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Research paper

Conformer-specific geminate recombination following methyl nitrite photolysis in solution

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ABSTRACT

The dynamics of the ultraviolet (UV) photoexcitation of methyl nitrite in weakly interacting perfluoromethylcyclohexane solution are investigated using transient absorption spectroscopy. UV excitation in the structured $S_1 \leftarrow S_0$ absorption band induces dissociation, with geminate recombination and vibrational cooling of syn and anti-conformers of methyl nitrite on a timescale of ~ 56 ps. Solvent-induced vibrational cooling favours relaxation to the higher-energy anti-conformer on entropic grounds, and subsequent inter-conversion to the lower-energy syn-conformer is prevented by a 3500 cm^{-1} barrier. UV excitation to the S_2 state produces a transient electronic absorption band resembling the absorption spectrum of NO_2 .

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1. Introduction

Ultrafast transient absorption spectroscopy of the intermediates and products formed by the ultraviolet (UV) photolysis of molecules in solution can provide rich information about how a solvent affects the photochemistry [1,2]. The photodissociation dynamics of isolated, gas-phase molecules offer a starting point for interpretation of many solution-phase measurements, but comparative liquid-phase studies also allow investigation of further dynamical behaviour such as solvent-cage induced geminate recombination that occurs after the bond dissociation is complete. The UV photolysis of methyl nitrite (MeONO) provides one such opportunity to explore solvent effects because there is an extensive body of prior experimental and theoretical work on its gas-phase photolysis, albeit with some controversy about the precise dissociation mechanism(s) [3–13]. Here, we present observations of the ultrafast dissociation and geminate recombination dynamics of MeONO dissolved in a liquid perfluorocarbon (PFC). A PFC was chosen for the solvent because it is weakly interacting and unreactive with any photochemical intermediates, and our recent studies have shown that detailed dynamical measurements are consequently possible [1,14].

The long-wavelength end of the UV absorption spectrum of gaseous methyl nitrite is presented in Fig. 1, and shows a structured $S_1 \leftarrow S_0$ transition extending to wavelengths as long as 400 nm.

The UV-excited methyl nitrite dissociates into a methoxy radical and nitric oxide with a quantum yield of approximately unity [15].



The lifetime of the S_1 state was determined to be 125 ± 50 fs by time resolved Laser Induced Fluorescence [4].

Syn and anti-conformers account for 60% and 40% of ground state MeONO molecules respectively at room temperature [17]. The anti-conformer lies 290 cm^{-1} higher in energy than the syn form [17], and interconversion is hindered by a $\sim 3500\text{ cm}^{-1}$ energy barrier [18]. The contributions of these two conformers to the structure in the $S_1 \leftarrow S_0$ UV band has been the subject of prior controversy. Tarte [19] proposed that each peak in the spectrum had contributions from both conformers; this assignment was subsequently supported by Huber and co-workers [3] and Reisler and co-workers [11], and formed the basis of a vibrational predissociation mechanism advocated by Schinke [20]. Pfab and co-workers [16] instead argued that the longest wavelength absorptions ($\lambda > 365\text{ nm}$) are uniquely attributable to the anti-conformer, as shown by the combs in Fig. 1. They supported their interpretation with temperature-dependent measurements, and matrix-isolation studies by Dick and co-workers [21] provided further evidence favouring the revised assignment. Shorter wavelength excitation of methyl nitrite to the S_2 state results in direct dissociation to a methoxy radical and nitric oxide along a purely dissociative potential [5,22].

Our investigation of the UV photolysis of MeONO dissolved in a liquid PFC, using ultrafast transient vibrational absorption spectroscopy (TVAS) and transient electronic absorption spectroscopy (TEAS), reveals prompt (sub-picosecond) photo-induced dynamics.

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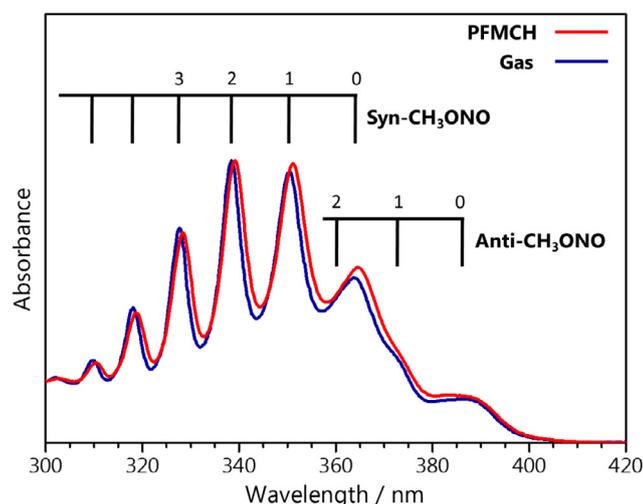


Fig. 1. UV absorption spectrum of gaseous methyl nitrite (blue) showing the $S_1 \leftarrow S_0$ band. The combs indicate the assignment of Pfab and coworkers [16] of vibronic features to progressions in the terminal NO stretch in the S_1 state for the syn (top) conformer and the anti (bottom) conformer (first three bands only). The corresponding spectrum of MeONO dissolved in perfluoromethylcyclohexane (PFMCH) is overlaid (red).

The syn and anti-conformers can be distinguished by TVAS, and wavelength dependent photolysis measurements support the assignment of the $S_1 \leftarrow S_0$ band structure by Pfab and coworkers. However, solvent caging of the photofragments hinders separation of the photofragments and we observe a remarkable propensity for conformer-specific geminate recombination and vibrational cooling dynamics.

2. Experimental

TEAS and TVAS measurements were undertaken using an ultrafast laser system and spectrometers which have been described in detail previously [23]. Methyl nitrite was synthesised using an established procedure [24]: nitrosylsulfuric acid was prepared by dissolving 10 g of sodium nitrite in 50 cm³ of concentrated sulfuric acid, and the nitrosylsulfuric acid was then slowly added to an ice-cooled mixture of 25 cm³ methanol and 25 cm³ water. The gaseous product was passed through an ice trap and the methyl nitrite was collected in a glass finger cooled by a dry ice – acetone trap. Methyl nitrite solutions were prepared by bubbling the vapour through perfluoromethylcyclohexane (PFMCH) which had been degassed by a freeze-pump-thaw method using liquid nitrogen as a coolant. Steady state UV–vis spectra of the solutions and gaseous MeONO were obtained using a Thermo Scientific GENYSIS spectrophotometer.

In time-resolved photochemistry studies, a peristaltic pump continuously circulated the methyl nitrate / PFMCH solutions through a stainless steel cell fitted with CaF₂ windows separated by 380- μ m PTFE spacers. UV excitation wavelengths were selected in the range from 248 to 385 nm; these photolysis pulses were of approximately 120 fs duration, with energies of 1 μ J/pulse, measured bandwidths of 9.0 and 5.5 nm at central wavelengths of 385 and 329 nm, and a repetition rate of 500 Hz. A spatially overlapped broadband UV–vis pulse (spanning wavelengths from \sim 350 to $>$ 800 nm) or IR pulse probed the photochemistry at a repetition rate of 1 kHz. UV–vis probe pulses were dispersed onto a 750-pixel array detector with 0.6 nm resolution, and IR pulses onto a 128-element MCT detector with 9.5 nm resolution. Time-resolved spectra were accumulated for time delays up to 1100 ps between the photolysis and probe pulses. The transient spectra were decom-

posed into constituent absorption features and time-dependent band intensities were extracted using the KOALA software package [25].

3. Results and discussion

The UV spectrum of methyl nitrite in perfluoromethylcyclohexane is compared with that for a gaseous sample in Fig. 1 and exhibits the same vibronic structure. There is a small increase in the widths of the spectral bands in solution, and a shift of these features by 0.6 nm to longer wavelength, but the spectrum indicates only modest perturbations to the electronic states of the MeONO by the PFC solvent.

TVAS of a methyl nitrite solution excited by a UV pulse at $\lambda = 385$ nm (the longest wavelength structured feature in the $S_1 \leftarrow S_0$ spectrum) is exemplified in Fig. 2 and shows a bleach feature centred at 1670 cm⁻¹ indicating depletion of ground state population by UV photolysis. The band is assigned to the terminal NO stretch of the anti-conformer of methyl nitrite [17]. However, no such bleach is seen at 1615 cm⁻¹ (beyond our baseline noise levels, which are 10% of the amplitude of the 1670 cm⁻¹ bleach feature) for the corresponding vibrational band of the syn-conformer. The absence of a syn-conformer bleach following excitation at 385 nm is consistent with the spectral assignment of the UV band system by Pfab and co-workers [16], as is shown by the combs in Fig. 1.

Moving to UV excitation wavelengths shorter than 365 nm introduces a bleach corresponding to the NO stretch of the syn-conformer, as expected on the basis of the band assignments in Fig. 1. The depth of the syn-conformer bleach increases relative to that for the anti-conformer with decreasing excitation wavelength. At all UV wavelengths investigated across the $S_1 \leftarrow S_0$ excitation (329–385 nm), significant bleach recovery is observed for the anti-conformer with increasing time delay between the photolysis and probe laser pulses. This bleach recovery is indicative of relaxation of a photoexcited state, or geminate recombination of photofragments held together by a solvent cage. Fig. 3 presents TVA spectra obtained following UV excitation at wavelengths of 248, 351 and 364 nm. Transient spectra obtained at other excitation wavelengths, and in tetrahydrofuran solution, can be found in the Supporting Information. At 364 nm, 90% recovery of the anti-conformer bleach feature occurs, and at 351 nm, which also corresponds to S_1 band absorption, 100% anti-conformer bleach recovery is followed by a further growth of the anti-conformer absorption of 20% of the maximum bleach intensity. In stark contrast, the recovery of the bleach feature associated with the syn-conformer feature is less than 25% at both these excitation wavelengths. These observations point to conformer-specific geminate recombination and vibrational cooling pathways.

The IR transition dipole moments differ for the terminal NO stretching modes of the syn and anti-conformers: the peak of the steady-state FTIR absorption band is 16% larger for the syn-conformer in PFMCH solution, but this conformer accounts for 60% of methyl nitrite at room temperature. NMR studies have shown that the equilibrium between syn and anti methyl nitrite is unchanged by solvents [26]. Scaling the IR absorption bands by the relative thermal populations of the conformers therefore implies a 27% larger absorption cross-section for the anti-conformer. Using this information in the analysis of the TVA spectra in Fig. 3 indicates that approximately 70% of the reformed ground state methyl nitrite adopts the anti-conformer structure, and only 30% returns to the syn-conformer after UV excitation across the S_1 band.

The preference for recombination to the anti-conformer, regardless of the UV excitation wavelength across the S_1 band

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