrade in 2009 the 5000 l/s cryogenic pump can now be separated from the source chamber by a gate valve. In the source chamber gas samples are injected by a suitable source. For the generation of molecular beams containing molecules with a low vapour pressure, a heatable reservoir has to be mounted directly on the source inside the vacuum. For refilling this reservoir, or simply for access of delicate sources needing servicing on a regular base, the source chamber has to be opened quite often. Due to the gate valve and due to the earlier installed valve separating the source chamber from the interaction chamber a quick service, breaking the vacuum only of the source chamber, can be performed without attending a long cycling up and down of the cryogenic pump.

Our planned measurements of alkyl peroxy radicals could not yet be started. A first measurement campaign will be conducted in December 2009, just in continuation to the current project period. But work with two beamline users with whom we have a close cooperation is also relevant for the general aim followed in this project. In cooperation with Tom Baer and Ingo Fischer we contributed to three publications, all having direct relevance for combustion chemistry [20, 22, 23].

Measurements at the SLS VUV beamline and at the University of North Caroline were dedicated to the dissociation of the ions of di-tert-butyl diazene and of di-tert-butyl peroxide

(DTBOO). The derivation of the formation enthalpy of the *t*-butyl peroxy radical, for which no experimentally reported values exist, could be achieved [20]. To this aim, the threshold energy at which DTBOO starts to dissociate into tert-butyl peroxy had to be measured. The experimental findings in both labs can be scrutinized with appropriate dissociation models to yield the dissociation channels of the excited precursor ions and their corresponding appearance energies. With the obtained results the enthalpies of *t*-butyl peroxy (TBOO) radical could be determined to be $\Delta_f H^0{}_0$ = 81.1 ± 3.9 kJ mol^{-1} and $\Delta_f H^0{}_{298}$ = 109.7 ± 3.9 kJ mol^{-1}. The evaluation hinges on the enthalpies of tert-butyl ions, the enthalpy of DTBOO, and the ionization energy of DTBOO. New measurements and calculations of DTBOO suggest an ionization energy of 8.32 eV. The formation enthalpy of tert-butyl ions was determined in Baer's group before and the heat of formation of DTBOO relies on published results.

The second publication together with Baer's group deals with Iodomethane [23]. The appearance of CH_3^+ ions by dissociative photoionization of CH_3I was already investigated thoroughly. Three earlier attempts to determine the exact value of this appearance energy produced contradictory results. High resolution (2 meV) measurements at the VUV beamline show an oscillatory behaviour of the ionization efficiency as a function of energy, indicating a complication due to the electronic A-state that lies close to the dissociation limit. Rydberg progressions converging to vibrationally excited A-state levels enhance the ionization efficiency whenever the excitation energy approaches the energy of the corresponding vibrational level. The room temperature iPEPICO experiment yields an accurate 0 K onset of 12.248 ± 0.003 eV, from which a $\Delta_f H^0{}_{298}$ (CH_3I) = 15.23 ± 0.3 kJ mol^{-1}, and a C–I bond energy in CH_3I of 232.4 ± 0.4 kJ mol^{-1} could be derived.

Ingo Fischer and his group carried out first iPEPICO measurements on three resonance stabilized radicals, 1-indenyl (Ind), 1-phenylpropargyl (1PPR), and 3-phenylpropargyl (3PPR) using the molecular beam and a pyrolysis source [22]. All these radicals are isomers of the composition C_9H_7. Up to now only approximate experimental ionization energies were available for either of the phenylpropargyl radicals. The adiabatic ionization energies (IE) for Ind (7.53 eV), for 3PPR (7.20 eV), and for 1PPR (7.4 eV) could be determined and agree with those obtained from ab inito calculations. No major change of the molecular geometry occurs upon ionization. The difference in the IE might allow a distinction of the three isomers in flames. The ionization energies and the photoionization efficiency curves of the brominated parent compounds (C_9H_7Br) were also measured.

Cooperations

The Swiss National Science Foundation (SNF) contributed to this project by supporting two dissertations with titles “Characterization of Vibrationally and Rotationally Excited Molecules by Two-Colour Resonant Four-Wave Mixing” and “Investigation of ultrafast molecular dynamics of combustion relevant species by time resolved non-linear Raman spectroscopy”. As mentioned above Andreas Walser and Margrete Meisinger submitted their theses successfully in fall 2008 and spring 2009, respectively.

A strong cooperation between the groups of Prof. Merkt, ETH and J.P. Maier, Uni Basel fosters experimental techniques that can be adopted to reach our goals. Good links are maintained with Prof. S. Leutwyler and H.-M. Frey, Uni Bern.

The in-house development of a VUV beamline at the SLS starts to produce results and thus provides a great synergy with our endeavours subsumed in the BFE project. With the chemical dynamics activity at SLS, a lot of knowledge and experience is brought to us by external groups. The relevance to our work is quite obvious in the close cooperation with Prof. Tom Baer (University of North Carolina) and Prof. Ingo Fischer (Universtät Würzburg).

Since 2007, we were involved in the preparative work for a proposal for a new COST Action. The Action dedicated to chemical kinetics was approved by the COST Committee of Senior Officials (CSO) in May 2009. The State Secretariat for Education and Research (SER) agreed to participate in the action and appointed us as a Swiss delegate to the steering and technical committees. SER will also support up to two projects within the framework of the COST action, financially.

Conclusion and Outlook

In the current report period, and in projects before, the molecular dynamics group established a solid competence on how to approach combustion chemistry on a fundamental molecular level. Our methods allow to determine the energy map and the elementary reaction channels that govern the progress of a combustion process. Alkyl peroxy radicals were in the main focus of our endaveour. Some of our results approach this aim, but we could not yet reach the very focal point of our objectives. The laser and synchrotron based spectroscopic instruments requested a longer implementation time than foreseen. We are optimistic that the now well established methods will demonstrate their full productive potential. We will be able to produce molecular data about radicals that were not yet subject to any experimental consideration. Due to a higher resolution compared to standard experiments and due to the imaging capability of the PEPICO set up, the VUV beamline will help to improve experimental results performed elsewhere that lack accuracy or that are not yet fully accepted. However, we continue to have doubts whether the alkyl peroxy “problem” can be solved appropriately comprehensive in the next three years, as this task is really very demanding.

The experimental challenge with peroxy radicals consist in the difficulty of a) their production in a molecular beam, b) their spectral bands lying in the far UV and c) to monitor the unstable and quickly dissociating peroxy ions with mass spectrometric techniques. Still, peroxy remains in our focus as we are persuaded, that the role of peroxy has to be understood for a correct assessment of low temperature combustion as well as of atmospheric chemistry. We also believe that there is no “work around” and that this task has to be tackled as soon as possible in spite of the mentioned discouraging facts.

Some of the pyrolytic sources developed by us will be treated in future under the aspect of “micro-reactor”. This will open a route to kinetic measurements that could produce directly “usable” thermochemical information though this information will be less robust than our basic experiments on the molecular level. We will start to connect “micro-reactors” to mass spectrometric measurements in order to register radicals, - a still rarely chosen approach to chemical kinetics. While industries are interested into an optimal yield in synthesis by micro-reactors, we are interested in the intermediate termination of an ongoing reaction. The interaction time in such a reactor can be adjusted by the reactor length and the flow velocity which in turn is adjustable by the diameter and the pressure across the reactor. At the outlet the reacted gas can expand into vacuum. After a few nozzle diameters all reactions cease due to a high enough rarefaction, - there are no more collisions -, and the intermediate radicals can be registered in a TOF mass spectrometer downstream. The basic idea is to map out the actual radical pools in a reacting gas in dependence of reaction time and stoichiometry and possibly on the catalytic action of reactor walls. We believe that such a set up is a very promising approach to real pressure, real temperature chemical kinetics.

In the next 4 years, starting in spring 2010, the PSI molecular dynamics group will engage in the COST Action CM0901 with title „Detailed chemical kinetic models for cleaner combustion”. COST - European cooperation in the field of scientific and technical research - is an inter-governmental European framework for international co-operation between nationally funded research activities. One of the motivations leading towards this proposal was the perceived absence of national and EU funding for a network about fundamental studies of chemical kinetics aiming at the understanding of combustion processes. Due to the initiative of Dr. Frédérique Battin-Leclerc (Nancy, France), Dr. Edward Blurock (Lund, Sweden) and Prof. John Simmie (Galway, Ireland) a research program could now be set up which is dedicated to the fundamental chemical aspects of combustion. Most of our investigations of radicals will in future be performed in this context.

We also will cooperate within the competence centre NCCR-MUST (National Competence Centre of Research - Molecular Ultrafast Science and Technology) which was submitted to SNF in fall 2009. The application for the NCCR obtained a good score in the first stage proposal round. Both environments, COST Action and NCCR will facilitate the co-operation with a comprehensive sample of European and Swiss groups sharing our interests.

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