Gas-phase femtosecond transient absorption spectroscopy

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A setup for measuring femtosecond transient absorption in the gas phase is reported. The apparatus is based on a 1 kHz amplified Ti:sapphire laser system and measures gas-phase transient absorption using a shot-to-shot normalization scheme with background subtraction. We have used this setup to examine the wave packet dynamics of the I2 B state in the vapor phase as a benchmark. The results are consistent with those reported by other groups using indirect transient absorption techniques.


I. INTRODUCTION

Transient absorption spectroscopy (TAS) has proven to be one of the most versatile techniques for studying ultrafast processes in chemistry and biology.1 In a typical ultrafast TAS experiment, a pump laser pulse initiates the dynamics of a system by generating a nonstationary state that evolves in time. A second delayed probe pulse then probes the dynamics by measuring the optical absorption due to an upward transition (or optical gain due to a downward transition) as a function of the pump-probe delay time. Although femtosecond TAS has been widely used in condensed-phase ultrafast studies, its application in the gas phase has not been fully recognized. On the other hand, many variants of femtosecond TAS have been developed over the years to measure transient absorption spectra indirectly in the gas phase and have played crucial roles in the development of femtosecond transition-state spectroscopy2,3 (FTS) and femtochemistry.4 The detection methods used in these indirect femtosecond TAS techniques include laser-induced fluorescence (LIF),5-7 ionization with mass8-16 or photoelectron kinetic-energy17-21 analyses, four-wave mixing22,23 (FWM) and coherent anti-Stokes Raman scattering (CARS).24,25 These techniques yield, in principle, information equivalent or similar to those given in the transient absorption spectra. However, in the femtosecond pump-probe LIF the final levels in the probing step need to be fluorescing. This requirement is not always satisfied for large molecules in which the higher electronically excited states are usually weakly or even not fluorescing. This problem is surmounted in the femtosecond pump-probe ionization spectroscopy in which one-photon or multiphoton absorption leading to ionization implements the probing. The advantages are its compatibility with mass and/or photoelectron kinetic-energy analyses. However, in the case of multiphoton ionization (MPI) the possible involvement of several upper electronic states may complicate the interpretation, and in the case of one-photon ionization the difficulty in producing high-photon-energy femtosecond pulses may limit the systems of interest to those of low ionization potentials. For femtosecond-FWM and femtosecond CARS the probing steps rely on third-order nonlinear processes and therefore the analyses of the transient spectra are somewhat involved.22,26 On the other hand, the direct femtosecond TAS method reported here measures the linear optical absorption of the probing transition itself, which should lead to a more straightforward interpretation. It does not require high-energy photons and is applicable for nonfluorescing systems. Thus, direct femtosecond TAS can complement other more popular techniques in exploring ultrafast dynamics in the gas phase.

In liquid-phase femtosecond TAS the solute concentrations are usually high enough to compensate for the very short path lengths required to minimize group velocity dispersion (GVD). In vapor-phase femtosecond TAS the molecular density is much lower, and therefore a much longer path length must be employed. Glownia et al. reported the first examples of gas-phase ultrafast transient absorption experiment with a subpicosecond time resolution.27-29 Since then, gas-phase femtosecond TAS had gone unnoticed, probably due to its seemingly poor sensitivity. Here, we report a setup for measuring transient absorption in the gas phase with ~100 fs time resolution and reasonable sensitivity. In our experiments the femtosecond pump and probe beams were collinearly overlapped in a ~20 cm gas cell in order to compensate for the low molecular density and attain detectable absorbance changes. The temporal resolution was not deteriorated by the long path length because the GVD effect in low-pressure gases is negligible. We have used this setup to examine the wave packet dynamics of the I2 B state in the vapor phase as a benchmark. In 1989 Bowman et al. employed femtosecond pump-probe LIF spectroscopy,5 an indirect variant of the transient absorption, and observed the I2 B-state wave packet dynamics. Since then I2 vibrational wave packet motion had been studied by many different ultrafast spectroscopic techniques, including femtosecond MPI,30,31 zero electron kinetic energy (ZEKE),30,31 degenerate four-wave mixing (DFWM),23 and CARS.24

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pump and probe pulse energies were about 10 and through a collinearly recombined by a dichroic mirror and focused roughly equal intensities. The pump and probe beams were frequency-doubled by another BBO crystal to obtain 400 nm pressor for GVD compensation.

The remaining part of the CPA output (800 nm) was frequency-doubled by another BBO crystal to obtain 400 nm femtosecond laser pulses that were subsequently divided by a beam splitter into the probe and reference beams with roughly equal intensities. The pump and probe beams were collinearly recombined by a dichroic mirror and focused through a f=200 mm lens into an ~20 cm long gas cell. The pump and probe pulse energies were about 10 and 1 μJ/pulse, respectively, before entering the cell, and the polarizations of the pump and probe beams were mutually perpendicular. After emerging from the cell, all three beams (pump, probe, and reference) were focused together onto the entrance slit of a small monochromator that served as a spectrometer. The pump and probe beams exiting the monochromator were then separately detected by two photodiodes. The output of each photodiode was fed into a boxcar integrator. An optical chopper (Thorlabs, MC1000) was placed in the pump-beam path to modulate the excitation by blocking every other pump pulse. A third photodiode was used to monitor the modulation phase.

In order to remove the background offset fluctuation the boxcar integrators were triggered at twice the repetition rate of the CPA and operated in the active base line subtraction mode. A four-channel digital delay pulse generator (Berkeley Nucleonics Co., Model 555) was used as the master clock to synchronize the entire system. The fundamental output of the pulse generator at 2 kHz triggered the boxcar integrators, the divided-by-two output (1 kHz) triggered the CPA, while the divided-by-four output (500 Hz) was used to synchronize the optical chopper. The boxcar integrator offset was recorded between successive probe/reference pulses and was subtracted from the subsequent probe/reference pulse signal. This procedure effectively minimizes the offset fluctuation of the boxcar integrators. The outputs of the two integrators, including the probe, reference, and between-pulse-offset signals, were read by a 16 bits analog-digital converter (National Instrument, PCI-6036E) and then transferred to a computer for absorbance change calculations using a shot-to-shot normalization scheme. The sample cell was an ~20 cm long glass tube with 2 mm thick quartz windows on both ends. A few grains of iodine crystals were sealed in the sample cell at room temperature to give an iodine vapor pressure of ~100 mtorr.

III. RESULTS AND DISCUSSION

Figure 2 shows the $I_2$ transient absorption transients ob-
tain using the setup described above. The transients are

dominated by a rapid oscillation with a period of \(\sim 310 \text{ fs}\)

which are characteristic of vibrational wave packet motion of the \(I_2 B\) state.\(^{32,33}\) The oscillation amplitude decreases with
delay time and diminishes at about 8 ps and then reappears
at about 14 ps. These dephasing and revival behaviors of
vibrational wave packet have been well documented in the
literature.\(^{32,33}\) In the present case, the femtosecond pump
pulse at 613 nm prepares a coherent superposition of several
vibrational eigenstates, i.e., a vibrational wave packet. The
different eigenstates evolve in time, causing the wave packet

to move back and forth in the \(B\)-state potential well with an
oscillation period determined by the average vibrational level
spacing.\(^{33}\) The probe pulse at 400 nm probes the wave packet
motion by measuring the transient absorption of the evolving
\(B\)-state wave packet to an upper electronic state, presumably the \(f_g\) state. The transient absorbance depends on the Franck-
Condon overlap which is modulated by the wave packet motion
in the \(B\) state, resulting in the observed rapid oscillation
with a period of about 310 fs, as shown in Fig. 2(A). Excita-
tion of iodine vapor at 613 nm accesses the \(B\)-state \(v'\)
\(\sim 10\) region (from \(v''=2\)) where the vibrational spacing is
about 110 cm\(^{-1}\), consistent with the observed 310 fs oscilla-
tion period. A Fourier transform (FT) power spectrum that
reveals the frequency content of the transient is shown in
Fig. 2(B) inset. Three major frequency components at 106.5,
108.5, and 110.5 cm\(^{-1}\) were identified. These are the results
of a series of nearest neighbor coherence and the observed
frequencies correspond to the vibrational level spacing of
successive levels near \(v'=10\). Because of anharmonicity a
phase mismatch accumulates among the evolving vibrational
eigenlevels and the wave packet gradually dephases. How-
ever, because the evolution of these eigenstates is coherent,
they can rephase at later time and reproduce the wave packet.
The revival time in Fig. 2(B) transient is about 20 ps, which
is consistent with the reciprocal of the frequency difference
of adjacent vibrational level spacing \((\sim 1.7 \text{ cm}^{-1})\) (Ref. 32)
around \(v'=10\). The lower oscillation amplitude in the re-
vived oscillation is due to rotational dephasing.

The transients shown in Fig. 2 are in good agreement
with those reported by Bowman \textit{et al.} using femtosecond
pump-probe LIF technique,\(^4\) i.e., an indirect transient absorp-
tion method. However, the next-nearest-neighbor coherence,
or the 2\(\omega\) components were not observed in our experiment.
This is due to the fact that our laser pulse width \((\sim 120 \text{ fs})\)
was almost a factor of 2 longer than those used in Ref. 5, and
therefore the coherent spectral width was not wide enough to
bring about 2\(\omega\) interference in our case. Fisher \textit{et al.}\(^{30}\) studied
the same system using femtosecond pump-probe ionization
spectroscopy with pulse widths comparable to ours, and
indeed, the femtosecond pump-probe MPI transients reported
in Ref. 30 are very similar to ours.

Although the transients shown in Fig. 2 were obtained
with the pump and probe beams collinearly overlapped and
focused, the signal did not only come from the small focal
volume. In fact, when the focusing lens was removed and the
two beams were collinearly overlapped along the beam path
in the cell, similar transients with \(\Delta OD\) of about an order of
magnitude lower were obtained. This phenomenon is prob-
ably due to the inhomogeneous beam profiles that result in
poor effective spatial overlap, and thus much lower \(\Delta OD\),
when the laser beams are not focused. For the experiments
described here a transient of \(S/N \sim 10\) and a maximum \(\Delta OD\)
of \(2 \times 10^{-3}\) can be readily obtained at a scanning rate of
1000-laser-shots average per delay position. This corre-
sponds to a lowest detectable \(\Delta OD\) of about \(2 \times 10^{-4}\) at
the same scanning rate. The high sensitivity and \(S/N\) ratio at-
tained with the present setup promise its future applications
to more complex molecular systems in the vapor phase. Note
that the temporal resolution was not deteriorated by the long
path length \((\sim 20 \text{ cm})\), suggesting that even longer path
lengths can be used for less volatile compounds. Recently,
we have successfully measured the vapor-phase transient ab-
sorption of \(\alpha\)-hydroxy acetonaphene (OHAP) excited at
320 nm and the preliminary results were consistent with
what we observed previously using femtosecond pump-
probe MPI detection.\(^{31}\) In conclusion, although the realiza-
tion of gas-phase femtosecond TAS is straightforward, the
high sensitivity and temporal resolution demonstrated here
suggest the applicability of femtosecond TAS to complement
other more widely used techniques in exploring ultrafast dy-
namics in the gas phase. Upgrading the present setup to en-
able broadband detection using a white-light continuum
probe is feasible and is now underway in our laboratory.

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