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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 nitrate 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.

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 Figure 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].

$$CH_3ONO(X^1A') \xrightarrow{UV} CH_3O^\bullet(X^2E) + NO^\bullet(X^2\Pi)$$
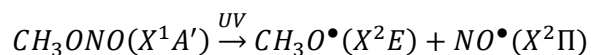
The lifetime of the S_1 state was determined to be 125 ± 50 fs by time resolved Laser Induced Fluorescence [4].
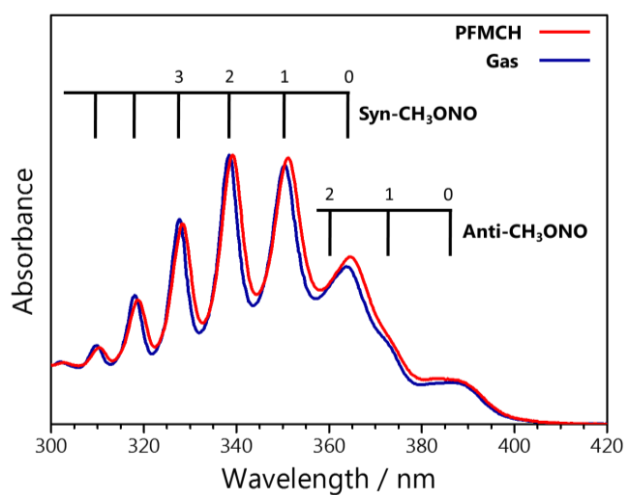

Figure 1: UV absorption spectrum of gaseous methyl nitrite (blue) showing the $S_1 \leftarrow S_0$ band. The combs indicate the assignment of Pfab and coworkers [16] of vibronic features to progressions in the terminal NO stretch in the S_1 state for syn (top) conformer and the anti (bottom) conformer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

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 ~3500 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 ($\lambda > 365$ 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

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[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. 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.

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 cm^3 of concentrated sulfuric acid, and the nitrosylsulfuric acid was then slowly added to an ice-cooled mixture of 25 cm^3 methanol and 25 cm^3 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 CaF_2 windows separated by 380-μm PTFE spacers. UV excitation wavelengths were selected in the range from 248 – 385 nm; these photolysis pulses were of approximately 120 fs duration, with energies of 1 μJ / 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 ~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 decomposed into constituent absorption features and time-dependent band intensities were extracted using the KOALA software package [25].

Results and Discussion

The UV spectrum of methyl nitrite in perfluoromethylcyclohexane is compared with that for a gaseous sample in Figure 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 λ = 385 nm (the longest wavelength structured feature in the $S_1 \leftarrow S_0$ spectrum) 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 Figure 1.
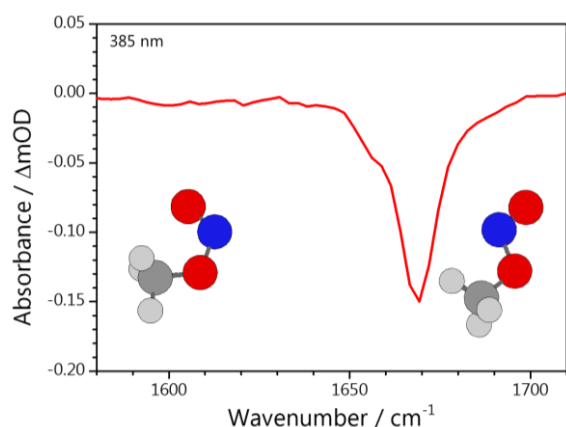

Figure 2: Transient vibrational absorption spectrum of methyl nitrite in PFMCH obtained at a time delay of 1.75 ps after 385 nm UV excitation. The bleach feature centred at 1670 cm^{-1} is assigned to the terminal NO stretch of the anti-conformer of methyl nitrite for which the structure is shown. A bleach corresponding to same vibrational mode of the syn-conformer, the structure of which is shown on the left, would be expected at 1615 cm^{-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 Figure 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. Figure 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 Figure 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 (329, 340, 351, 364, 385 nm), is unlikely to be determined by the geminate recombination step because the nascent, recombined MeONO has an internal energy greatly in excess of the barrier to conformer exchange. Instead, it may be explained by the higher entropy of the anti-conformer [27]. In the gas phase, the enthalpy and entropy changes for conversion from the syn to the anti-conformer are $\Delta H = 3.5 \, kJ \, mol^{-1}$ and $\Delta S = 8.5 \, J \, K^{-1} \, mol^{-1}$ [17]; hence, the anti-conformer becomes favoured at temperatures above 410 K. The energy released by UV photoexcitation and geminate recombination will heat the local solvent environment as it dissipates from a reformed MeONO molecule, providing an entropic driving force towards the anti-conformer to overcome the enthalpic preference for the syn-

conformer. Previous UV irradiation experiments on methyl nitrite in an argon matrix, but without ultrafast time resolution, showed a similar result: the anti-conformer abundance remained almost constant [12], which was attributed to UV-assisted conversion of syn to anti-methyl nitrite. Our measurements show that the conformational selectivity in the re-formation of ground state molecules is determined by the dynamics of the recombination process and vibrational cooling which sample widely from the available microstates of the system.

The degree of recovery of ground state anti-methyl nitrite after excitation is consistent across the S_1 state, and occurs with a time constant of 56.0 ± 8.5 ps which could correspond to either $S_1 \rightarrow S_0$ internal conversion, or dissociation and geminate recombination, followed by loss of the excess energy to the solvent bath and vibrational cooling. A similar time constant is obtained for the recovery of the syn feature(see Supporting Information). The large quantum yield for CH_3O + NO from gas-phase photolysis of methyl nitrate [15] suggests that the dissociation and recombination pathway will dominate in the PFC solution, but our TVAS measurements were unable to detect an unambiguous transient absorption by nitric oxide. However, the integrated absorption cross-section of gas phase nitric oxide is significantly smaller than for the corresponding terminal N-O stretching mode in methyl nitrite [28].
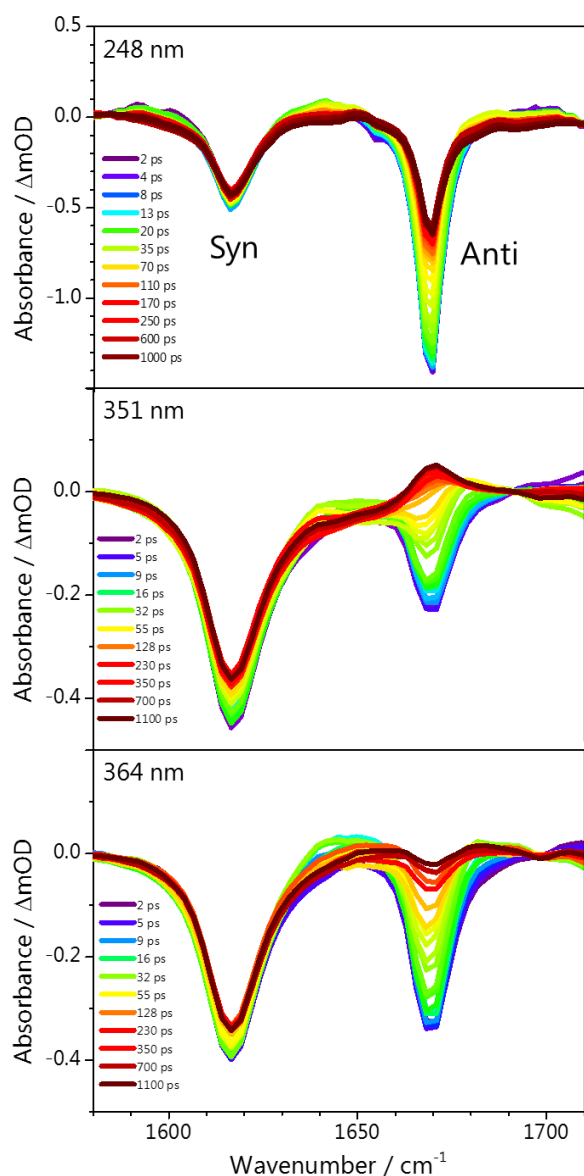
Figure 3: Transient vibrational absorption spectra of solutions of methyl nitrite in PFMCH excited by three different wavelengths of UV light. The spectra were obtained in the 1580 – 1710 cm^{-1} range spanning the absorption bands of the terminal NO stretching modes of syn and anti MeONO. Spectra are shown for time delays from 2 – 1100 ps (see inset colour keys) after UV excitation at 248 nm (top), 351 nm (middle) and 364 nm (bottom).

The 3500 cm^{-1} barrier for conformational interchange on the electronic ground state [18] is much smaller than the UV photon energy (>27500 cm^{-1}) and the MeO-NO bond dissociation energy of 14620 ± 350 cm^{-1} [29]. Geminate recombination will initially deposit an excess energy in the MeONO molecule corresponding to this bond energy, and dissipation to the solvent bath over a timescale of >50 ps allows time for the cooling molecules to explore a wide conformational space before trapping into the syn or anti conformer structures. The conformational preference we

observe is therefore likely to be established in the early stages of this vibrational cooling when there is sufficient thermal energy to favour the anti-conformer on entropic grounds.

The top panel of figure 3 shows the TVA spectra obtained after absorption of 248 nm light. This shorter wavelength excitation corresponds to absorption to the S_2 electronic state of methyl nitrite. The bleach in the terminal NO stretching band of anti-methyl nitrite partially recovers, with a time constant of 59.7 ± 5.2 ps which matches the ground-state recovery timescale measured after excitation in the $S_1 \leftarrow S_0$ band. The similarity of the time constants suggests the same mechanisms of bleach recovery, but incomplete repopulation of the ground state also indicates that a significant fraction of the excited state molecules break apart and avoid geminate recombination. The purely dissociative nature of the S_2 potential energy surface along the MeO-NO coordinate promotes rapid dissociation and high fragment recoil speeds, allowing more of the photofragments to escape their solvent cage and diffuse apart. These arguments support geminate recombination, as opposed to internal conversion of the photo-excited parent molecule, as the main mechanism for methyl nitrite recovery.
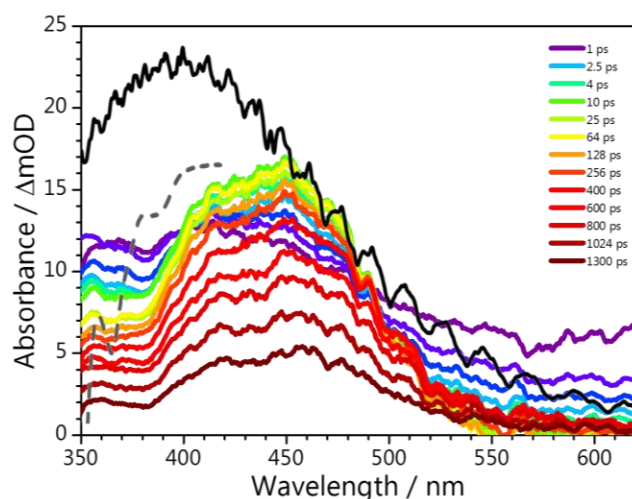

Figure 4: Transient electronic absorption spectra of a solution of methyl nitrite in PFMCH after UV excitation at 248 nm. Spectra are shown with increasing time delay from 1 ps (purple) to 1300 ps (dark red). The black line shows the steady state gas-phase absorption spectrum of NO_2 [30] and the grey dashed line is the inverted spectrum of methyl nitrite.

TEA spectra of methyl nitrite solutions showed no observable excited state or photoproduct signals after UV excitation to the S_1 band, suggesting that the excited state lifetime is too short to give measureable excited state absorption or stimulated emission features. However, excitation to the S_2 state at 248 nm produced the time dependent absorption features shown in figure 4. The electronic absorption spans most of the 350 – 600 nm wavelength range of the probe light at early time delays, but narrows with increasing time delay to leave a distinct band peaking at 450 nm.

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The signal at wavelengths above 560 nm decays with a 2.2 ± 0.6 ps time constant which matches the 2.3 ± 0.4 ps time constant for growth of 450-nm feature. This band then decays on a timescale greater than 1 ns. Kinetic traces are shown in the Supporting Information.

A number of candidates might account for the transient features in the electronic spectra, the rapid rise of which suggests a primary photoproduct. For example, a bound triplet state of methyl nitrite [22] could form through rapid geminate recombination, although this would require a spin change in the photofragment radical pair. An excited state of the methoxy radical could also explain the signal, and fluorescence measurements have previously shown a small quantum yield of $\tilde{A}$-state methoxy radicals when exciting methyl nitrite in the S_2 band [8, 31]. However, a more plausible assignment is to NO_2 because of the similarity of the observed spectrum at later times to the steady-state UV absorption spectrum of gaseous NO_2 (as shown in Figure 4). Whitaker and co-workers recently proposed a direct route from gaseous MeONO to Me + NO_2 photofragments when exciting to the S_1 state [32], but our liquid-phase measurements only observe a signal attributable to NO_2 after excitation of MeONO to the S_2 state. The transient absorption features evident to longer wavelengths in Figure 4 at early times might then correspond to nascent, vibrationally hot NO_2 photofragments. The loss of signal intensity below 400 nm, where NO_2 continues to absorb, can be explained by an overlapping bleach of the electronic absorption band of methyl nitrite.

Conclusions

Ultrafast transient vibrational absorption spectroscopy of solutions of MeONO in perfluoromethylcyclohexane shows a strong propensity for recovery of ground state MeONO molecules in their anti-conformation, despite this conformer lying higher in energy than the syn-conformer. The known gas-phase photochemistry of MeONO suggests that the most likely mechanism for recovery of ground state molecules is dissociation to MeO + NO on the S_1 state and geminate recombination of the radical pairs, followed by cooling of $\sim$14600 cm^{-1} (corresponding to the bond dissociation energy of MeO-NO) of internal energy to the surrounding solvent. This relaxation takes $\sim$56 ps. For most of this time, the internal energy of the excited MeONO molecules exceeds the 3500 cm^{-1} barrier to conformational interchange, but entropic factors favour relaxation to the anti-conformer. The TVA spectra support the assignment of Pfab and coworkers of the bands seen in the structured $S_1 \leftarrow S_0$ electronic absorption spectrum of gaseous methyl nitrite. Shorter wavelength excitation of methyl nitrite in solution accesses the S_2 state, and TEA spectra indicate a photolysis channel leading to NO_2.

Acknowledgements

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