Time-Resolved Infrared Pump-Probe Spectroscopy of ClNO in Acetonitrile

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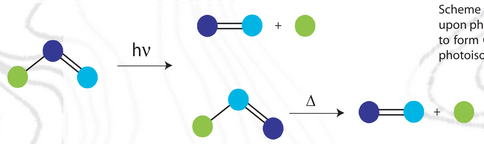
Introduction

Understanding the fundamental aspects of phase-dependent photochemical reactivity is a central challenge in environmental chemistry. For example, the environment-dependent reactivity of haloxides, such as chlorine dioxide (OClO), has attracted a significant amount of attention due to the contribution of these compounds to the stratospheric chlorine budget.[1] Photoexcitation of gaseous OClO results primarily in the formation of OCl and O.[2] In contrast, ClOO production is observed in low temperature matrixes.[3] Finally, in solution OCl/O, Cl/O_2 and photoisomer production are all observed.[4] Similar complexity is observed in nitrosyl-halide chemistry, and our lab has recently investigated the photochemistry of nitrosyl chloride (ClNO)(Scheme 1).



Scheme 1: The reaction pathways available to ClNO upon photoexcitation. In the gas phase dissociation to form Cl and NO dominates, whereas in matrixes photoisomerization to form ClON is observed.

The photochemistry of solution phase ClNO was recently investigated using femtosecond pump-probe spectroscopy.[5] In these studies photoinduced depletion of ClNO and recovery via geminate recombination was observed. In addition, photoproduct formation in all solvents (acetonitrile, chloroform, and dichloromethane) was found, but definitive assignment of the photoproducts was not achieved. To address this issue, we have initiated a series of FTIR and ultrafast TRIR studies of ClNO photochemistry in solution.

Experimental Setup

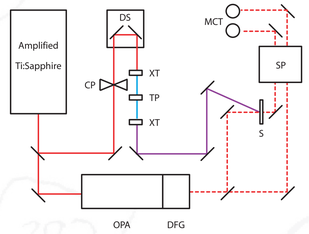


Figure 2: A schematic of the UV-pump, IR-probe spectrometer used in this study. The following abbreviations have been used: CP: mechanical chopper, DS: delay stage, XT: BBO crystal, TP: time plate, OPA: optical parametric amplifier, DFG: difference frequency generator, S: sample, SP: spectrograph, MCT: a pair of LN_2 mercury/ cadmium/ telluride detectors.

Results and Discussion

Static FTIR Absorption

The solvent-dependence of the N-O stretch fundamental transition frequency was studied. The transition demonstrates a positive solvatochromic shift that is linear with solvent polarity ($E_T(30)$ scale). A corresponding decrease in the N-Cl stretch fundamental frequency is also observed in the resonance Raman spectrum.[6]

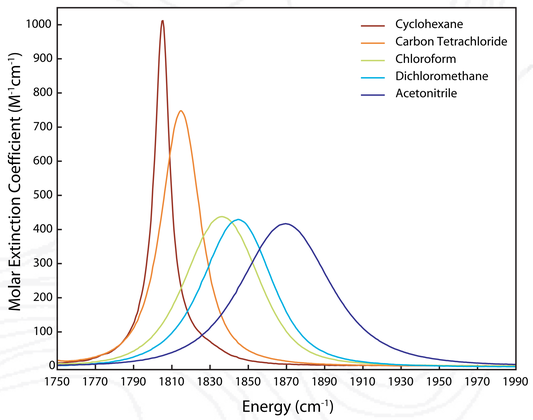
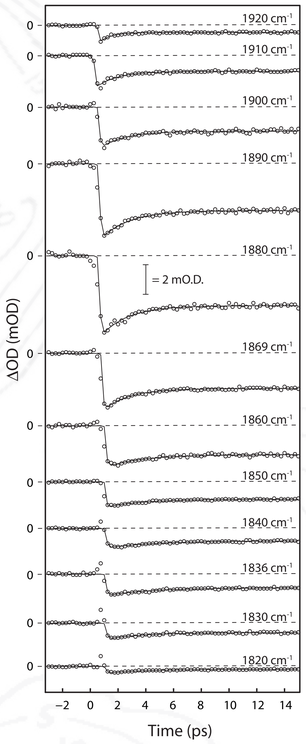


Figure 1: IR absorption spectra of ClNO in the region of the NO stretch fundamental transition in various solvents. As the solvent polarity is increased, the frequency of the transition increases consistent with an increase in the NO bond strength and corresponding decrease in strength of the NCl bond.

Time-Resolved IR Absorption Study



Following 266-nm excitation, a reduction and subsequent recovery in optical density is observed at all probe wavelengths. Additionally, at probe wavelengths between 1820 cm^{-1} and 1840 cm^{-1} an initial increase in optical density is evident, peaking at 0.75 ps. The depletion is consistent with loss of ground-state ClNO due to photolysis and the recovery indicates partial geminate recombination of the photoproducts. The maximum reduction in optical density is at 1880 cm^{-1}, and most of the evolution is completed within ~5 ps. There is no evolution in the band shape as observed despite the fact that it is asymmetric and shifted relative to the absorption band. This may indicate little to no excess vibrational energy is being deposited into the NO stretch of geminately recombined ClNO.

Figure 3: Optical density evolution of ClNO dissolved in acetonitrile following photoexcitation at 266 nm. Measured at probe frequencies ranging from1820 cm^{-1} to 1920 cm^{-1}.

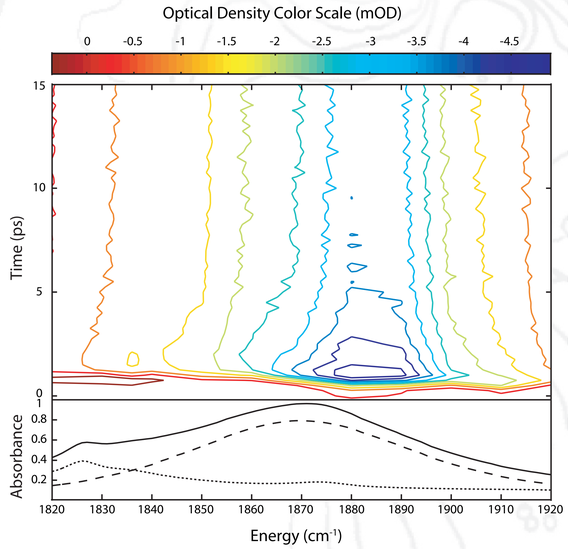


Figure 4: Contour plot of TRIR optical-density evolution observed in the region of the NO-stretch fundamental transition of ClNO dissolved in acetonitrile following 266-nm photolysis. The color scale representing the change in optical density is provided at the top of the figure. The bottom panel presents FTIR spectra of the sample (solid), acetonitrile only (short dashed), and the NO-stretch (long dash).

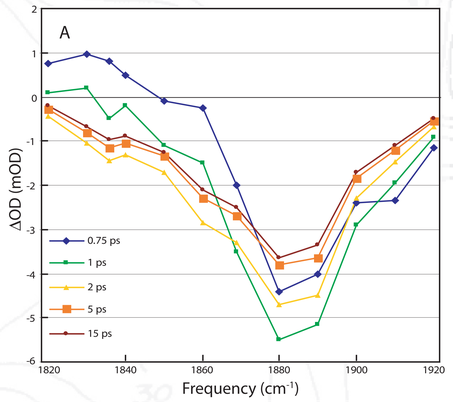
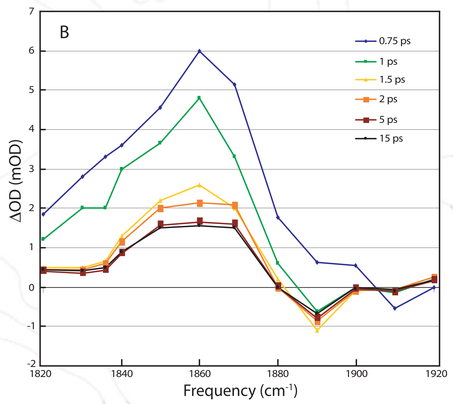


Figure 5: A) The absolute change in optical density measured at specific delay times following photoexcitation of ClNO at 266 nm. B) Optical-density increase corresponding to photoproduct formation following ClNO photolysis. The increase in optical density is centered at 1860 cm^{-1}, roughly 10 cm^{-1} lower in frequency than the NO-stretch fundamental in ClNO. This feature decays on the 5-ps timescale to a value of 2 mOD that remains constant out to the longest delay times investigated (50 ps).



The maximum reduction in optical density does not correspond to the peak of the N-O stretch fundamental. Therefore, an optical density increase must exist on the low frequency side of the N-O stretch. To investigate this possibility, ClNO depletion was removed by adding back the ground-state absorption spectrum until the reduction in OD for probe frequencies > 1900 cm^{-1} was removed (Figure 5 B). The peak of the absorptive feature occurs at 1860 cm^{-1} and may correspond to the photoisomer (ClON), free NO, or vibrationally excited ClNO produced by geminate recombination.

ClːACN Charge-Transfer Complex

The weak absorption feature appearing below 1836 cm^{-1} in Figure 5 B suggests possible modification of the solvent modes upon formation of the chlorine-acetonitrile (Cl:ACN) charge-transfer complex. To further investigate this possibility we have probed the C-N stretch of acetonitrile (Figure 6).

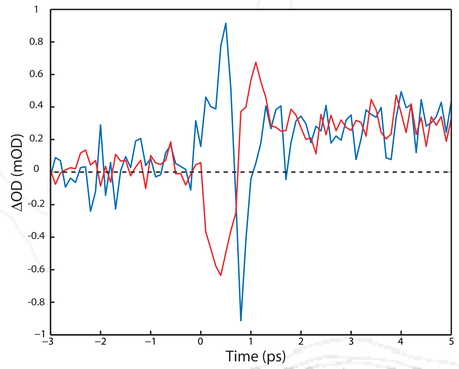


Figure 6: TRIR optical density evolution following ClNO photolysis in acetonitrile. The probe frequencies employed are on the high-energy (blue, 2260 cm^{-1}) and low-energy (red, 2240 cm^{-1}) side of the CN-stretch fundamental transition (2250 cm-1).

Conclusions

We have observed the unexpected environment-dependence of the NO stretch of ClNO. The linewidth is significantly increased and the frequency dramatically blue-shifted wih increasing solvent polarity. We have observed the photo-induced depletion and subsequent geminate recombination following photoexcitation of ClNO. Formation of a photoproduct is seen, which we have assigned as the first observation of the photoisomer, ClON, in solution phases.

References:

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Acknowledgements:

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