

ULTRAFAST SPECTROSCOPY OF AZOBENZENE

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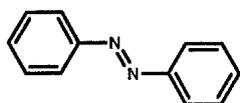
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INTRODUCTION

Photoisomerisation is a fundamental reaction class which has wide importance in pure and applied chemistry, and in nature. The classic example of a photoisomerisation reaction is provided by stilbene, for which the mechanism and dynamics have been elucidated since the development of ultrafast spectroscopic techniques.¹ These studies have been extensive, including our own past work at RAL on mode-specific vibrational excitation and relaxation as studied by time-resolved resonance Raman spectroscopy.² Another textbook example of photoisomerisation is provided by azobenzene, for which only very early attempts at direct study by time-resolved spectroscopy had been reported³ prior to our recent work in York,⁴ in stark contrast with the large number of studies reported for the isosteric stilbene molecule. In the past, the mechanism of azobenzene photoisomerisation and its wavelength dependence have been debated almost exclusively on the basis of steady-state studies, with an in-plane inversion mechanism proposed for isomerisation from the $S_1(n\pi^*)$ state and an additional rotation mechanism, similar to that for stilbene, proposed for isomerisation from the $S_2(\pi\pi^*)$ state.⁵



In York, we have used femtosecond time-resolved UV-visible absorption (TRVIS) spectroscopy⁶ to observe the photochemistry of trans-azobenzene directly for the first time.⁴ On UV excitation to the $S_2(\pi\pi^*)$ excited state, the first-formed species was identified by a band at ca. 390 nm which decayed in ca. 900 fs. A second component in the decay, prominent at shorter wavelengths, was similar to that of ca. 15 ps observed for the recovery of the bleach of the ground-state UV absorption band. Drawing on the results of steady-state experiments and ab initio calculations⁷ reported in the literature, our interpretation of these results is that rotation on the S_2 potential energy surface occurs in ca. 900 fs to form a 'bottleneck' state (S_2^\ddagger or S_1^\ddagger) which is relatively long lived, and which results in the relatively long time of ca. 15 ps for ground-state recovery (Fig. 1).

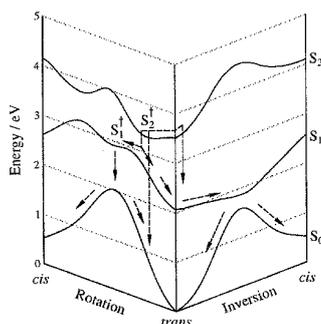


Fig. 1 Proposed mechanism for azobenzene photoisomerisation.^{4,7}

Following these initial experiments, we wished to extend our studies of trans-azobenzene to visible excitation to the $S_1(n\pi^*)$ excited state. The excitation wavelengths required (400-500 nm) are not readily available using our amplified dye laser apparatus in York, and so these studies have been carried out at RAL. The aim was to pump the molecule into the S_1 state and to use ultrafast TRVIS spectroscopy to study the photochemistry.

EXPERIMENTAL

The OPA system in the LSF Ultrafast Spectroscopy Laboratory was used at a repetition rate of 40 kHz and provided both pump (ca. 25-600 nJ) and probe (ca. 6-90 nJ) pulses (ca. 600 fs instrument response function) at various wavelengths. The beams were overlapped in a 0.5-mm path length cell through which a solution of trans-azobenzene in n-hexane was flowed. The pump beam was chopped at ca. 2 kHz, and the probe beam was sampled by two photodiodes, detecting both sample and reference signals. The data were collected, by lock-in amplifier, as kinetic traces at single probe wavelengths.

RESULTS AND DISCUSSION

Our initial experiments at RAL were essentially a repeat of our earlier studies at York: trans-azobenzene was excited at 260-280 nm, into the $S_2(\pi\pi^*)$ state (Fig. 2), and the TRVIS kinetics were probed at 390, 420, and 490-700 nm. The time resolution at RAL was inferior to that at York, and this precluded a detailed analysis of the fast component observed at ca. 390 nm. Nevertheless, the observed kinetics could be fitted by a dual exponential decay with lifetimes of ca. 900 fs and 10 ps; these results essentially confirmed the earlier work at York, within the constraints of the RAL apparatus at the time of our visit.

The principal aim of the visit was to study the photochemistry of trans-azobenzene on excitation to the $S_1(n\pi^*)$ state. On pumping at 503 nm, at low excess energy above the S_1 origin (Fig. 2), excited-state absorption was observed at 390-420 nm. These probe wavelengths comprised the rather limited range

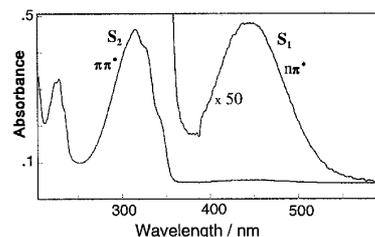


Fig. 2 Ground-state UV-visible absorption spectrum of trans-azobenzene in n-hexane.

that was available under these particular experimental conditions. The 'spectrum' obtained across this limited range, scaled for changes in alignment and energy which occurred as the laser system was tuned, is shown in Fig. 3.

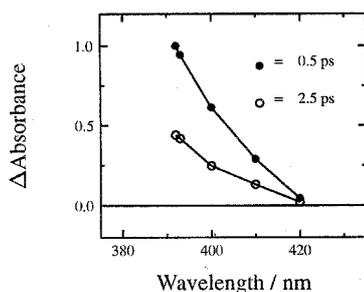


Fig. 3 Scaled TRVIS spectrum of trans-azobenzene. Pump 503 nm.

All of the TRVIS kinetics obtained within this limited probe range showed a single exponential decay of ca. 2.5 ± 0.2 ps, as shown in Fig. 4. This figure also serves to illustrate the high signal-to-noise ratio obtained, and also the excellent fit of these data on 503-nm pumping to a single exponential decay. The transient absorption at 390-420 nm and the lifetime of ca. 2.5 ps may be assigned to the $S_1(n\pi^*)$ state of trans-azobenzene.

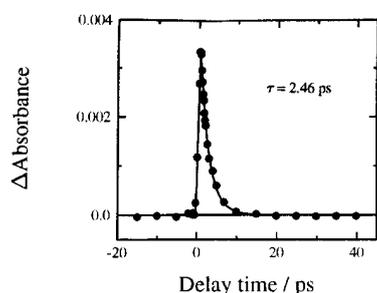


Fig. 4 TRVIS kinetics of trans-azobenzene. Pump 503 nm. Probe 392 nm.

Experiments were also carried out with excitation at 390-420 nm, at high excess energy above the S_1 origin (Fig. 2). Transient absorption was observed throughout the range 370-600 nm, using the much wider probe wavelength range available with these experimental conditions. The significantly different experimental arrangements resulting from tuning the OPA system required the TRVIS data to be scaled; the resulting 'spectrum' comprised a strong peak at ca. 400 nm and a weaker peak at ca. 520 nm, the latter shown in Fig. 5.

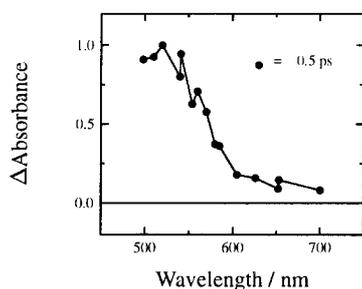


Fig. 5 Scaled TRVIS spectrum of trans-azobenzene. Pump 420 nm.

The TRVIS kinetics obtained on excitation at ca. 400 nm were different from those obtained on excitation at ca. 500 nm or at ca. 300 nm. They did not fit to a single exponential decay, but did fit reasonably well to a dual exponential decay: a fit with components of ca. 0.6 and 2.4 ps is illustrated in Fig. 6, with the decay on pumping at 503 nm also shown for comparison, but fits of similar quality could be obtained with different combinations of lifetimes and amplitudes.

This second, faster component observed on excitation at ca. 400 nm may arise from rotation on the S_1 surface at these high

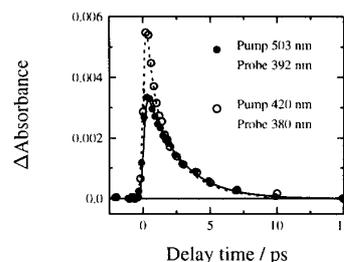


Fig. 6 Scaled TRVIS kinetics of trans-azobenzene.

excess energies, but is not interpretable from the current set of data. We plan further work to address this question.

CONCLUSION

Ultrafast TRVIS studies have established that the lifetime of the $S_1(n\pi^*)$ state of trans-azobenzene is 2.5 ps. An additional decay component has been observed when pumping trans-azobenzene to high excess energies above the S_1 origin; the interpretation of this effect requires further experiments. A paper on this work shortly will be submitted for publication.⁸

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