

Interfacial Carbonyl Groups of Propylene Carbonate Facilitate the Reversible Binding of Nitrogen Dioxide

Jessica B. Clark and Heather C. Allen*

Department of Chemistry & Biochemistry, The Ohio State University, Columbus, Ohio 43210,
USA

Corresponding Author

* Heather C. Allen, allen@chemistry.ohio-state.edu

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Measurement of NO₂ Concentration

The concentration of NO₂ delivered to the liquid surface was determined using FTIR spectroscopy. To achieve this, the Teflon cell described in the main text was replaced by a 10 cm path length linear gas cell equipped with two ZnSe windows (Pike Technologies, part #: 162-2200). Using the gas purification system described in the main text, 50 mL/min N₂ and 5 mL/min zero air were flowed through the linear cell and to exhaust for 5 days before the experiment was started. After 5 days, the flow of 100 mL/min N₂ and 5 mL/min air through the cell was collected as background spectrum. Immediately following this, the NO₂ flow was set to 40 mL/min and spectra were acquired every 10 min. Spectra were collected using 128 scans and 4 cm⁻¹ resolution. The intensity of the NO₂ peaks was monitored over time as the gas flowed through the cell. A constant intensity was reached after 30 min and the intensity of the NO₂ peak at 1602 cm⁻¹ was used along with Beer's Law to calculate the concentration of NO₂. The average spectrum of NO₂ after 30 min flow through the linear cell during two trials is plotted in Figure S1. The absorbance (A) of the NO₂ peak occurring at 1602 cm⁻¹ was determined to be 5.91×10^{-4} . Using Beer's law ($A = \epsilon bc$), the known 10 cm path length (b), and the previously reported absorption cross section (ϵ , 4.71×10^{-19} cm²/molecule)¹ of NO₂ at 1602 cm⁻¹, the concentration was determined to be 5.1 ppm.

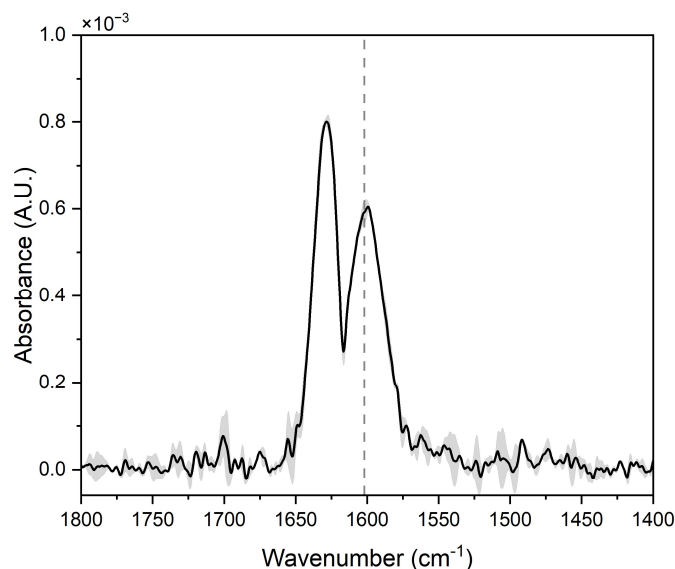


Figure S1. FTIR spectrum of NO_2 gas used to determine its concentration for surface studies. Dashed reference line included at 1602 cm^{-1} to indicate peak position of the absorbance used in the calculation. The spectrum is an average of two trials, with the standard deviation plotted as shading.

Spectral Pre-Processing

Following calculation of RA as described in the main text, a Savitzky-Golay filter was applied to all IRRAS spectra to improve the signal-to-noise ratio. The filter used 30 adjacent data points (15 cm^{-1}) to fit the noise to a second order polynomial function. The spectra were then all baseline corrected using OriginLab's built-in baseline correction functionality. Within the "peak analyzer" tab, the "subtract baseline" procedure was selected. To define the baseline, 7 anchor points were selected between 2300 and 800 cm^{-1} in regions of the spectrum where no vibrational modes occurred. The initial anchor points chosen for all IRRAS spectra were 806 , 990 , 1310 , 1450 , 1730 , 2060 , and 2238 cm^{-1} . Minute adjustments to these initial anchor points were made for each individual spectrum to ensure that the points represented the average of the noise in that particular region. The anchor points were then fit using a linear function to define the baseline, which was then subtracted.

Time-Resolved Spectra of PC Surface Before NO₂ Exposure

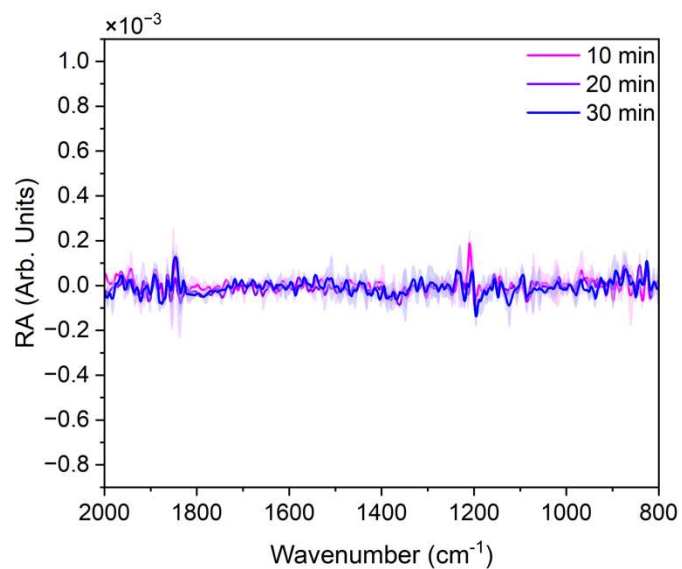


Figure S2. IRRAS spectra of 100 mL/min N₂ and 5 mL/min air flowing over the PC surface for 30 min. Spectra are an average of two trials, with the standard deviation plotted as shading. These results demonstrate that the flow of N₂ and air over the PC surface does not disrupt the vibrational modes of PC over time.

Propylene Carbonate Peak Assignments (IRRAS)

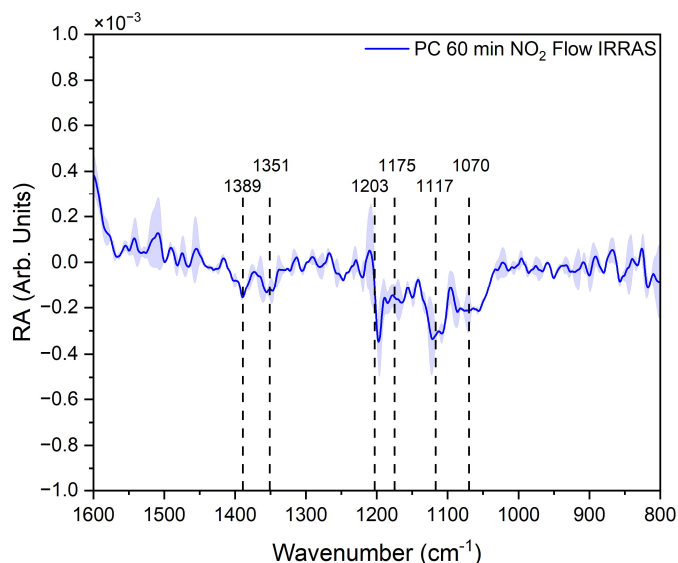


Figure S3. IRRAS spectra of the low frequency peaks observed when 5.1 ppm NO₂ was flowed over the PC surface for 60 min. Spectra are used to assign the observed peaks to the vibrational modes of PC. Dashed reference lines are included at the center of each band, and the position (in cm⁻¹) is labeled above the reference line.

Table S1. Summary of the low frequency peaks observed in the IRRAS spectrum of the PC surface during 60 min of NO₂ flow. Peaks are assigned by comparison to a previous study that combined *ab initio* calculations with experimental ATR-FTIR spectra of PC to make the vibrational assignments.

This Work (IRRAS, cm ⁻¹)	Literature (ATR-FTIR, cm ⁻¹) ²	Assignment ²
1389	1389	CH bend/rock
1351	1354	HCCH bend
1203	1225	CH ₂ rock
1175	1184	CH ₂ rock
1117	1120	In-plane ring + carbonate str. (O=COO)
1070	1077	In-plane asym. ring str.

Attenuated Total Reflection (ATR)-FTIR Spectroscopy Experiments

The spectrum of bulk PC without exposure to NO₂ was acquired using attenuated total reflectance (ATR)-FTIR. A Perkin Elmer diamond/KRS-5 universal ATR assembly was used with a Perkin Elmer Spectrum 100 FTIR spectrometer. The spectrum of the crystal following cleaning with ethanol was used as the background for all spectra. Propylene carbonate was transferred from the septum-sealed bottle using a syringe and 5 drops of the

liquid were deposited onto the ATR crystal. The spectrum of the PC sample was collected using 128 scans and 4 cm⁻¹ resolution. This process was repeated for a second trial and the average is plotted in Figure 5 of the main text.

Diethyl Sebacate (DES) Experiments

DES was selected for comparison as it contains similar functional groups to PC but is a linear molecule. Additionally, DES has been used as a model ester-containing molecule for previous studies of atmospheric heterogeneous reactions.^{3,4} Structural changes of the DES surface induced by NO₂ were observed in two of the four total trials. Despite the lack of reproducibility, the average of the first two trials are presented in Figure S4 to provide support to the PC experiments which were reproducible in all cases. The IRRAS spectrum of the DES surface during 40 min flow of NO₂ is presented in Figure S4 as spectrum A. The IRRAS spectrum of the PC surface during exposure to NO₂ is included in Figure S4 as spectrum B for comparison. When the DES is exposed to NO₂, the carbonyl stretch is the only mode that is affected as indicated by the appearance of the intense positive band at ~1740 cm⁻¹. This band also exhibits the same doublet peak structure as PC when exposed to NO₂. These results provide additional support for carbonyl specific interactions of NO₂ at organic ester interfaces. The two trials of DES exposed to NO₂ that did not exhibit perturbations to the carbonyl mode are presented in Figure S5.

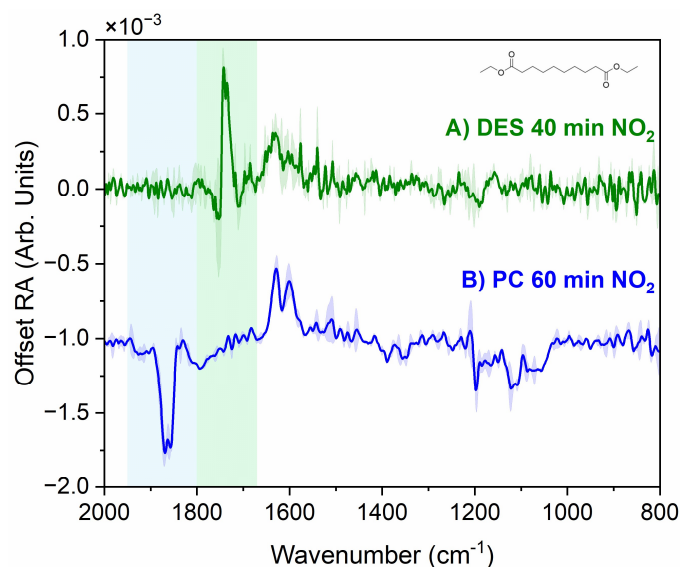


Figure S4. IRRAS spectrum of the DES surface during 40 min flow of 5.1 ppm NO₂ (green, A). IRRAS spectrum of the PC surface during 60 min flow of 5.1 ppm NO₂ is included for comparison (B, blue). Spectra plotted are an average of two trials and the standard deviation is plotted as shading. Spectra are offset for clarity and the carbonyl region of DES and PC are highlighted with green and blue shading, respectively.

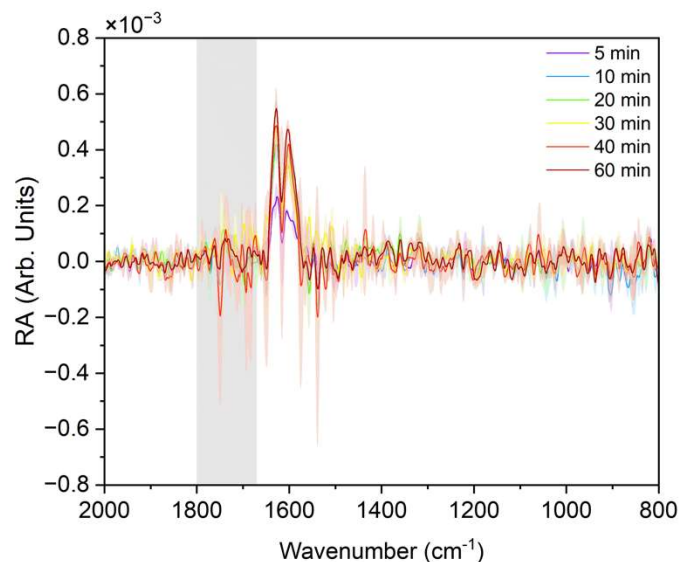


Figure S5. Time-resolved IRRAS spectra of NO₂ flowing over the surface of DES. The spectra presented are an average of two trials with the standard deviation plotted as shading. Only peaks belonging to NO₂ (1600 and 1630 cm⁻¹) are present in the spectra and no perturbation to the carbonyl is observed. This is in contrast to the carbonyl mode observed in the additional two replicated of DES and NO₂ presented in Figure S4 above.

Determination of Water Content in PC using Raman Spectroscopy

Raman spectroscopy was used to evaluate the water content in the pure PC sample as well as determine the amount of water removed from the PC surface when following 120 min of air flow over the surface of a 0.091 mole fraction water-in-PC solution. Spectra were acquired using a custom-built Raman spectrometer (described elsewhere⁵) with 532 nm excitation. Spectra are collected by averaging 150 exposures with a 0.1 s exposure time. For studies of pure PC, the liquid was transferred from the septum-sealed bottle directly into the quartz cuvette and sealed with a cap equipped with a silicone gasket. These steps were taken to limit water contamination within the sample. For studies of PC/water solutions, 20 mL of PC was transferred to an acid-cleaned vial and mixed with the appropriate mass of water to achieve a 0.091 mole fraction of water in PC. An aliquot of this sample was taken and placed in a quartz cuvette then used to acquire the Raman spectrum of the solution before gas flow experiments. After the spectrum was acquired, the aliquot was returned to the original vial and used for the IRRAS flow experiments. Following the 120 min flow of N₂ and air over the PC/water surface, an aliquot of the sample was taken again and the Raman spectrum after the flow experiments was acquired. The OH stretching region in the Raman spectra of pure PC, 0.091 mole fraction PC/water before flow experiments, and PC/water after flow experiments is plotted in Figure S6. The OH stretching region is convoluted with the CH stretching modes of PC as observed from 3100 – 3350 cm⁻¹ in the Raman spectra. When water is added to PC, a sharp band at ~3550 cm⁻¹ grows in along with a shoulder at ~3650 cm⁻¹. We have investigated the structure of water in PC that gives rise to these bands in a previous publication and find that these bands result from mostly unassociated water

molecules.⁵ Here, the absence of these peaks in the pure PC spectrum (Figure S6, black) indicate that the water content is below the limit of detection. When considering the PC/water spectra before (Figure S6, dark blue) and after (Figure S6, light blue) 120 min of air flow over the surface, there is a marked decrease in the OH stretching band intensity of $\sim 2/3$. While the intensity of Raman bands does not correlate linearly with concentration, we can conclude that water was removed from this system during the flow experiments. Moreover, these results support that the changes observed in the IRRAS spectra during N_2 and air flow over the PC/water solution is due to dehydration of the surface.

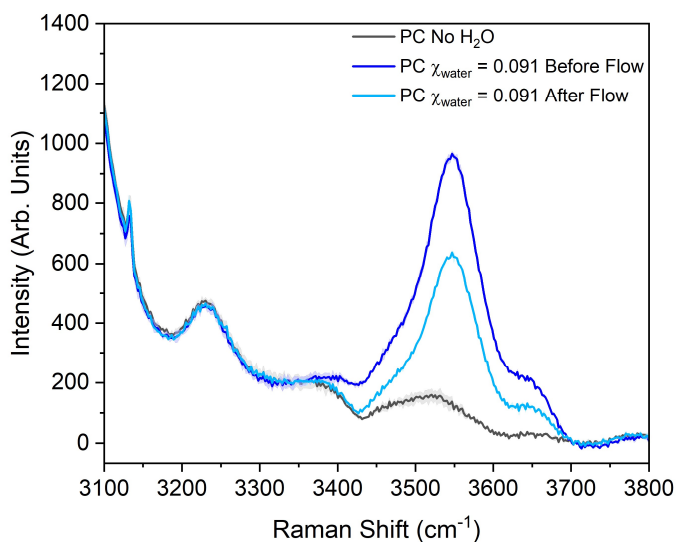


Figure S6. Raman spectra in the OH stretching region of pure PC (black), 0.091 mole fraction of water in PC before flow experiments (dark blue), and 0.091 mole fraction of water in PC after flow experiments (light blue).

IRRAS Spectra of NO₂ Flow Over PC/Water Solution

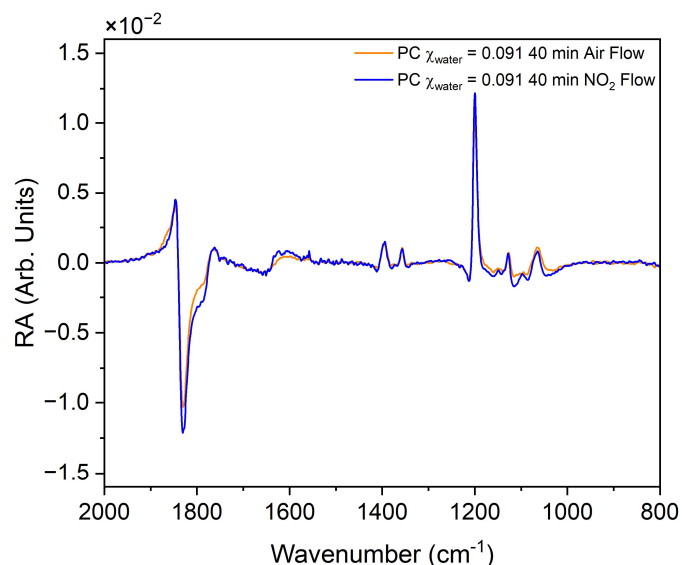


Figure S7. IRRAS spectra of the PC + H₂O surface after 40 min of dehydration (orange) and 40 min of NO₂ exposure (blue). The reference used to calculate RA for the dehydration spectrum is the initial reference spectrum taken at time 0. The reference used to calculate RA for the NO₂ exposure is the spectrum taken after 40 min flow of N₂ and air over the surface (sample spectrum used in orange trace). The IRRAS spectra can then be compared as they represent the same duration of gas flow over the surface. The changes caused by dehydration vs. those caused by the presence of NO₂ cannot be deconvoluted.

References

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