Time Resolved Infrared Absorption Study of the Solvent Dependent Vibrational Relaxation of Chlorine Dioxide

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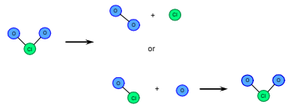
Abstract

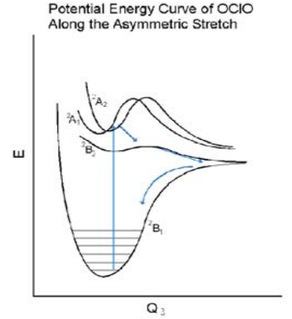
Halooxide photochemistry is of interest due to the importance of these compounds in atmospheric chemistry. Chlorine dioxide (OClO) has received attention since it is a reservoir for atomic chlorine in the stratosphere.[1] Photoexcitation of OClO promotes the following reactions:



Time-resolved resonance Raman (TRRR) and transient absorption studies have provided insight into the formation and and subsequent relaxation of ground-state OClO produced by recombination of the primary ClO and O photofragments. TRRR studies have shown that although recombination is rapid (< 300fs), the excess vibrational energy available to OClO upon recombination does not appear along the symmetric-stretch coordinate until ~5 ps after recombination. This observation suggests that the excess energy must be initially deposited along another coordinate. Transient absorption studies have been interpreted in terms of initial energy deposition along the asymmetric-stretch coordinate.[2-4] However, direct evidence confirming that the asymmetric-stretch coordinate participates in geminate recombination and vibrational relaxation has yet to be reported.

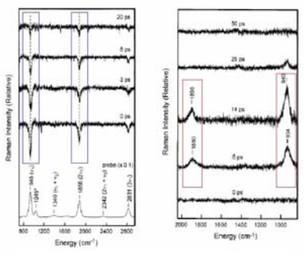
We have performed UV pump/IR probe studies to monitor the vibrational population dynamics along the asymmetric-stretch coordinate of OClO following recombination.[2] The dynamics of OClO dissolved in three solvents (H_2O, D_2O, and acetonitrile) were investigated. Following 401-nm photoexcitation, probe wavelengths ranging from 1094 cm^{-1} to 1014 cm^{-1} in H_2O and D_2O and from 1094 cm^{-1} to 960 cm^{-1} in acetonitrile were used to monitor vibrational energy deposition and relaxation along the asymmetric-stretch coordinate. The vibrational-relaxation dynamics were modeled using the Isolated Binary Collision (IBC) model and the perturbative expansion model as described by Benjamin and coworkers in their molecular dynamics (MD) studies.[5,6,8] For OClO in H_2O and D_2O, the IBC model is not capable of reproducing the observed evolution in optical density. Instead, the perturbative approach provides a more accurate reproduction of the relaxation dynamics. In contrast, the dynamics in acetonitrile are not well represented by either model. This behavior is attributed to mode-specific relaxation involving the methyl-rock of acetonitrile. The results presented here provide a detailed description of the role of the asymmetric-stretch coordinate in the geminate recombination and vibrational-relaxation dynamics of OClO.

Potential Energy Curve of OClO Along the Asymmetric Stretch



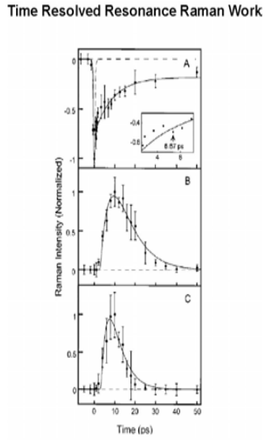
Excitation of ground-state OClO results in population of the $^2A_2$ which undergoes internal conversion to the $^2A_1$ and $^2B_2$ and from the $^2B_2$ it is believed that the photofragments recombine to form vibrationally hot OClO. PE surfaces are adapted from Peterson and coworkers.[7]

Time Resolved Resonance Raman Work



Time resolved Stokes (left) and anti-Stokes (right) Spectra of aqueous OClO. The negative intensity in Stokes data corresponds to depletion of ground-State OClO, while the appearance of anti-Stokes Intensity is indicative of symmetric-stretch vibrational excitation and relaxation.

Time Resolved Resonance Raman Work

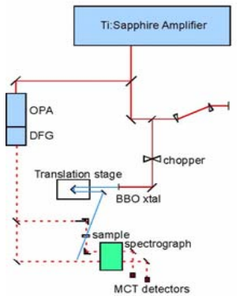


(A) Intensity of the OClO symmetric-stretch fundamental Stokes transition as a function of time. Recovery of ground-state OClO is biphasic with a fast (300-fs) time constant corresponding to geminate recombination and a slower (9-ps) component corresponding to vibrational relaxation.

(B/C) Intensity of the OClO symmetric-stretch fundamental (B) and overtone (C) anti-Stokes transitions as a function of time. Intensity appears with a time constant of 5 ps and decays with a time constant of 9 ps.

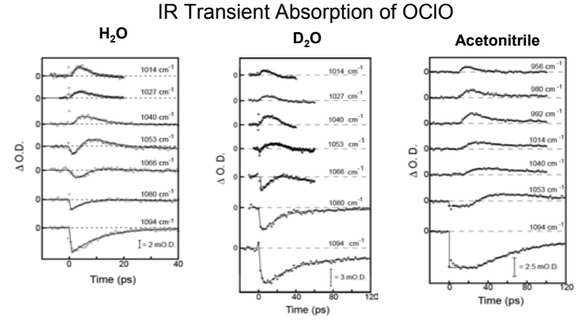
These data demonstrate that the recovery of ground-state OClO via geminate recombination occurs in 300 fs, but vibrational excitation along the symmetric stretch does not occur until 5 ps. Therefore, following geminate recombination, the initial vibrational energy must be deposited along another coordinate, presumably the asymmetric stretch.

UV Pump IR Probe Apparatus

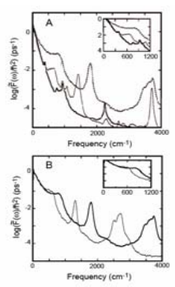


An amplified Ti:sapphire laser produces 802-nm pulses with a temporal width of 40 fs. One half of the amplifier output is frequency doubled to produce the pump field at 401 nm. The other half of the output is used to pump an optical-parametric amplifier to provide 1479 nm and 1761 nm signal and idler fields. Difference frequency generation of the signal and idler is performed to provide the 9.2 micron probe beam. Using a spectrograph, 30 cm^{-1} frequency components of the IR field are selected following interaction with the sample to monitor the pump-induced evolution in optical density. The instrument response as determined by the photoinduced change in transmittance through a thin silicon wafer is 120 ± 50 fs.

IR Transient Absorption of OClO



MD Results[8]

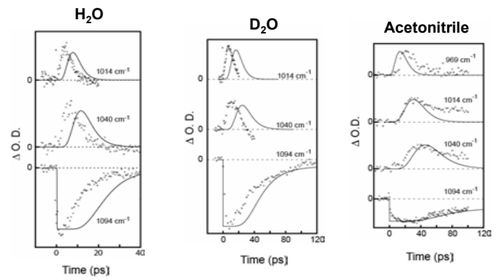


IBC Modeling of Vibrational Relaxation

One basic theoretical treatment of vibrational relaxation is the Isolated Binary Collision (IBC) model in which the level-dependent vibrational-relaxation rate constants are defined as follows:

$$k_{n\to n-1} = nk_{1\to 0}$$

In the above expression, n is the vibrational level quantum number, and $k_{0\to 1}$ is the relaxation rate from n = 1 to n = 0. Vibrational level populations were calculated using a standard master equation approach with the initial population of the n = 15 level after geminate recombination. Comparison of the predicted evolution to experiment demonstrates that the collisional model does not accurately reproduce the vibrational relaxation dynamics.



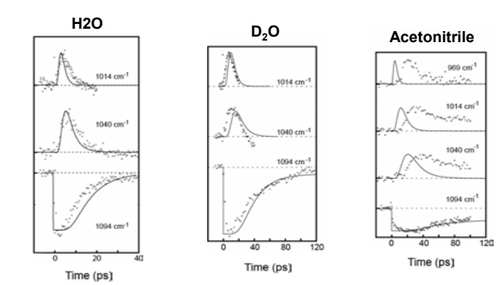
Perturbation Model

A second model employed to model the vibrational-relaxation dynamics was derived from the molecular-dynamics studies of Benjamin and co-workers. This model states that the linear dependence of the relaxation rate constants with level (n) is augmented by an additional term that represents the force of the solvent along the coordinate of interest:[5,6,8]

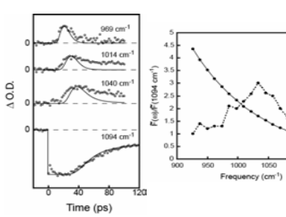
$$k'_{ij} = k_{ij}\tilde{F}_{q,q'}(\omega_{ij})\hbar^{-2}$$

$$\tilde{F}_{q,q'}(\omega_{ij}) = \int_{-\infty}^{\infty}\langle f_q f_{q'}\rangle e^{i\omega_{ij}t}dt$$

Values for $\tilde{F}_{q,q'}(\omega_{ij})$ were obtained from the classical MD simulations of Benjamin and coworkers. [8] Comparison of the predicted evolution to experiment demonstrates that the perturbation model does a better job of reproducing the vibrational relaxation dynamic in H_2O and D_2O, but not in acetonitrile. It should be noted that the agreement in quantitative, and that the absolute rate constants predicted by this model are roughly five-fold greater than the experimentally-determined values.



Modified Acetonitrile Model



A 10-ps delay was introduced after photoexcitation to reproduce the temporal lab before the observation of ground-state population in the data.

$\tilde{F}_{q,q'}(\omega_{ij})$ values were determined through manual fitting of the data. (shown right)

Reproduction of experiment requires substantial modification of the MD results, presumably due to mode-specific coupling to methyl rock of acetonitrile.

Conclusion

- Energy deposition following geminate recombination is along the asymmetric-stretch coordinate.
- Consistent with MD, vibrational relaxation in H_2O is more rapid compared D_2O, and the slowest relaxation is observed in acetonitrile.
- Neither the IBC nor the perturbation model well predicted the vibrational dynamics of OClO in acetonitrile. Modification of $\tilde{F}_{q,q'}(\omega_{ij})$ from MD is required to reproduce the experimental results.

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