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INVESTIGATION OF REACTIONS AND SPECIES DOMINATING LOW TEMPERATURE COMBUSTION

Jahresbericht 2007

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BFE Projekt-/Vertrag-Nummer	101969/152433
BFE-Projektleiter	Stephan Renz
Dauer des Projekts (von – bis)	1.12. 2006 –30.11. 2009
Datum	8. Dezember 2007

ZUSAMMENFASSUNG

Die unter dem abgekürzten Titel “Peroxy” laufende Projektarbeit hat das Ziel, eine gute spektroskopische Basis zur Erfassung der Alkyl-Peroxyl Radikalen zu erstellen. Peroxy Radikale bestimmen das Zündverhalten brennbarer Kohlenwasserstoffen/Luft Gasgemische. Im Rahmen der Untersuchungen müssen unter Umständen auch die Edukte und Produkte der Peroxy Radikalen vermessen werden. Dazu gehören Alkyl Radikale, Olefine, Aldehyde und Hydroperoxide.

Bis heute gibt es keine vollständigen spektroskopische Datensätze von Peroxy-Radikalen. Um diese Lücke zu schliessen, entwickeln wir aufwändige spektroskopische Messmethoden und spezielle Molekularstrahlapparaturen, in denen die zu untersuchenden Radikale in einer gut definierten sauberen Umgebung dargestellt werden können. Im nahezu stossfreien Molekularstrahl bleiben die bei tiefen Temperaturen gebildeten Radikale stabil, bis sie gezielt mit Licht angeregt und zur Dissoziation gebracht werden können. Für diese Dissoziationsprozesse in Abhängigkeit der Anregungsenergie interessieren wir uns besonders, da durch sie die Bindungsenergien und damit Aktivierungsenergien und Bindungsenthalpien bestimmt werden können.

Mit Hilfe einer neuen Versuchsanlage konnten FWM (Four wave mixing) und CRD (cavity ringdown) Signale von Radikalen mit einem Signal/Rausch Verhältnis (S/N) von im Allgemeinen besser 100 erzielt werden. Mit eienr besonders sorgfältigen Justierung gelang der Nachweis von C_2 – Molekülen sogar mit einem S/N Abstand von 10^8. Auf Grund dieser hervorragenden Empfindlichkeit konnten anschliessend auch C_2^- Anionen mit einem gut interpretierbaren Spektrum direkt nachgewiesen werden, - nach unserer Kenntnis das erste Mal überhaupt. Diese demonstrierten Empfindlichkeit ist ein wesentlicher Schritt in Richtung Vermessung von Peroxy Radikalen.

Die Anwendbarkeit von dreifach resonanten fs – FWM Methoden konnte anhand von H_2CO demonstriert werden. Die Anwendung derselben Messmethode auf Di-tert-buytyl Peroxy ergibt Hinweise, dass offenbar Butyl-Peroxy Radikale gebildet werden. Dieses Resultat ist ein erster Einstieg in die Spektroskopie der Peroxy-Radikale.

Einleitung

Die unter dem abgekürzten Titel “Peroxy” laufende Projektarbeit hat das Ziel, eine gute spektroskopische Basis zur Erfassung der Alkyl-Peroxy Radikalen zu erstellen. Peroxy Radikale bestimmen die Zündung eines brennbaren Gasgemisches. Je nach Brennstoff, dauert es länger oder kürzer bis sich eine Flamme entwickelt hat. Sobald die Flamme bei hoher Temperatur brennt kann sie mit einer vergleichbar einfachen Kinetik beschrieben werden kann. Bei niederen Temperaturen dagegen sind die ablaufenden Prozesse ausserordentlich komplex und hängen stark von der anfänglichen Zusammensetzung des Brennstoffs ab.

Mit spektroskopischen Messungen können wir insbesondere die Bildungsenthalpien der Peroxy Radikalen experimentell bestimmen. Bisher wurden entsprechende Angaben meist nur theoretisch mit aufwändigen Modellen gewonnen, deren Genauigkeit nicht genügend genau abgeschätzt werden kann. Allerdings, auch die experimentelle Bestimmung solcher Grössen gelingt kaum auf Anhieb. Unter Umständen müssen auch Edukte und Produkte der Peroxy Radikalen vermessen werden. Dazu gehören Alkyl Radikale, Olefine, Aldehyde und Hydroperoxide. Um ein Bild von der Art und Verteilung der sich anfänglich in einer Flamme bildenden Radikalen (Radikalen-„Pool“) zu gewinnen, müssen alle einzeln nachweisbar sein. Als wichtiger Indikator für den momentanen Zustand einer Flamme gilt insbesondere auch das Molekül Formaldehyd, das ein wichtiger Gegenstand unserer Forschung bleiben wird.

Bis heute sind die spektroskopischen Daten von Peroxy-Radikalen eher dürftig. Um eine bessere Wissensbasis zu erstellen müssen aufwändige und und für Peroxy massgeschneiderte spektroskopische Messmethoden zum Teil noch entwickelt werden. Für diese Arbeiten müssen Peroxy Radikale in definierter Form vorliegen. Flammen, in denen Peroxy-Radikale unter anderem gebildet werden, eignen sich als Messumgebung nicht, da die Vielzahl von parallel ablaufenden Prozessen die heiklen Messungen stören würden. Speziell entwickelte Molekularstrahlapparaturen werden eingesetzt, um die zu untersuchenden Radikale in einer gut definierten, sauberen Umgebung darzustellen. Mit diesen Techniken können kurzlebige Moleküle bei sehr tiefen Temperaturen hergestellt werden. Da im Molekularstrahl keine Stösse auftreten, bleiben die Radikale stabil, bis sie gezielt mit Licht angeregt und zur Dissoziation gebracht werden können. Für diese Dissoziationsprozesse in Abhängigkeit der Anregungsenergie interessieren wir uns besonders, da dadurch die Bindungsenergien und weiter die Bindungsenthalpien bestimmt werden.

Die in der letzten Projektperiode fertig gestellte Interaktionskammer ist mit Erfolg in Betrieb genommen worden. Die Molekularstrahlquelle ist auf einer XYZ Translationsbasis mit Vakuumdurchführungen montiert, so dass sie während des Betriebes justiert werden kann. Die Quelle ist heizbar, damit auch bei Raumtemperatur flüssig oder sogar fest vorliegende Stoffe in den Molekularstrahl eingebracht werden können. Zusätzlich wurde die Quelle statt der herkömmlich runden, mit einer schlitzförmigen Öffnung ausgerüstet, um das Interaktionsvolumen von Laserstrahlen und Molekularstrahl Zu vergrössern. Allerdings müssen auch grössere Pumpen eingesetzt werden, da der ausgedehnte Molekularstrahl zu einem grösseren Gasdurchsatzführt. Weiter gelang es, eine Entladungsanregung, mit der aus geeigneten Molekülen die gewünschten Radikale erzeugt werden, in die neue Schlitzdüse einzubauen. Dank der insgesamt verbesserten Versuchsanordnung konnten FWM (Four wave mixing) und CRD (cavity ringdown) Signale mit einem Signal/Rausch Verhältnis (S/N) von mehr als 100 erzielt werden. Mit einer sorgfältigen Optimierung der Entladungsparameter und der exakten Einstellung der FWM Laserstrahlen-Geometrie gelang der Nachweis von C_2 – Molekülen sogar mit einem S/N von 10^8. Auf Grund dieser hervorragenden Empfindlichkeit konnten danach auch C_2^- Anionen mit einem gut interpretierbaren Spektrum direkt nachgewiesen werden, - nach unserer Kenntnis das erste Mal überhaupt. Dieses Resultat ist auch darum bemerkenswert, weil der Nachweis gelang, obschon die Dichte der Anionen als eher gering angenommen werden muss. Mit der so demonstrierten Empfindlichkeit sind wir der Vermessung von Peroxy Radikalen wesentlich näher gekommen. Allein, die Herstellung von Peroxy-Radikalen ist herausfordernd. Mit einer weiteren Radikalenquelle die erlaubt, reinen Sauerstoff durch ein zweites Ventil zu dem vorher mit einer Entladung angeregten Gas beizufügen, wurden erste Experimente durchgeführt. Bisher gelang es H_2CO, HCO und CO aus mit der Entladung angeregtem Methan und O_2 herzustellen.

Die Anwendbarkeit von dreifach resonanten, zeitaufgelölsten fs – FWM Methoden konnte anhand von H_2CO demonstriert werden. Bei Anregung im UV-Gebiet werden mehrer Dissoziationswege ausgehend vom elektronischen S_1 Zustand von H_2CO angesprochen. Die Lebensdauer bezüglich Dissoziation hängt von der Anregungsenergie ab und bewegt sich im Bereich von ps bis ns. Die Anwendung der selben Messmethode auf Di-tert-buytyl-peroxy ergibt Hinweise, dass tatsächlich Butyl-Peroxy und nicht wie erwartet Butoxy Radikale gebildet werden. Dieses Resultat ist ein erster Einstieg in die Spektroskopie der Peroxy-Radikale über die bis heute bestehenden Grenzen hinaus.

Projektziele

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, - among them the aldehydes. We intend to directly measure the formation and dissociation enthalpies that up to now were only indirectly inferred from kinetic experiments or derived in 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.

Dissociation properties of alkyl peroxy radicals play an important role in atmosphere and in combustion processes. However, even relatively simple reactions like the combination of ethyl radicals with dioxygen, i.e.

$$CH_3CH_2 + O_2 \rightarrow [CH_3CH_2OO]^* \rightarrow CH_2CH_2 + OOH \quad (1),$$
$$\rightarrow CH_3CHO + OH \quad (2) \text{ or}$$
$$\rightarrow c\text{-}CH_2CH_2O + OH \quad (3)$$

are not well understood. A comprehensive understanding of the mechanism for these gas-phase reactions would likely allow an extrapolation to more complex hydrocarbon systems. Unfortunately, the spectroscopic characterization of peroxy radicals, like CH_3CH_2OO, is very difficult and complex measurement techniques have to be invoked.

A flame in which peroxy radicals are present is not suited for these delicate investigations. As a consequence, radicals have to be prepared by specially designed sources that yield a sufficient concentration for optical detection. The preparation of very cold molecules in a molecular beam in which collisions among molecules can be neglected is optimally suited to perform spectroscopic investigations of multiatomic molecules.

The aim of this project is two fold:

- Measurement of molecular features such as binding energies and micro canonical rates for 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.

Our PHOFEX-experiments (Photo Fragment Excitation) developed for H_2CO are continued to obtain a comprehensive map of state to state dissociation data. The results will be checked against predictions obtained with unimolecular dissociation models. For the comparison of measurements with theory we enter a close cooperation with theoreticians working in this field.

Femtosecond CARS experiments (Coherent Anti-Stokes Raman Spectroscopy) will be performed to assess excitation to high lying vibrational states of H_2CO and , if possible, of HO_2 and alkyl peroxy radicals.

The knowledge base for peroxy radicals is not yet sufficient to directly apply e.g., PHOFEX and fs-CARS techniques. Even if the techniques work, we do not expect them, to yield the full range of information we got in the treatment of H_2CO. Our efforts will therefore concentrate on a first approach to measurements of ground state vibrational frequencies and the energy of dissociation limits.

Experiments at the SLS/VUV beam are scheduled to assess the character of alkyl peroxy ion states. The dissociative photo-ionization techniques available in the VUV may be suited to determine the ground state dissociation threshold directly. Moreover, a clear picture about the alkyl peroxy ions, stable or dissociative, is an important ingredient for future mass spectrometry in combination with laser spectroscopic measurements.

According to the double fold aim we expect two results:

- Contribution of an important data set, mandatory to obtain a sound understanding of H_2CO, and possibly HO_2, dissociation. The complementarity of fs- and ns-measurement techniques should be clearly exemplified with these molecules. The measurements will help to harden unimolecular dissociation models that can then be applied to other molecules with more trust than now.

- Dissociation paths and energies of HO_2 and alkyl peroxy radicals. The combination of synchrotron VUV spectroscopies and laser spectroscopic measurement will yield more exact values of dissociation energies of peroxy radicals and the identification of dissociation channels. These data will improve the knowledgebase for current theoretical efforts dedicated to combustion modelling.

Durchgeführte Arbeiten und erreichte Ergebnisse

Slit Assembly for the Radical-Source: DFWM and TC-RFWM spectroscopy of HC_4S, C_2 and C_2^- in a Molecular Beam Environment

In a recent development the discharge source mounted on the translation stage was equipped with a slit assembly allowing a laterally extended molecular beam providing a spatially greater overlap of the molecular beam with the laser beam. With this set up a much bigger signal was obtained providing a signal-to-noise ratio (S/N) of ~100 for four-wave mixing (FWM) and cavity ring-down (CRD) spectroscopy. With a careful optimization of the discharge parameters and with an accurate alignment of the degenerate FWM (DFWM) experiment overwhelming S/N ratios up to 10^8 were obtained for C_2 in the molecular beam. This excellent sensitivity allows us also, to detect with a DFWM method C_2^- anions for, - to our knowledge -, the first time. Actually, the excellent observed S/N of 10^4 in spite of the extremely low C_2^- - densities bodes well for assessing the important class of peroxy anions[1] with our experimental approach.

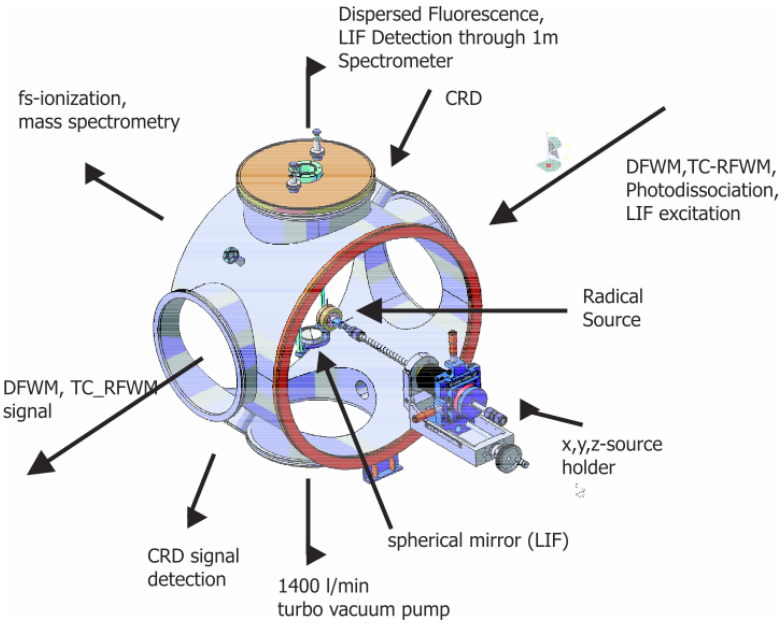

Figure 1: Molecular beam apparatus for multiplex spectroscopy.

The new molecular beam apparatus, designed for multiplex spectroscopy (DFWM, TC-RFWM, LIF, CRD, fs-ionization/mass spectrometry) has been described in earlier reports and in a recent publication[2]. For quick reference the main features are repeated here. Fig. 1 depicts the interaction chamber of our molecular beam apparatus together with a schematic representation of the different applied spectroscopic measurements methods. A molecular beam is generated by supersonic expansion through a pulsed valve which is mounted on a xyz-translation stage. For solid or liquid substances exhibiting a too low vapour pressure at ambient temperatures, the source holder is heatable by two heating loops. The valve operates at 10 Hz and creates a gas pulse with about 500 µs duration.

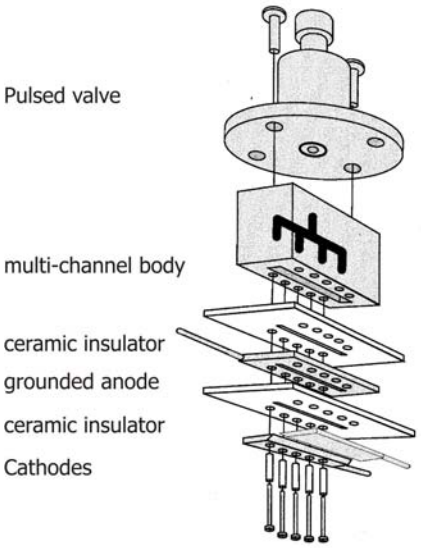

Figure 2. Discharge source with a rectangular orifice.

Figure 2 shows an additional option of the instrumentation: A slit-source assembly. The device has been designed originally for cavity ring-down spectroscopy by Maier's group in Basel.[3] A multi-channel body is mounted on a pulsed valve regulating the gas flow. Gas proceeds through a ceramic insulation layer towards the anode, a slotted stainless steel plate providing two sharp jaws along the slit length. Another set of jaws downstream separated with a ceramic spacer from the anode serves as cathode. The cathode is rapidly charged to a high negative voltage at the time when an arriving gas pulse exhibits an optimal pressure. The geometry of the electrodes limits the discharge to a region upstream of the expansion.

The emerging molecular beam containing radicals and other transient species is crossed perpendicularly by the three input beams which establish a forward BOXCARS configuration for DFWM experiments (Figure 3). I_1 and I_2 are the pump beams, I_p and I_s the probe and signal beams, respectively. The beams propagate almost parallel to the larger dimension of the expanding rectangular molecular beam. Significant enhancements in sensitivity and resolution are thus obtained over that recorded with a conventional free jet source having a circular nozzle orifice. The increase of the S/N ratio by a factor of ≈ 100 is mainly due to the increase of the effective interaction length of the nearly collinear laser beams with the slit-jet expansion.

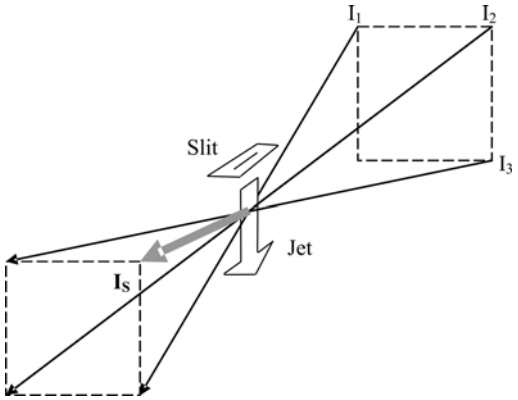

Figure 3. Forward BOXCARS arrangement of input and signal laser beams for a FWM experiment.

Initial experiments have been performed on HC_4S[4] and C_2. To date, measurements on the combustion relevant C_2 by four-wave mixing techniques have been carried out only in high-temperature (3000 K) oxy-acetylene flames. HC_4S has been chosen for the collaboration with the Basel group according to their interest in sulfur-terminated carbon chains having a high relevance in astronomy due to a relative large abundance in space. In a recent publication[4], we illustrate that the two-color approach, applied to the d $^3\Pi_g$-a $^3\Pi_u$ system of C_2 and the Ã $^2\Pi_{3/2}$ - $\widetilde{X}\,\Pi_{3/2}$ electronic transition of HC_4S, provides a spectroscopic tool for unambiguous assignment of photonic transitions while offering the possibility of disentangling overlapping components. The potential of using four-wave mixing in slit-jet discharges for studying radicals at low temperature is thus asserted.

Further improvements have been achieved by carefully adjusting the delay of the pulsed discharge (≈ 5 kW peak) in respect to the opening of the pulsed valve. In fact, a S/N ratio of ≈ 10^8 could be achieved for the C_2 radical.

The extraordinary well performing experimental facility set up in our laboratory opens a most sensitive approach to detailed spectroscopic studies of transient and internally cold transient and radical species in a collision-free environment. Recently, we succeeded in producing a degenerate four-wave mixing signal with C_2^-, a species representing the important class of molecular anions. Figure 4 shows, for the first time to the best of our knowledge, a rotationally resolved DFWM spectrum and a simultaneously obtained LIF signal of the B $^2\Sigma_u^+$ - X $^2\Sigma_g^+$ electronic transition of C_2^-. In addition, a simulation with PGOPHER[5] using published molecular constants[6] is shown in Figure 4 (inverted trace). The abundance of the negatively charged carbon dimer relative to the neutral is roughly 1%. Nevertheless, still an excellent S/N ratio of ≈ 10^4 is obtained which is sufficient to even perform the doubly-resonant variant of the FWM method: two-color resonant four-wave mixing (TC-FWM).

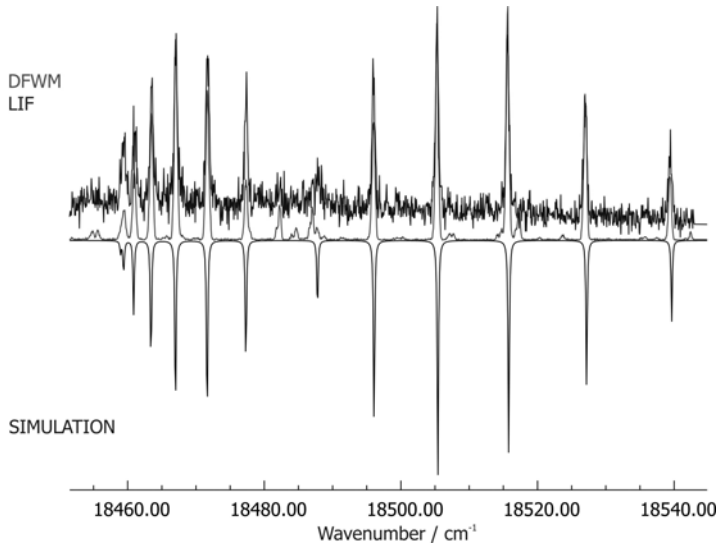

Fig. 4: DFWM (middle trace) and LIF (uppermost trace) of the C_2 anion obtained upon discharge and slit source expansion in the molecular beam. In addition a simulation of the spectrum at ≈ 100 K is shown (inverted lowest trace).

It is important to mention that the production of negatively charged radicals in a molecular beam at an abundance sufficient for (nonlinear) optical spectroscopy is a major step towards generation and characterization of peroxyl-radicals. In fact, neutral species in the ground state may selectively be produced from the anion by photo detachment[1]. Moreover, negative peroxy radicals are stable and thereby suited for investigation in a mass spectrometer, whereas positive ions seem to dissociate immediately.

Double-Valve Discharge Source

As discussed in the previous report of this project, oxygen containing precursor molecules have generally a deteriorating effect on the discharge. As a consequence, we have designed a novel

source for oxygenated transient species, like peroxy-radicals. A gas pulse from a second valve providing an oxygenated precursor (O_2, NO_2 etc) starts after an adjustable delay relative to the precursor gas pulse and discharge trigger. Radicals and other reactive species are allowed to react for a few μs prior to supersonic expansion.

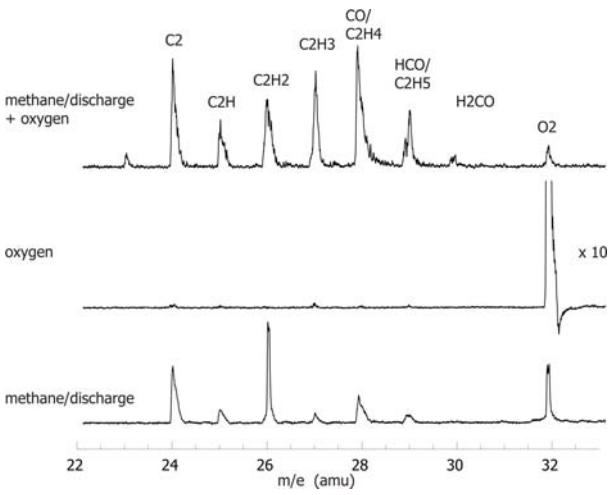

Fig. 5: fs-ionization/mass spectrometry in combination with the double-puls/discharge source. The upper trace shows the resulting mass spectra for a discharge in a methane/Ar mixture and the subsequent admixture of O_2. Radicals reacting with O_2 produce significant abundances of CO, HCO and H_2CO. The bottom trace shows the same mass spectrum without an O_2 gas pulse. The middle trace is observed with an O_2 pulse only.

In the period of this report, the oxygenation of hydrocarbon species could be achieved. Figure 5 shows a fs-ionization/mass spectrometric analysis of the species present in the molecular beam when a discharge is struck in methane and O_2 is added downstream. The bottom trace is obtained by fs-ionization of the skimmed molecular beam which is generated by supersonic expansion of a 10 % methane in a ≈ 5 bar Ar mixture after being excited by an electric discharge. A typical series of C_2H_x (x=0,…,5) species is observed in this mass range. The minor peak at m/e = 32 amu is due to oxygen impurities in the vacuum system. The middle trace is measured by actuating the second valve of the reaction chamber backed by a pressure of ≈ 4 bar neat oxygen. Apart from the O_2 peak at m/e = 32, no significant masses are present. If both valves and the discharge assembly are actuated at optimized time delays, the mass spectrum reproduced in the upper trace is observed. Compared to the neat methane trace, a significant increase of CO, HCO and H_2CO are detected which originate from reactions of the radicals produced by the discharge with O_2. For example, CH_3 + O_2 is likely to produce the formaldehyde molecule, H_2CO, and OH.

Further experiments with different precursors and reactant gases are necessary to develop the full potential of the double-valve source design for peroxy-radical production. Measurement series with varying relative precursor concentrations and delay times between valve openings and discharge have to be conducted. Initial optical measurements are planned by four-wave mixing, CRD, LIGS and LIF techniques on the peroxy A-X transition in the IR. For a current study on methane detection by LIGS[7], the near-infrared radiation has been obtained by Raman shifting the output of a dye laser in molecular hydrogen at 5 bar. For experiments in the IR wavelength range, we plan to use a similar approach. Instead of the first Stokes shift, however, the second order is needed. Consequently, to increase the efficiency of the process, higher pressures of gaseous H_2 might be required (≈ 20 bar).

Sensitive methods for the detection of weak transitions in the near-infrared are required to address the first excited electronic state of proxy-radicals. Therefore, a new, highly sensitive method is being developed in our laboratory: laser-induced grating spectroscopy. The potential of the method was demonstrated[7] on the extremely weak overtone/combination bands of methane at 11170 cm^{-1} and 11980 cm^{-1}.

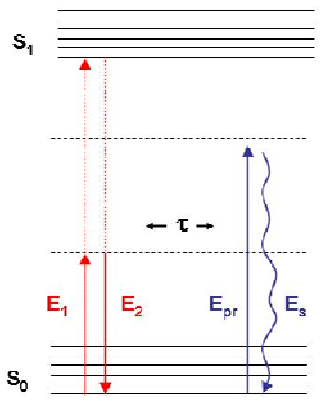

Fig. 6: Electronically resonant and non resonant time resolved transient grating excitation scheme.

Fs-Spectroscopy

In this part of the project we aim to apply ultrafast highly intense femtosecond (fs) laser pulses to produce and to investigate alkylperoxyl radicals by means of time resolved four wave mixing (FWM) methods. The approach of time resolved four wave mixing involves the coherent interaction of three deliberately delayed laser pulses with a molecular ensemble. The thereby induced macroscopic polarization acts as a source of a fourth coherent signal that is radiated from the medium at the delayed time τ (see Fig.6). In this report we confine ourselves on time resolved “transient laser induced gratings”, - a variant of FWM. This measurement method can be set up in an electronically resonant or non resonant configuration. The corresponding energy diagram of the experiment is shown in Figure 6.

In the non resonant case we simultaneously apply two 800 nm pulses (E_1, E_2), not reaching an electronically excited state of a molecule (indicated as S_1). The excitation occurs only within the ground electronic state (S_0) and consequently only ground state dynamics are probed by the delayed laser pulse E_{pr}. In the resonant case we tune the frequency of both initial pulses to an electronic resonance and excited state contributions should dominate in the signals. To achieve a higher selectivity the probe laser wavelength can also be tuned to match a specific resonance, but here, if not especially mentioned, it is simply chosen for an optimized detection (e.g. sensitivity of photomultiplier).

Alkoxy (RO) and alkylperoxy (ROO) radicals can be produced, - alternatively to the above mentioned processes -, by direct photo dissociation of particular di-alkyl-peroxides (ROOR). In many cases, di-alkyl-peroxides and hydroperoxides are stable enough (explosion hazard) to be introduced directly into a molecular beam source. The simplest hydroperoxide is HOOH. It dissociates to HOO when excited with light below 200 nm. Excitation at longer wavelength predominantly produces OH.

HOOH is safely available when stabilized at concentrations of 35% in aqueous solution. A stainless steel reservoir connected to an optically accessible cell was filled with the solution without further purification. The cell was filled up to a total pressure of ~ 50 mbar.

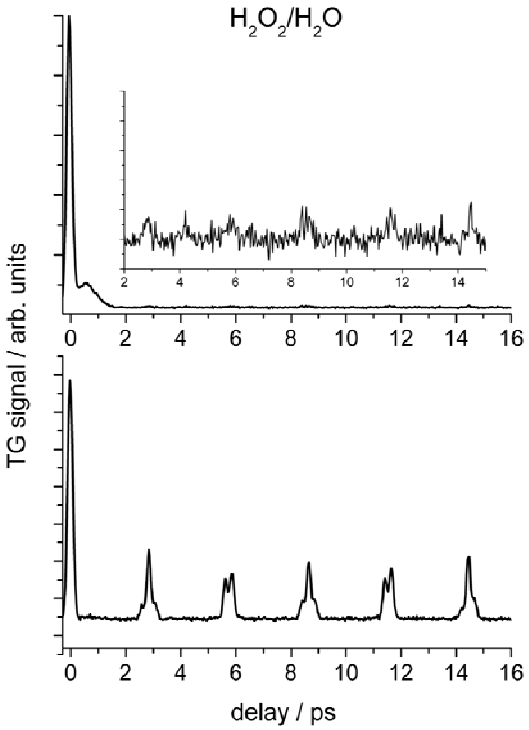

Fig. 7: Top: Time resolved transient grating signals from mixed H_2O_2/H_2O vapor. Bottom: The same experiment after keeping the aqueous solution one day in the stainless steel reservoir. The signal shows a clear beating pattern from O_2 only.

Figure 7 shows two transient signals, which have been derived from mixed H_2O_2/H_2O in the gas phase. The sample in both experiments origins from the same fill of aqueous solution. The top trace in Fig 7. corresponds to the measurement performed immediately after filling, whereas the bottom trace was obtained after leaving the solution in the stainless steel reservoir for one day. The dominant signal contribution in the lower trace stems from O_2, which could clearly be identified by the characteristic rotational recurrences of the diatomic molecule indicating that H_2O_2 most probably dissociates at the metal surface of the reservoir to oxygen. Unfortunately the presence of a large amount of water hinders a clear signal interpretation of the transient (top trace) characteristics at short delay times. This early time response is mainly characterized by a zero delay time coherence spike followed by a rotational feature fading out whine about 1 ps due to fast dephasing of the initially excited rotations. Even in the absence of rotational recurrences, i.e when fast dephasing prevails, it might be possible to determine the main rotational constants (A,B,C) of a molecule from curves as shown in the top of Fig. 7. Hence, in some cases the early time response can suffice to differentiate between precursor and daughter molecules. In the case of HOOH, OOH and H_2O, all having comparable moments of inertia, this discrimination is not clear.

However, more success can be expected from di-tert-butyl-peroxide molecule (DTBOO) that, in spite of its much bigger size, exhibits, like all peroxyl compounds, an electronic structure and symmetry comparable to HOOH. In the configuration of DTBOO the H atoms in HOOH are replaced by tert-butyl (C_4H_8) groups (Fig. 8). With the molecular configuration proposed in NIST chemistry webbook (http://webbook.nist.gov/chemistry/), we calculat the moments of inertia and the main rotation constants using the Gaussian'98 software package. Similar calculations can be done for the tert-butoxy (TBO), tert-butyl (TB) and tert-butyl peroxide (TBOO) molecules, which are the most prominent candidates involved in the DTBOO dissociation (Table 1).

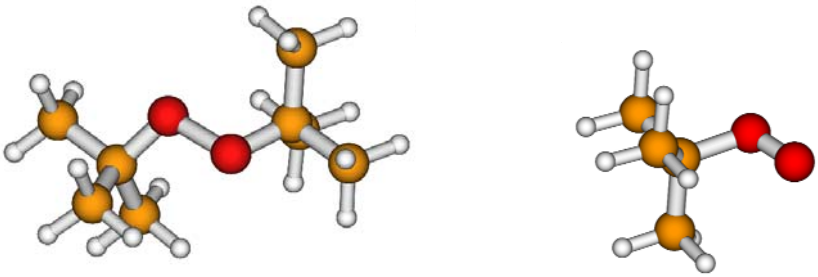

Fig. 8: Structure of di-tert-butyl peroxide and tert–butyl peroxide from NIST Database.

	A / cm^{-1}	B / cm^{-1}	C / cm^{-1}
DTBOO	0.0246	0.02478	0.0751
TBOO	0.0956	0.0950	0.1498
TBO	0.0783	0.0743	0.0480
TB	0.2768	0.2703	0.1480

Tab.1: Calculated main rotational constants of DTBOO, TBOO, TBO,TB.

Figure 9 shows an electronically non resonant transient grating signal derived from a 50 mbar DTBOO vapor sample and four simulated signals using the rotational constants of TDBOO, TBOO, TBO and TB, respectively. All molecules are treated as symmetric top (which is a good approximation due to Table 1) and centrifugal distortion has not been included.

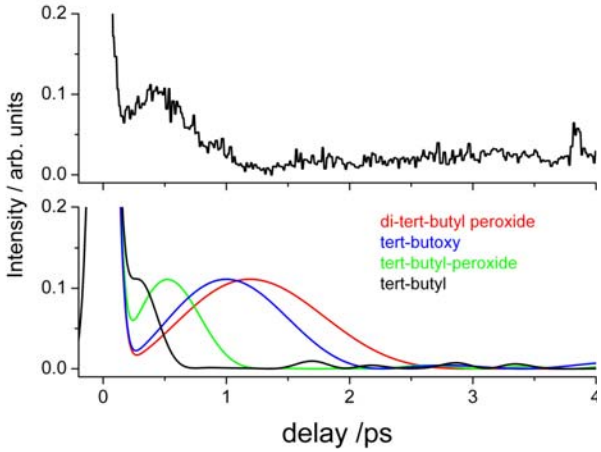

Fig. 9: Non resonant time resolved transient grating signal from 50 mbar TDBOO vapor, compared to simulations achieved by using main rotational constants of each species.

Interestingly, within the approximation of undistorted rotations, the best accordance with the measured signals could be achieved with the constants of TBOO. The most prominent absorption in DTBOO is in the UV spectral range between 340 and 230 nm. Resonant transitions correspond to a non-bonding orbital configuration and break the molecule symmetrically at the RO-OR bond, producing vibrationally 'hot' TBO radicals. The absorption of photons below ~ 230 nm wavelength opens a direct dissociation channel yielding TBOO radicals as products. The associated absorption cross section is approx. 10 times higher, $\sigma(200\ nm) \sim 2x10^{-19}\ cm^2$ than that at longer wavelengths. However, the excitation of DTBOO with 800 nm laser pulses is below the energy required to induce the dissociation from an electronically excited state by a single photon absorption step. Therefore, the question arises what is the origin of the TBOO signal?

It is conceivable that due to the high intensity of the 800 nm pulses an efficient multiphoton transition to the excited molecular states occurs, which is followed by a direct dissociation within the duration of the laser pulses. For comparison we repeated the experiment with light at shorter wavelength, possibly resonant with a low lying dissociating state. According to the term scheme depicted in Figure 10. An increased production of TBO over TBOO would be expected. The excitation laser wavelength was thus tuned to 295 nm inducing a $\pi^* \rightarrow \sigma^*$ transition yielding the O-O bond rupture.

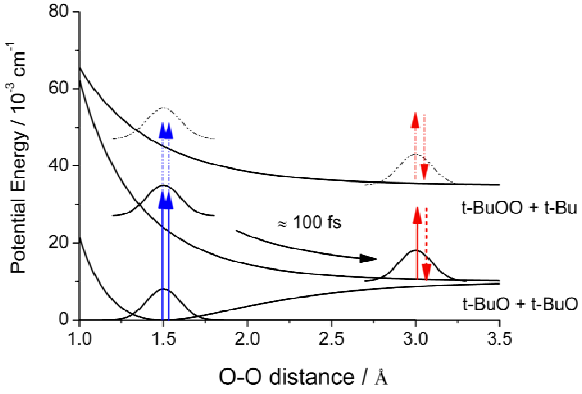

Fig. 10: Two possible resonant fs-TG excitation schemes using UV laser pulses to form the grating.

Astonishingly, the early time response of the resonant and the non resonant transient obtained with TDBOO appears similar (Fig. 11). Evaluation of the transient signals do not support a higher TBO production in the resonant case as expected. Thus, the anticipated resonance seems not to play a major role in the observed dissociation mechanism.

Excitation wavelengths around 200 nm, as additionally indicated in Figure 10 (arrow extension), promise to be a more clear cut approach to TBOO. The high absorption cross section at these wavelength and the direct production of TBOO radicals promise to be more interpretable. However, these wavelengths are much more difficult to produce since non linear doubling crystals are typically limited to ~ 210 nm. We started to assemble a sum frequency device that mixes tripled 800 nm fs laser output (~ 266 nm) with the 800 nm fundamental output in a BBO crystal, yielding 200 nm fs light pulses. The corresponding four wave mixing and mass spectrometric experiments are in preparation.

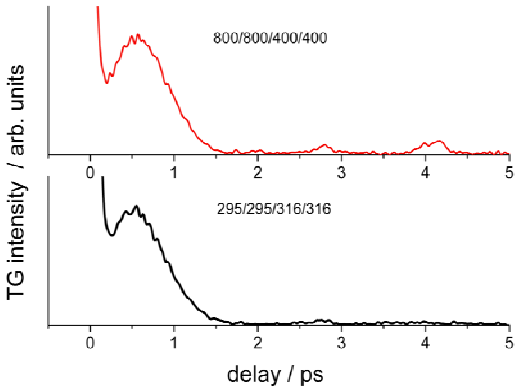

Fig. 11: Non resonant (top) and electronically resonant (bottom) fs-TG signals from a TDBOO sample.

The UV resonant transient grating technique benefits from electronic resonances. The general idea is to increase the selectivity by resonantly enhanced contributions to the detected signals. In the case of DTBOO we observed contributions either from the ground electronic state of DTBOO, or from the dissociation products or from both. Excited state dynamics could not be assigned to the observed transients, which is also an indication for the pure dissociative electronically excited state and a fast dissociation within the 100 fs pulse duration.

However, expanding our singly resonant studies[8] aiming at the polyatomic formaldehyde molecule, we now demonstrated successfully the applicability of a fully resonant UV-fs-transient grating method. H_2CO comprises multiple dissociation channels, starting from the excited S_1 electronic state. The lifetime in S_1 depends on the excitation energy but is in the order of ps to ns. Fs-time resolved UV transient grating signals from excited state H_2CO at energies around the HCO production threshold (~ 30330 cm^{-1}) have been measured. The sample conditions were set to a pressure of 30 mbar and a temperature of ~ 80 °C. In contrast to the DTBOO signals the time resolved UV transient grating signals reflect the molecular dynamics in the excited state including relaxation processes.

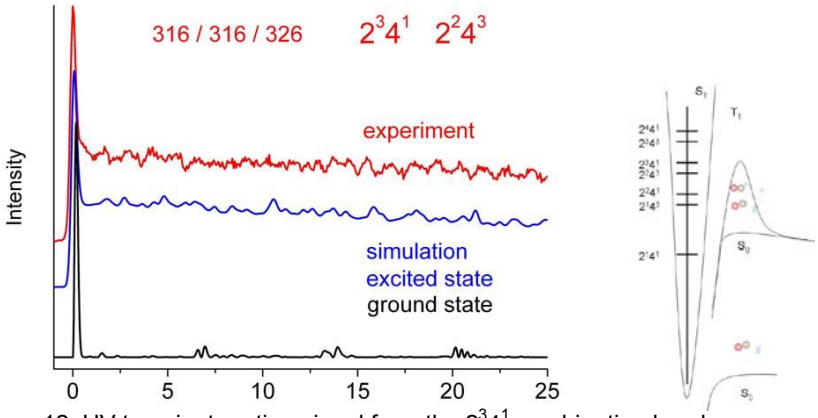

Figure 12: UV transient grating signal from the 2^34^1 combination band. Pump wavelength: 316 nm, probe wavelength: 326 nm. The insert on the right shows the potential energy surfaces of H_2CO, indicating the position of different vibrations.

A typical all UV fs TG signal, its simulation and a potential energy scheme where the asymmetric stretch ($\nu 2$) and bending ($\nu 4$) combination bands (2^n4^m) of H_2CO are indicated is shown in Fig. 12. The chosen resonance to the 2^34^1 combination band is energetically below the triplet barrier but well above the HCO threshold. Ground state contributions, which are typically observed as rotation recurrences seem to be much weaker in intensity using the resonant excitation scheme. The rotational dynamics in the ground electronic state can be observed with a non resonant excitation scheme[8].

Nationale Zusammenarbeit

The SNF supports this work in the frame of two dissertations with project titles “Characterization of Vibrationally and Rotationally Excited Molecules by Two-Color Resonant Four-Wave Mixing” and “Investigation of ultrafast molecular dynamics of combustion relevant species by time resolved non-linear Raman spectroscopy”.

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, Uni Bern.

The in-house development of a VUV beamline at the SLS provides a great synergy with our endeavours subsumed in the current BFE project.

Internationale Zusammenarbeit

With the chemical dynamics activity at SLS, a lot of knowledge and experience is brought to us by external groups with whom we are going to perform experiments. In a close cooperation with Tom Baer from University of North Carolina we will establish a Photo-Electron Photo-Ion Coincidence (PEPICO) apparatus to measure the formation enthalpies of a range of organometallic complexes. In 2008 we will start a cooperation with Prof. Ingo Fischer, Uni Würzburg who works on allyl and propargyl radicals, which are relevant for soot production in combustion processes.

The success of the fs experiments has led to a cooperation with Dr. Arnulf Materny, University of Bremen, where fs-CARS experiments have been performed on benzene to explore energy transfer processes and rotational effects in liquids and in the gas phase.

The interpretation of measured dissociation data needs more theoretical investigations on the potential surfaces of molecules as well as the refinement of existing dissociation models. With Prof. R. Marquardt from University of Strassbourg we plan to perform a comprehensive investigation of molecular state manifolds by sophisticated ab initio computations.

Bewertung 2007 und Ausblick 2008

The envisaged project on peroxyl radicals is very ambitious and still bears many risks. With a new contract BFE supports our work towards the goal to assess the role of peroxy radicals and other species dominating ignition. The technical effort to achieve a suitable experimental environment is considerable and time consuming. The search for suitable precursors for peroxy radicals production in a suitable experimental environment allowing fs-spectroscopic or mass spectrometric measurements will remain our prime focus in 2008. More experiments are needed for an unambiguous mass spectrometric identification of species and to assess advantages and drawbacks of the femtosecond laser ionization.

Femtosecond pump probe methods, CRD- and PHOFEX-techniques will continuously applied to further scrutinize the dissociation paths of H_2CO leading to H_2 + CO and H + HCO, respectively. The experience gained with H_2CO will then be transferred to the spectroscopic assessment of peroxyl radicals, HOO being the prime candidate to which not only our measurement techniques but also a lot of available theoretical work can be applied.

Currently we install the chemical dynamics beamline at Swiss Light Source (SLS). In spring 2008 first pilot experiments well be performed. Within the frame of one of those pilot projects PEPICO measurements on H_2O_2 will be realised.

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