Ultrasensitive ultraviolet-visible 20 fs absorption spectroscopy of low vapor pressure molecules in the gas phase

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We describe an ultrasensitive pump-probe spectrometer for transient absorption measurements in the gas phase and in solution. The tunable UV pump and the visible (450–740 nm) probe pulses are generated by two independently tunable noncollinear optical parametric amplifiers, providing a temporal resolution of 20 fs. A homebuilt low gain photodetector is used to accommodate strong probe pulses with a shot noise significantly lower than the overall measurement noise. A matched digitizing scheme for single shot analysis of the light pulses at kilohertz repetition rates that minimizes the electronic noise contributions to the transient absorption signal is developed. The data processing scheme is optimized to yield best suppression of the laser excess noise and thereby transient absorbance changes down to $1.1 \times 10^{-6}$ can be resolved. A collinear focusing geometry optimized for a 50 mm interaction length combined with a heatable gas cell allows us to perform measurements on substances with low vapor pressures, e.g., on medium sized molecules which are crystalline at room temperature. As an application example highlighting the capability of this instrument, we present the direct time-domain observation of the ultrafast excited state crystalline at room temperature. As an application example highlighting the capability of this instrument, we present the direct time-domain observation of the ultrafast excited state intramolecular proton transfer of 2-(2'-hydroxyphenyl)benzothiazole in the gas phase. We are able to compare the resulting dynamics in the gas phase and in solution with a temporal precision of better than 5 fs. © 2008 American Institute of Physics. [DOI: 10.1063/1.2834877]

I. INTRODUCTION

Pump-probe spectroscopy with femtosecond time resolution is a powerful tool for investigating molecular dynamics and kinetics in systems that are of interest to chemistry and biology. In prominent cases it provided the crucial breakthrough in understanding the underlying mechanisms. Molecular processes are usually governed by intramolecular properties as well as interaction with the surrounding medium; thus in most situations it is impossible to exclude a priori the relevance of the environment. High level ab initio quantum chemical descriptions usually consider the isolated molecule, i.e., the diluted gas phase situation. To understand the interplay between intra- and intermolecular dynamics, it is therefore most important to disentangle them. This can be done most simply by investigation of the isolated molecule in the gas phase and comparison to its behavior under condensed phase conditions. With the advent of quantum control and quantum computing, the role of coherence, vibrational as well as electronic, and the nature of dephasing processes become more and more important. In this context, the comparison of gas phase and condensed phase results is particularly interesting if a time resolution is achieved which allows the observation of conformational changes and vibronic wavepacket dynamics.

In the gas phase, very sensitive detection techniques are necessary due to the low particle densities. In most cases, photoionization and mass selective detection have been utilized as probe processes since ions and electrons can be detected with almost single particle efficiency. In the condensed phase, however, ionization techniques cannot be applied and one has to resort to optical signals. Transient absorption spectroscopy has proven to be a very suitable probing technique since it is sensitive, gives absolute numbers for molecular observables such as concentrations or transition strengths, and provides in practice a superior time resolution compared to most other techniques. However, comparison of absorption experiments in the condensed phase with ionization experiments in the gas phase is not straightforward because both techniques probe different properties of the molecules and project the wave function of the system onto very different final state manifolds. Moreover, the photoionization process needs probe pulses far in the ultraviolet, which are difficult to generate with a suitably broad bandwidth and extreme time resolution.

To overcome this dilemma, we have developed a transient absorption spectrometer that extends this technique to low pressure gas phase samples. A low pressure situation is typical for samples of chemical interest, since the large mol-
molecules investigated possess a very low vapor pressure even at elevated temperature. Our instrument provides the required sensitivity and a time resolution suitable for observing coherent molecular wavepacket motions. The progress results from the combination of four strategies tackling different critical points of the experiment (see Sec. II). (i) A focusing geometry with a long Rayleigh range gives an optimized overlap of the pump and probe beams and a usable path length of 50 mm. (ii) An improved detection scheme and adapted amplification electronics allow us to observe changes in the absorbance down to $1.1 \times 10^{-6}$. (iii) A differentially pumped, heatable gas cell allows us to reach sufficiently high vapor pressures even for crystalline molecular substances. (iv) The high time resolution is achieved by using noncollinearly phase matched optical parametric amplifiers (NOPAs) as sources of pump and probe pulses, which provide tunable sub-20-fs pulses over the full visible spectrum. Absorption bands of small and medium sized molecules, which are usually in the ultraviolet (UV) spectral region, can be addressed by sum frequency mixing or second harmonic generation without sacrificing time resolution. As an example demonstrating the capabilities of this instrument, we present a comparison of the direct time-domain observation of the excited state intramolecular proton transfer (ESIPT) of 2-(2′-hydroxyphenyl)benzothiazole (HBT) (i) in the gas phase and (ii) in cyclohexane solution (see Sec. III). The measurements in both phases have been performed immediately one after another by simply exchanging the sample cells. In both cases, the temporal overlap of the pump and probe (time zero) can be determined with a precision better than 5 fs. To the best of our knowledge these are the first transient absorption measurements in gas phase with a time resolution of 20 fs.

II. DESIGN AND IMPLEMENTATION OF THE EXPERIMENTAL SETUP

A. Required sample length

In this section we discuss the requirements for transient absorption measurements in the gas phase on medium sized molecules, such as organic molecules with three or four aromatic rings. We assume excitation densities well below saturation and the probe wavelength $\lambda$ outside the absorption spectrum of the molecule. In the case of an optically thin sample with an optical density (OD) of $OD_0(\lambda_{\text{pump}})$ at the pump wavelength $\lambda_{\text{pump}}$, the transient optical density change $\Delta OD$ for the pump-probe signal can be approximated by

$$\Delta OD(\lambda, \tau) \approx \epsilon^*(\lambda, \tau) OD_0(\lambda_{\text{pump}}) \Phi_{\text{pump}},$$

(1)

where $\epsilon^*(\lambda, \tau)$ is the molar extinction coefficient of the molecules transferred by the pump pulse from the electronic ground state to some excited state and $\Phi_{\text{pump}}$ is the fluence of pump photons per unit area. $\epsilon^*$ effectively describes electronic relaxation, chemical processes, vibronic wavepacket motion, and solvation. It typically depends on the probe wavelength $\lambda$ and the pump-probe delay $\tau$. In the gas and solution phases, the effective $\epsilon^*$ is expected to be similar. For a molecule exhibiting an ultrafast reactive process, all lines will be homogeneously broadened and, in addition, the broad spectral width of the femtosecond pulse smoothens out any possible gas phase line structure. Therefore, to get the same pump-probe signal amplitude, the product of the sample optical density times the pump photon fluence has to be kept constant when going from the solution to the gas phase. For solution experiments, $OD_0(\lambda_{\text{pump}})$ is typically 0.3 OD. The fraction of excited molecules $\epsilon \Phi_{\text{pump}}$ should be kept at or below the 5% level to avoid sequential multiphoton effects. $\epsilon$ is the molar extinction coefficient of the ground state molecules, which is typically comparable to $\epsilon^*$. Taking the pump beam radius into account, this constraint eventually limits the pulse energy that can be used for the experiment. The maximum absorbance change that can be induced is thus typically 0.01 OD. Since a signal-to-noise ratio of 100:1 is desirable to characterize molecules exhibiting complex wavepacket dynamics, a detection sensitivity of at least 100 $\mu$OD is needed.

The substance HBT, which we use to demonstrate the performance of our setup, is crystalline at ambient temperature with vanishing vapor pressure. We performed a series of cw absorption measurements, showing that we need a sample length of 50 mm and a temperature of approximately 110 °C to get an optical density of 0.15. In secs. II C, II D, and II F, it is discussed in detail how these requirements can be fulfilled.

B. Overview of the setup

A schematic of the experimental apparatus is shown in Fig. 1. The pump-probe spectrometer is based on two noncollinearly phase matched optical parametric amplifiers (NOPA 1 and NOPA 2) which generate tunable visible pulses with a bandwidth suitable for pulse durations down to 10 fs. The laser source is a regenerative Ti:sapphire amplifier system (CPA 2001; Clark-MXR Inc.) delivering pulses at 1 kHz repetition rate with 775 nm center wavelength, 150 fs duration, and 950 $\mu$J energy. A fraction of 220 $\mu$J of the CPA pulses is used to pump each of the NOPAs. A vari-
able fraction of 60–100 μJ is split off for chirped sum frequency mixing (SFM) with the output of NOPA 1 to generate tunable UV pump pulses with energies up to 3 μJ. The CPA pulses are stretched in a 70 mm long block of SF57 glass to a length of approximately 380 fs and focused by an f = 200 mm lens into a β-barium borate (BBO) crystal cut for type I phase matching. The NOPA 1 pulses are focused by an f = 200 mm spherical mirror into the SFM mixing crystal. For broadband UV spectra, a 60 μm thick BBO crystal was used, whereas for high UV pulse energies, a 135 μm BBO crystal was employed. In the latter case the bandwidth of NOPA 1 was limited to approximately one-half of the acceptance bandwidth of the crystal. Without sacrificing output power, the bandwidth of NOPA 1 can be easily decreased by chirping the continuum seed. To generate distinct NOPA spectra with a center wavelength between 700 and 740 nm and a bandwidth suitable for 30 fs, a glass block of 1 cm LF7 proved suitable. For the experiments presented below, pump center wavelengths of 325 and 350 nm are chosen according to the first absorption maximum of HBT and the half maximum in its red wing, respectively. However, it can be set anywhere in the spectral region between 285 and 375 nm, which is particularly well suited to excite medium sized molecules. To compress the s-polarized UV pulses, they are sent through a sequence of two antireflection coated fused silica prisms with an apex angle of 45° (PC-UV). The transmission through the UV compressor is more than 90%. A chopper is placed in the UV beam path to block every second pump pulse for a shot to shot referencing procedure. The arrival time of the pump pulse at the sample, and thereby the delay time between pump and probe pulse, is adjusted via a hollow retroreflector mounted on a motorized, computer controlled translation stage (delay) with a positioning accuracy and a reproducibility of 0.1 μm (M-014.D01; Physik Instrumente GmbH) resulting in a 0.67 fs timing resolution. The maximum travel of the stage allows one to measure pump-probe delay times of up to 150 ps.

The pulses from NOPA 2 are used for transiently probing the molecular sample. A thin achromatic half-wave-plate for the visible (RAC 3.2.10L; B. Halle Nachf. GmbH) is used to rotate the polarization of the probe light and to measure the molecular dynamics under different polarizations. After transversing a standard double-pass prism compressor of fused silica Brewster prisms (PC-VIS), they are matched in diameter and convergence via a telescope and irises fused silica Brewster prisms. The transmitted energy of the probe beam is measured with a second photodiode module. This integral detection without wavelength dispersion results in an optimal time resolution and avoids signal contributions (coherent artifacts) during the temporal overlap of the pump and probe pulses that would mask the dynamics around time zero. The pump energy, and thereby the synchronization signal for the shot to shot referencing procedure, is measured by a third photodetector. To determine the time zero of the pump and probe pulses, a difference frequency cross correlation is measured in a 10 μm thick BBO crystal. A detailed description of the procedure is given in Sec. II G.

To record ultrafast wavepacket dynamics on a time scale up to 6 ps, the pump-probe delay is scanned with a constant step size of typically 3 or 5 fs. To measure short and long time scale dynamics within one scan, a linear-logarithmic time scale is applied. For pump-probe delays between −1 and 1 ps, a constant step size is chosen, which is then exponentially increased such that the same number of data points is recorded between 0 and 1 ps as between 1 and 10 ps and so forth. The variation in the step size is smooth and continuous around 1 ps.

C. Focusing geometry

For the following discussion we assume an ultraviolet pump and a visible probe beam.

To optimize the pump-probe signal, the waist of the probe beam in the sample should be definitely smaller than the waist of the excitation beam. In most femtosecond experiments in solution, the sample thickness is in the range of 50 μm to 1 mm to avoid deterioration of the temporal resolution due to group velocity mismatch. The pump radius at the focus is typically on the order of 50 μm and the probe radius of 35 μm. In this regime, the probe focus can be placed easily within the pumped volume; the whole sample lies within the Rayleigh range of the beams and the overlap is guaranteed over the total thickness [see Fig. 2(b)]. Due to much lower particle densities in the gas phase, the sample and the overlap region can be extended to several centimeters without loss of time resolution. Accordingly, the Rayleigh range has to be extended to the length of the sample [see Eq. (1)]. This results in larger focus diameters and a lower fluence of photons. To be able to optimize the setup for the pulse duration rather than for the pulse energy (see choice of SFM crystal discussed above), a minimal waist of the pump pulse has to be found, which results in a sufficiently long Rayleigh range and an adequate excitation density with moderate pulse energies [see Fig. 2(c)]. A suitable focusing geometry can be found with Fig. 2(a). The curves represent the combinations of Gaussian UV pump beam radii w_{UV} and probe radii w_{vis} at the focus for which the 1/e² border of the probe beam intersects the 1/e² border of the pump at the given distance z_X from the focus [see Fig. 2(b)]. The curves are labeled by the distance z_X in millimeters. Assuming Gaussian beams with M^2 > 1 (Ref. 18) and w_{vis} < w_{UV}, the intersection distance z_X can be written as
In Fig. 2 the pump wavelength $\lambda_{\text{UV}}$ is set to 325 nm and the probe wavelength $\lambda_{\text{vis}}$ to 560 nm. According to the experiment, the beam quality parameters $M^2_{\text{UV}}$ and $M^2_{\text{vis}}$ were set to 1.7 and 1.4, respectively. Within a region extending over $2z_R$ around the focus, the probe beam is smaller than the pump. The Rayleigh lengths of the pump $z_{R,\text{UV}}$ and probe $z_{R,\text{vis}}$ beams which depend quadratically on the focal beam radius can also be read from the diagram [Fig. 2(a)]. The hatched area in Fig. 2(a) indicates the region for which the focal pump radius is below 125 $\mu$m. The gray area in the figure indicates the actual parameter region of the experiment. It shows that with a pump radius of 125 $\mu$m, we can achieve intersection distances up to 30 mm, and thereby overlap regions up to 60 mm by choosing a focal probe radius of about 95 $\mu$m. The quite large focal radii call for a weak focusing regime which was implemented with a focal length of 500 mm (see Sec. II B). The focusing geometry and beam quality parameters were verified with a beam camera. The $M^2$ values are in good agreement with parameters found previously for NOPA beams.

From Eq. (1) it follows that the pump energy $E_{\text{pump}} \propto \Phi_{\text{pump}} (w_{\text{UV}}^4)$ in the gas phase experiment should be chosen such that the fluence of pump photons is the same as for the solution phase focusing geometry. The increase of the focal diameter by a factor of 2.5 implies an increase of the pump energy by a factor of 6, yielding an absolute value of 450–500 nJ at the sample, which is readily achievable.

D. Photodetectors and data acquisition

For the highest possible detection sensitivity of the transmission changes, the pulse energies of the probe and the reference beam are measured with two matched homebuilt photodetectors. The probe and reference pulse energies are typically 5–10 nJ; thus the detectors are designed to allow the direct measurement of pulse energies up to 2 nJ. In the experiment, the pulses are only slightly attenuated by suitable optical filters. At 500 nm, the 2 nJ correspond to $5 \times 10^9$ photons and a shot noise limit of $1.7 \times 10^{-5}$ results (a typical photodiode quantum efficiency is $\sim 70\%$). Assuming a Gaussian spatial profile, the $1/e^2$ beam diameter of the pulses on the photodiode should be at least three times smaller than the dimension size of the active area to detect the pulse energy with an accuracy of more than $10^{-5}$. On the other hand, the input pulses should not be focused too tightly onto the detector to avoid local saturation.

A schematic of the amplifier circuit is shown in Fig. 3. It transforms the photogenerated charge into a voltage at the 1 V level and leads to a signal duration long enough for an accurate analog-to-digital conversion (ADC) without the need for a boxcar integrator or a sample and hold unit. A large area $(5 \times 5 \text{ mm}^2)$ photodiode (S1227-66BQ; Hamamatsu Photonics K.K.) is reversely biased with 5 V. Even for this large area photodiode, the dark current ($25 \text{ pA}$) on the time scale of the output signal ($50 \mu$s) is orders of magnitude below the shot noise limit of the probe pulses. The charge carriers generated instantaneously by the laser pulse in the photodiode are stored on the internal capacitance of the diode and on the capacitor $C_1$ connected in parallel, resulting in a total capacitance of 2 nF. For a pulse energy of 1 nJ, the charge generated on the photodiode corresponds to 150 mV, which is well below the bias voltage and even the bandgap of silicon. The capacitance is discharged via $R_1$ and $R_2$ in parallel, giving a time constant of 22 $\mu$s. A trim potentiometer connected in series to $R_1$ allows to precisely match the time constants of two detectors. The ac coupling via $C_2$ reduces the influence of background cw light. The voltage drop across $R_2$ is amplified by a factor of 8.4 with an operational amplifier (LT1220; Linear Technology Corp.). Here any amplifier which has a low input offset voltage and a low input bias current can be chosen. The gain is rolled off at 50 kHz with an $RC$ low pass circuit in the feedback loop.
The detector output signal is linear to the input pulse energy up to 1 V output. The two detectors for signal and reference pulses, terminated with 50 Ω, are sampled by a two channel, 14 bit, high speed digitizer (NI 5122; National Instruments) over a period from 20 μs before to 80 μs after the laser pulse at a sampling frequency of 10 MHz, i.e., a 0.1 μs spacing. The baseline is determined from the first 20 μs and subtracted from the subsequently sampled points. The signal is then integrated from 3 to 40 μs after the laser pulse, giving a numerical value proportional to the pulse energy. This procedure eliminates baseline problems, reduces high frequency noise by a factor of 10, and gives an effective 14 bit resolution. For a single dark channel, we find shot to shot standard deviations of 5 × 10⁻⁵. The photodiode detecting the pump pulse is read synchronously with a second ADC board (PCI-MIO-16E4; National Instruments).

E. Data processing and noise suppression

The noise observed in a pump-probe spectrometer consists of three main components: laser excess noise, shot noise, and electronic noise of the detectors and the data acquisition device. The latter two contributions have been addressed in the preceding section. We will now show that the laser excess noise is the dominant part, and therefore discuss in detail our measures to decrease the influence of the laser fluctuations.

The output of a NOPA can have intensity noise as low as the pump laser (typically around 1% rms) if the amplification is driven properly into saturation. The UV pump pulse generated in the SFM process has about twice the noise of the pump laser. Although in principle it should be possible to eliminate laser excess noise for the probe pulse by normalizing it to the reference channel, in practice it is difficult to reach the shot noise limit. Experimentally, we find that our shot to shot referencing procedure reduces the estimate for the normalized standard deviation (rms noise) by a factor of β=25 (data not shown) and thus the laser excess noise remains the dominant noise source.

An analysis of the fluctuations of the laser system can help optimize the data acquisition and processing strategy. For kilohertz ultrafast laser systems, they are not purely statistical but typically dominated by low frequency contributions. A signal processing that simply sums over a statistical but typically dominated by low frequency components imply that consecutive laser shots are strongly correlated.

We consider the normalized noise \( n_i \) given by the deviation \( n_i = (E_i - \overline{E}_i)/\overline{E} \) of the individual pulse energy from the average as displayed in Figs. 4(a) and 4(b) on a short and a long time scale. \( E_i, i=1,\ldots,N \), are successively recorded pulse energies, and \( \overline{E} \) denotes the average and \( \overline{E} \) the quadratic mean value. For our laser system, the standard deviation of the normalized noise is in the long time limit less than 0.01, i.e., 1% rms. The Fourier transformation of the ensemble shown in Fig. 4(b) is displayed in Fig. 4(d). Figure 4(c) shows a scatter density plot of \( n_i \) vs \( n_{i+1} \) indicating a strong linear correlation between successive pulses. The Pearson product moment correlation function

\[
r = \frac{\text{cov}(n_i; n_{i+1})}{\text{var}(n_i)}
\]

(Ref. 22) is well suited to analyze our data and a perfect correlation would yield a value of +1 while a perfect anticorrelation would render −1. For our pump laser system we typically find a value of \( r > 0.93 \).

The high shot to shot correlation is exploited by a shot by shot referencing method with the pump beam blocked for every second laser shot (see Sec. II B). At one shot the probe signal (sig) and reference signal (ref) are recorded for the excited sample \( (\text{sig}^*, \text{ref}^*) \) and at the next shot without excitation \( (\text{sig}_{i+1}^*, \text{ref}_{i+1}^*) \). The signals for \( N \) pairs of laser shots are measured for every delay time \( \tau \) between the pump and probe, where typical values of \( N \) are 300–500. From these numbers, the excitation induced transmission change \( \Delta T \) is calculated relative to the transmission without excitation \( (T_0) \):

\[
1 + \frac{\Delta T(\tau)}{T_0(\tau)} = \left[ \frac{\text{sig}^*}{\text{ref}^*} \right]_N \left[ \frac{\text{sig}_{i+1}^*}{\text{ref}_{i+1}^*} \right]_N^{-1},
\]

(3)

\[
\Delta \text{OD}(\tau) = -\log \left[ 1 + \frac{\Delta T(\tau)}{T_0(\tau)} \right].
\]

(4)

The difference in optical density \( \Delta \text{OD} \) can be computed with Eq. (4) from the normalized difference transmission signal given by Eq. (3). For the sufficiently small changes in the transmission observed in these studies, \( \Delta \text{OD} \) can be approximated quite well by

\[
\Delta \text{OD} = \left( \frac{\Delta T/T_0}{\ln(10)} \right) = -\frac{(\Delta T/T_0)}{2.3026}.
\]

(5)

For further elucidation of the influence of the laser noise on the signal noise, we let \( P_i = P_0(1+n_i) \) and \( Q_i = Q_0(1+m_i) \) be the probe and pump pulse energies for the \( i \)th laser shot of the experiment, suffering from the normalized noises \( n_i \) and

![Fig. 4. Normalized shot to shot deviation of the pump laser system over 0.1 s and 5 s. (c) Scatter density plot of the pulse energy deviation vs energy deviation of the consecutive shot. (d) Fourier transform of the data shown in (b) plotted on a log-log scale.](image)
m_i, respectively. From Eq. (1) it follows for small signals that the pump induced transmission change of the sample is linear in the pump energy ΔT_i ≈ Q_i. Then the signal detected by the probe photodiode \( \sigma_{2i} \propto P_2(T + \Delta T_2) \) can be expressed as

\[
\sigma_{2i} \propto P_2(T(1 + n_{2i}) + P_0\Delta T(1 + n_{2i} + m_{2i} + n_{2i}m_{2i}))
\]  

for the excited sample and as

\[
\sigma_{2i+1}^0 \propto P_0(T(1 + n_{2i+1})
\]

for the sample without excitation (after Ref. 23). The reference channel suffers from a slightly different noise \( n_i' \):

\[
\sigma_{i+1}^0 \propto P_0(1 + n_i')
\]

With \( \delta_{2i}(n_{2i} - n_{2i}' - (n_{2i+1} - n_{2i+1}') \), Eq. (3) can be rewritten to first order in terms of noise as

\[
1 + \frac{\Delta T(\tau)}{T_0(\tau)} = 1 - \langle \delta_{2i}/N \rangle + \frac{\Delta T(\tau)}{T_0(\tau)}(1 + \langle m_{2i}/N - \langle \delta_{2i}/N \rangle).
\]

Since \( \langle \delta_{2i}/N \rangle \) is a difference between different detectors and consecutive laser shots, it can be assumed to be mostly uncorrelated to \( \langle m_{2i}/N \rangle \). The standard deviation for the pump-probe signal is thus given by

\[
\sigma\left[\frac{\Delta T(\tau)}{T_0(\tau)}\right]^2 \approx \sigma(\langle \delta_{2i}/N \rangle)^2 + \frac{\Delta T(\tau)}{T_0(\tau)}\sigma(\langle m_{2i}/N \rangle)^2 + \sigma(\langle \delta_{2i}/N \rangle)^2.
\]

The second term \( \sigma(\langle \delta_{2i}/N \rangle) \) determines the detection sensitivity whereas \( \sigma(\langle m_{2i}/N \rangle) \) limits the signal-to-noise ratio of the transient transmission measurement. In the case of large transient transmission signals, the transmission change should be corrected for the pump noise. This can be done by dividing \( \Delta T(\tau)/T_0(\tau) \) by the ratio of the pump pulse energies averaged over the data point for the delay \( \tau \) and the long term average of the pump pulse energies.

We next want to go one step further and obtain an analytical expression for \( \sigma(\langle m_{2i}/N \rangle) \) and \( \sigma(\langle \delta_{2i}/N \rangle) \). It can be shown that \( \sigma(n_{2i} - m_{2i+1})^2 \approx 2(1 - r)\sigma(n)^2 \) and therewith \( \sigma(\delta_{2i}/N)^2 = \beta^2 - 2(1 - r)\sigma(n)^2 \). From the shot to shot correlation \( r \), the simplest estimate for a correlation over a k-shot distance is \( r^k \). Using this relationship, one can estimate the correlation \( \langle \delta_{2i}/\delta_{2j} \rangle = r^{j-2i} \langle \delta_{2i} \rangle \) and obtain a closed form expression for the total correlation within the sample. This gives an upper estimate for the standard deviations in Eq. (9):

\[
\sigma(\langle \delta_{2i}/N \rangle)^2 \leq \frac{2(1 + r^2)}{N(1 + r)}\beta^2\sigma(n)^2,
\]

\[
\sigma(\langle m_{2i}/N \rangle)^2 \leq \frac{1 + r^2}{N(1 - r)}\sigma(m)^2.
\]

With \( N = 500 \), \( \beta = 25 \), \( r = 0.9 \), \( \sigma(n) = 0.01 \), and \( \sigma(m) = 0.02 \), Eqs. (10) and (11) can be evaluated to \( \sigma(\langle \delta_{2i}/N \rangle)^2 \approx 2 \times 10^{-5} \) and \( \sigma(\langle m_{2i}/N \rangle)^2 = 3 \times 10^{-3} \).

Comparing these values to the ones obtained experimentally (see Sec. III C), it can be seen that the probe induced noise as well as the signal-to-noise ratio match within a factor of 2. The following relation becomes apparent: When employing a shot to shot referencing procedure, a high shot to shot correlation is obviously advantageous for the referencing. On the other hand, a high correlation over many laser shots reduces the number of uncorrelated shots in the sample, and averaging over the sample is less effective. For the probe induced noise [see Eq. (10)] these two effects fairly cancel out \([(1 + r^2)/(1 + r) \approx 1]\), whereas the pump induced noise [see Eq. (11)] is only reduced by the effective number of uncorrelated laser shots in the sample, which is about 10% of \( N \) since \((1 + r^2)/(1 - r^2) \approx 10\). This dilemma can be avoided by a fast scanning measurement scheme. 24 Our apparatus will be augmented in this way in the future.

In summary, the estimation in this section and the preceding one shows that the fluctuations and, in particular, the correlations of pump and probe pulses are the limiting factors for the signal-to-noise ratio and the sensitivity of the transient absorption signal. The detector shot noise and the precision of the data acquisition only contribute a small fraction. Therefore efforts aimed at reducing the laser noise will directly lead to a further improvement of the described setup.

### F. Gas cell

Medium sized molecules are typically obtained as crystalline samples at room temperature and have to be heated to achieve reasonable vapor pressures. If this is done in a cell, some of the substance condenses on the walls and windows and forms a thin layer. At the points where the light beams enter or exit the cell, they interact with this layer and eventually destroy the molecules. Since the molecules on the windows are immobile, the effect accumulates quickly and opaque spots appear that absorb the pump energy. We were not able to prevent this from happening by differentially heating the windows.

To circumvent this problem, a heatable gas cell has been constructed with windows protected by an inert gas flow (see Fig. 5). The cylindrical glass cell containing the sample is placed within an aluminum casing. Holes of 1.5 mm in diameter are drilled through the middle of the cell windows so the light beams can enter and exit the cell without passing through glass, and thereby through a layer of sample substance. A few windings of heating tape are wrapped around the cell and the temperatures of up to 150 °C can be readily achieved. An extra winding of the heating tape is placed near each window to heat them slightly more than the central part of the glass cell. This prevents molecules from occluding the holes.

The light beams enter the aluminum casing via 1 mm thick fused silica windows at the endings of two 100 mm long tubes. A baffle with a 4 mm hole separates each tube into two chambers. The outer chamber is flushed with dry nitrogen from a cylinder while the inner one is pumped. In this way, a constant flow of nitrogen is adjusted through the baffle which efficiently keeps sample molecules from diffusion.
ning to the windows and condensing there. The cell is operated at a pressure around 2 mbars, which is about ten times higher than the vapor pressure of the sample to avoid pumping a significant amount of sample out of the cell. Under these conditions the mean time between collisions is well above 10 ns, which is a factor of 100 longer than the time scale we examine with our pump-probe experiments.

G. Determination of time zero

Especially for ultrafast processes, the exact onset of the pump induced photochemical reaction contains valuable information and should be determined as precisely as possible. To do so, we measure alternately (i) the cross correlation between pump and probe pulses in a 10 μm thin BBO crystal and (ii) a short scan of the molecular dynamics around time zero. From consecutive measurements of the cross correlation, one can determine (see below for necessary corrections) the time zero during the actual molecular experiment. We find that the time zero drifts between consecutive measurements are less than 2 fs. Proper interpolation makes this small effect negligible.

A number of precautions have to be taken to ensure the desired precision in the determination of time zero.

1. All cross correlation measurements are performed with the crystal placed at the same physical position (focus) where the centers of the gas cell and flow cuvette are during the experiment.

2. To actually measure the cross correlation, the sample cell is replaced by a compensation window of the same material and nominal thickness as the entrance window of the cell. This window accounts for the dispersion and group velocity mismatch (GVM) of the pump and probe in the front cell window. The GVM is ~250 fs/mm for fused silica. The dispersion influences the achieved temporal resolution and the compressors are adjusted accordingly.

3. The cross correlation determined by (2) has to be corrected for the difference in thickness of the compensation window and the cell window and for half the GVM induced by the sample.

4. To measure the difference in thickness of the compensation window and the sample cell entrance window, the cell is disassembled and only the front window is placed into the beam path. Alternate cross correlations with the cell window and the compensation window are then performed as described above. We found that the compensation window used for measurements with the gas cell introduces 20.3 fs more group delay than the sample cell window. In the case of the solution cell, the compensation is 3.8 fs too small (for 325 nm pump and 595 nm probe, see Fig. 6).

5. In experiments performed with the gas cell, the GVM of the pump and probe half way through the evacuated cell is smaller than through the additional air, which the beams transverse when the cell is taken out for cross correlation measurements. The shift of time zero due to the evacuation of the cell has been determined experimentally. For the experiments presented in Fig. 6, we found that the cross correlation is shifted by 33 fs to smaller delays by evacuation of the cell. Since only half of the cell length enters into the spectroscopic measurement, we obtain a correction value of 16.5 fs.

6. For the solution experiments, the GVM of half of the thickness of the sample is computed from GVM data for solvents determined in our laboratory. The flow cuvette used for the experiment presented in Sec. III has an optical path length of 120 μm. For a layer of 60 μm of cyclohexane, we obtain a cross correlation shift of 17.8 fs to later times for the wavelengths given above.

Although individual cross correlation measurements can be performed with a precision of better than 2 fs, due to concatenation of measurements the final accuracy is approximately 5 fs.

Figure 6(a) shows the initial dynamics for HBT measured in the gas phase and in solution. The cross correlation measurement obtained with the respective compensation window is taken as time zero [see dash-dotted line in the lower part of Fig. 6(a)]. As indicated, the gas phase signal appears too early and the solution phase one too late. The contributions to the deviation discussed above are shown to scale in the figure.

In Fig. 6(b) the experimental curves for HBT in the gas phase and in solution are displayed with proper correction of time zero. It turns out that within the precision of the measurement, the initial rise of the emission is in both cases equally fast. From such an observation we can deduce a detailed model of the influence of the solvent environment on the primary dynamics of the excited state intramolecular proton transfer.
III. PERFORMANCE OF THE SPECTROMETER: ULTRAFAST EXCITED STATE INTRAMOLECULAR PROTON TRANSFER

A. Transient absorption spectroscopy of 2-(2'-hydroxyphenyl)benzothiazole

As a first experiment with the new gas phase pump-probe spectrometer, the ultrafast intramolecular proton transfer in HBT is investigated. The process occurs on a time scale of 50 fs and is associated with rich wavepacket dynamics. Since the transient absorption of HBT in the nonpolar and inert solvent cyclohexane is very well characterized, a comparison to the transient absorption in the gas phase is ideal to identify gas phase specific features for the process. Here some results are presented to document the performance of the spectrometer. A detailed discussion of the molecular dynamics will be presented elsewhere.

Figure 7 shows a comparison of transient absorption curves of HBT in the gas phase and in cyclohexane solution excited at 325 nm and probed at 490 nm. The measured cross correlation was 39 fs and the UV pulses had an energy of 450 nJ. The gas cell was heated to ~110 °C. To switch between the gas phase and solution experiments, the gas cell is replaced by a flow cuvette with an optical path length of 120 μm and a 200 μm thick fused silica entrance window. Additionally a compensation window is inserted in the beam to account for the different thicknesses of the gas and flow cell windows. Since no other adjustments are necessary, the setup is optimally suited to compare directly the dynamics in the gas phase and in the condensed phase. The solution measurements are in excellent agreement with previous experiments performed on a liquid jet. The results show that the pump-probe spectrometer allows for the precise measurement of complex ultrafast dynamics in the isolated as well as in the soluted molecule.

B. Temporal resolution

The cross correlation trace presented in Fig. 7 has a width full width at half maximum of 39 fs. A conservative analysis shows that processes which are as fast as 20 fs can be reliably detected with deconvolution techniques or by fitting a model function that takes the cross correlation into account to the data. The achieved time resolution is also suitable to observe coherent motions in skeletal modes of molecules. These are seen as the oscillating signal contributions in both recordings shown in Fig. 7. In the first picoseconds they are dominant over the more common exponential signal decays. In the present configuration, the UV pump pulse with a length of 30 fs is mainly responsible for the cross correlation width. In the SFM process the spectral phase of the visible input beam is linearly transferred to the UV. It is therefore possible to correct for higher order spectral phase distortions with chirped mirrors or adaptive optics in the visible beam path. This should allow for UV pump pulses with durations in the order of 10 fs, further improving the time resolution by a factor of 4. It has already been demonstrated that the tuning range of the probe pulses can be readily extended into the near infrared while maintaining the time resolution.

C. Sensitivity, signal-to-noise ratio, and dynamic range

To verify the sensitivity under realistic conditions and to determine the minimal detectable absorbance change, the noise of a typical pump-probe trace of HBT in gas phase is analyzed in Fig. 8. Five successive scans with an excitation wavelength of 350 nm and a probe wavelength of 570 nm were performed. Each data point of each scan is computed from 421 pairs of laser shots with and without excitation. The scan is recorded with a time step of 5 fs between successive data points. Afterward, the scans are averaged and the resulting curve is smoothed by adjacent averaging of five data points, corresponding to less than the ratio of the cross correlation width to the time resolution.
correlation width over the time step, and thereby not deteriorating the temporal resolution. A statistical analysis of the signal before time zero returns a standard deviation, i.e., a detection sensitivity of the instrument of $1.1 \times 10^{-6}$ OD, meaning that changes in the absorbance down to almost 1 µOD can be detected on the 1σ level. This is two orders of magnitude or more better than previous work; even so much less pump pulse energy is used.\textsuperscript{28,29} The corresponding shot noise limit is less than a factor of $-10$ lower. With a maximum reasonable absorption change of 0.05 OD, the dynamic range, i.e., the ratio of the largest over the smallest detectable absorbance change within one scan is 45 000:1. For a pure exponential decay this would mean that it can be observed over ten decay time constants.

For the analysis of the signal after time zero, a multiplexponential decay model function is fitted to a part of the measured trace which is expected to be a smooth decay without oscillatory contributions [see Fig. 8(b)]. Subtracting the fitted model function from the measured data gives the deviation of the measured data points from the smooth decay [see Fig. 8(b), lower panel] which can be identified to a good approximation with the noise of the data. Figure 8(c) shows a histogram of the deviations which exhibit roughly a Gaussian distribution. The standard deviation σ of the noise accounts to $2.9 \times 10^{-6}$. In addition to the fundamental noise of the setup, determined from the analysis of the data before time zero, the noise of the pump pulse is superimposed on the signal after time zero. Assuming that the noise components are independent, it can be computed to $2.7 \times 10^{-6}$. A detailed analysis of measurement traces at different signal amplitudes shows that the pump noise scales fairly linearly with the signal amplitude. This is in good agreement with the theory presented in Sec. II E. Comparing the pump noise to the average signal of $0.36 \times 10^{-3}$ in the regime analyzed above, this gives a signal-to-noise ratio of 43 dB (140:1). The high signal-to-noise ratio allows us to detect weak oscillatory contributions to the signal, which can originate from coherent nuclear wavepacket dynamics, and to observe these oscillations that typically decay faster than the population over a longer time scale, and thus determine frequency and damping time more accurately. The detection scheme presently does not correct for the fluctuations of the pump light. Precisely measuring the pump pulse energy and implementing such a correction might well push the signal-to-noise ratio up to 50 dB (300:1).

The demonstrated extremely high sensitivity and signal-to-noise ratio together with the superior temporal resolution allow for the first time the direct comparison of the ultrafast dynamics of chemical reactions proceeding in the isolated gas phase and in solution. It should therefore help further our fundamental understanding of the various contributions to the processes. Furthermore we believe that the setup does allow the measurement of dynamics in single molecular layers which are most important in the rapidly developing field of molecular electronics and organic light emitting diodes.

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\textsuperscript{14} We use the following definition of the optical density: OD= $-\log_{10}(E_f / E_0)$, with $E_0$ the energy of the incident light pulse and $E_f$ the transmitted energy.