

Studies of Ter-Butyl-Peroxy and Hexadiyne by dispersed fs-FWM methods

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Hexadiyne and Peroxy radicals are investigated by non linear, femtosecond, Four Wave Mixing (FWM) techniques. Both species are relevant in the context of first aromatic ring formation and ignition mechanisms, respectively. Recording spectrally dispersed fs-FWM signals unveils molecular features not accessible with the common pump probe technique.

Introduction

Unimolecular dissociation is the extension of a chemical bond to infinity and occurs typically on the sub picosecond timescale of molecular vibrations. There exists a large variety of spectroscopic techniques that employ ultrashort laser pulses to monitor fast dynamic processes in molecules [1-3].

Di-Tert-Butyl-Peroxide

Di-tert-butyl peroxide (DTBOO) a sufficiently stable molecule is a good candidate as precursor for the production and investigation of $C_4 - OO$ peroxy radicals. The most prominent absorption ($\pi^* \rightarrow \sigma^*$) in DTBOO is in the UV spectral range between 340 nm and 230 nm. In order to learn more about the state manifolds connecting to the states of the fragments we started single photon, vacuum ultraviolet, measurement at the SLS/VUV beamline. The VUV absorption of DTBOO has been measured in the currently installed PEPICO endstation. Hydrocarbon compounds can be introduced into the endstation vessel at pressure up to 40 mbar without any risk of contamination of the beamline optics maintained in vacuum at 10^{-9} mbar. The absorbance for photon energies ranging from 5.43 to 9.76 eV is shown in Figure 1 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 increases above 5.63 eV (below 220 nm) by orders of magnitude and a relative

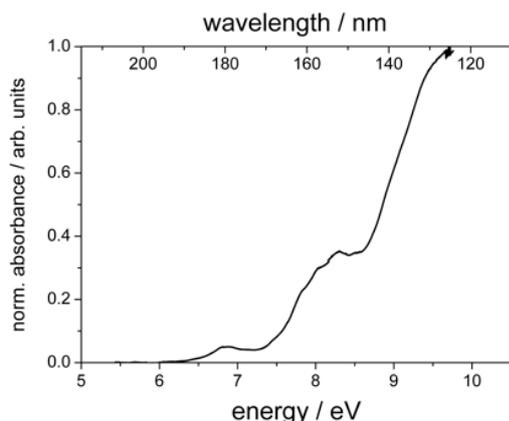


Fig. 1: VUV absorption signal from 5.43 to 9.76 eV.

maximum is reached at 6.8 eV (~ 180 nm), which is in the vicinity of the dissociating B^2A'' state. The IP of DTBOO is at 8.78 eV [4] which is also clearly seen by the appearance of a second plateau in the absorption spectrum of Fig.1. The weak-modulation of the absorbance just below the ionization threshold energies may indicate the presence of several Rydberg states.

Photo excitation is expected to excite DTBOO to a non-bonding orbital configurations breaking the molecule symmetrically at the O-O bond, thus producing vibrationally 'hot' TBO (ter-butoxy) radicals. The absorption of photons below ~ 230 nm wavelength, however, correlates to a direct disso-

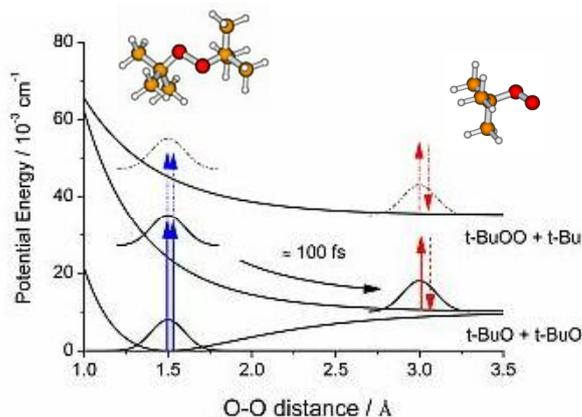


Fig.2: DTBOO fs-FWM excitation scheme

ciation channel yielding $TBOO^*$ radicals (ter-butylperoxy) as products (Fig. 2).

Setting the excitation laser wavelength to 295 nm yielded similar signal characteristics in the resonant approach compared to a fully off-resonant excitation. Astonishingly, the early time response of the resonant and the non-resonant transients obtained with TDBOO appears similar. 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.

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Hexadiyne

The origin of the soot production remains an interesting process that is not yet fully explored. In the case of aliphatic fuels (alkanes, acetylene, ethylene) a first ring must be formed by a sequence of elementary reactions. Ring formation is the key process for the production of polyaromatic hydrocarbons in flames [5]. It is believed that chain lengthening of acetylene leads to the formation of unsaturated radicals, which might stabilize by ring-closure [6]. Based on RRKM calculations it was concluded that chemically activated intermediates can form aromatic rings faster than bimolecular collisions, and therefore fundamental dissociation, isomerisation or H atom loss reactions gain importance [7].

Benzene formation is assumed to occur by recombination ('self-reaction') of C_3H_3 radicals [8-10] via the "loose" transition states of 1,5-hexadiyne, 1,2-hexadiene-5-yne and 1,2,4,5-hexatetraene. Calculations of the potential energy surfaces (PES), temperature dependent branching ratios and rate coefficients of the propargyl recombination reaction were accomplished by Miller and Klippenstein [11]. There is a general agreement that these intermediates are the primary recombination products that interconvert and isomerize to secondary products eventually leading to benzene [12]. The thermal rearrangement of 1,5-hexadiyne, e.g., has been investigated between 210° to 350° C. Isomerization has been observed over the whole temperature range towards a single product, which has been identified as 3,4-dimethylenecyclobutene [13].

With infrared and Raman spectroscopy, Hopf and coworkers [8, 9] investigated the conformation and vibrational spectra of 1,5-hexadiyne (bi-propargyl), 1,2-hexadiene-5-yne (propargylallene) and 1,2,4,5-hexatetraene (biallenyl), in detail. It is known that the dominant conformer in the vapour phase of all three species is the trans-configuration. Usually a trans-conformation is recognizable due to the mutual exclusion of infrared and Raman bands. However, this is not true for the conformers of benzene. Both band types show characteristic lines of trans- and gauche-conformers, e.g., of bipropargyl.

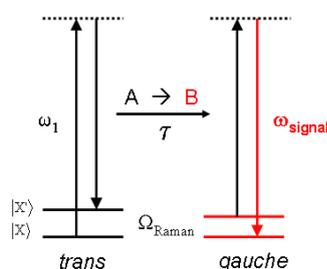


Fig.3: Fs-FWM excitation scheme. All transitions may occur on one conformer or partitioned, as indicated, on two distinct conformers.

We registered dispersed off-resonant fs-time resolved four wave mixing (fs-FWM) signals obtained in a gaseous 1:1 mixture of pentane and 1,5-hexadiyne (total pour pressure is ~10 mbar). Fs-FWM

vides information about molecular dynamics - e.g. isomerization steps - occurring in the ground electronic state of the molecule upon photoexcitation. The method involves three nonlinear electric field interactions with a molecular ensemble to create a resulting fourth wave (Fig. 3). Two laser pulses interact simultaneously with the molecular sample and coherently excite a ro-vibrational ensemble of states that is covered by the spectral width of the laser pulses. Rotations and low energy torsion or

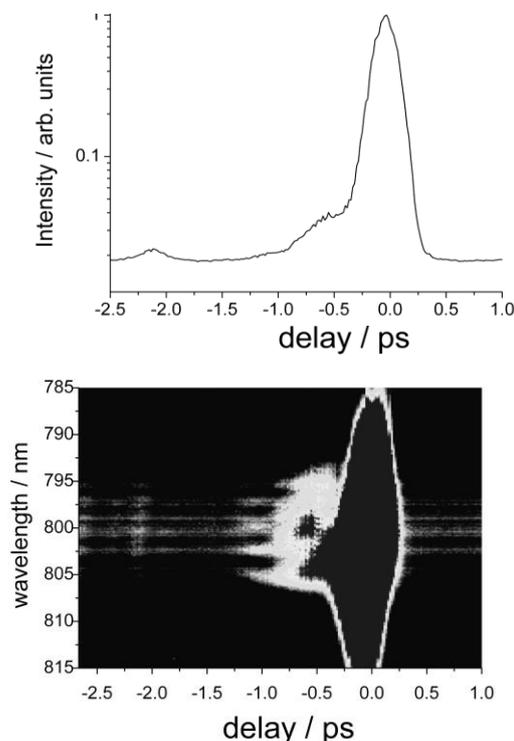


Fig. 4: Top: Frequency integrated fs-FWM signal from a 1,5 hexadiyne/pentane mixture. Bottom: Dispersed fs-FWM signal. The delay between pump and probe evolves to the left.

bending vibrations are thus possibly excited. The third, delayed probe-laser pulse interrogates the evolution of the molecular ensemble. In the present experiment all laser pulses have the same wavelength (~800 nm), a typical duration of ~100 fs and a spectral width of ~11 nm (fwhm).

The early time response ($\tau = \pm 150$ fs, Fig.4 top) is mainly characterized by a time-zero coherence spike followed by ($\tau = < -150$ fs) a rotational feature, which is caused by a fast dephasing of the initially excited rotations. From these signals it is possible to determine even in the absence of rotational recurrences the main rotational constants (A,B,C) of a molecule with a one- to two-digit accuracy. Hence, in some cases the early time response can be a sufficient indication to differentiate between molecules. However molecules, such as pentane and 1,5 hexadiyne have analogue rotational constants and therefore can not be readily distinguished by this method.

When the fs-FWM signal is spectrally dispersed additional information about the involved molecules is gained. Weak spectral features are observed in the dispersed signal (Fig 4 bottom) at delays < 1 ps that are not discernible in the undispersed, one dimensional presentation (Fig 4 top). At a delay position of e.g. 0.7 ps, the spectral analysis of the signal fields enables the distinction between the mixed 1,5-hexadiyne sample and

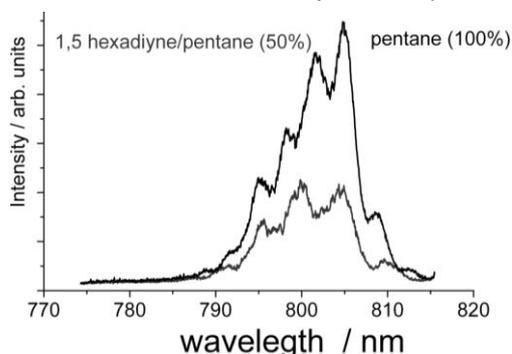


Fig. 5: Fs-FWM signal spectrum from pure pentane (100%) and from the 1,5-hexadiyne/pentane mixture (50%) at 0.7 ps probe delay.

pure pentane (Fig. 5). The observed spectral peaks at this delay are separated by ~ 75 cm^{-1} and ~ 50 cm^{-1} , respectively. Figure 6 (top) shows a “wavenumber” plot of the measurements shown in Figure 5. The abscissa shows the Fourier transformed signal along the delay time τ while the ordinate scales relatively to the carrier frequency of the signal pulse at ~ 1250 cm^{-1} : beating frequencies are presented as a function of the signal spectrum.

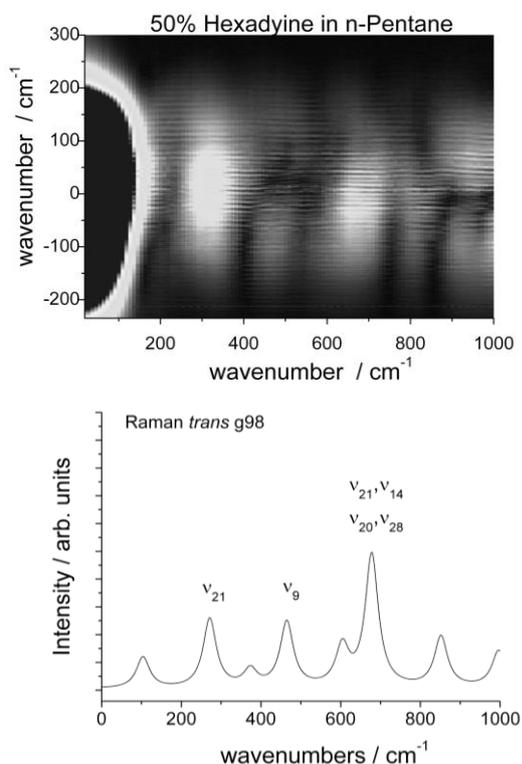


Fig. 6: **Top:** “2D- wavenumber” plot of the signal in Figure 2 bottom. **Bottom:** Raman spectrum of trans-1,5 hexadiyne.

We observe partial accordance between the calculated Raman spectrum (Fig. 6 bottom) of *trans*-1,5-hexadiyne and the 2D-experiment. The low frequency mode appearing at ~ 320 cm^{-1} was expected from the experiment as the bandwidth of the laser is broad enough to cover this energy. However, the appearance of higher frequency components that are not, or only weakly, covered by the bandwidth of the laser pulses still needs more considerations.

The signal field in off-resonant degenerated FWM typically reflects the spectral profile of the input beams. Therefore, in the absence of isomerization processes we expect signal contributions replicating the spectral distribution of the input. However, if dynamics are effective between the input field interactions, as indicated in Figure 3. spectral departures from the input profile may become apparent, and may be interpreted adequately. Currently, detailed analysis of the measured data is in progress.

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