

SOLVENT MEDIATED PHOTOPHYSICAL OUTCOMES OF BROWN CARBON CHROMOPHORES

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Abstract:

Nitrogen-heterocyclic chromophores such as 2-phenylpyrrole (2PhPy) are prototypical, molecular chromophores found in brown carbon (BrC) aerosols in the Earth's atmosphere. BrC aerosols are increasingly recognized as important contributors to radiative forcing in the atmosphere due to their optical absorption properties in the UV and visible wavelength ranges. In this study, the photophysical and structural changes of 2PhPy from sequential addition of water solvent molecules were investigated. In doing so, we aim to reveal the solvent-mediated photophysical outcomes and develop a molecular-level understanding of the local-solvation interactions at the BrC aerosol interface. Single-conformation spectroscopy methods were carried out to reveal the extended hydrogen-bonding topology of the mass-selected clusters with isomer selectivity. Our results are compared with several theoretical methods for detailed analysis of the photophysical outcomes at the aerosol interface.

Introduction

An aerosol is formed when a very small quantity of liquid or solid particles is suspended in gas.¹ Since aerosols occupy a size regime that is between bulk liquid and individual gas phase molecules, they have distinctive properties not seen in either bulk liquid or in pure gases. In part due to these unique properties, aerosols are vital areas of research. It is particularly critical to study aerosols that are present in Earth's atmosphere, since these particles contribute substantially to Earth's climate, due to their absorption of solar radiation, as seen in **Figure 1**. Through indirect and direct effects, aerosols affect how much solar radiation Earth's atmosphere absorbs, and they can lead to atmospheric warming. When aerosol particles absorb light, energy is retained in the atmosphere causing an increase in temperature.² Clouds can also form from aerosol particles. Clouds, in turn, can absorb or scatter solar radiation, further impacting the atmosphere.³ Furthermore, aerosols can affect the reflectivity of clouds, which can impact the overall radiative forcing of the Earth's

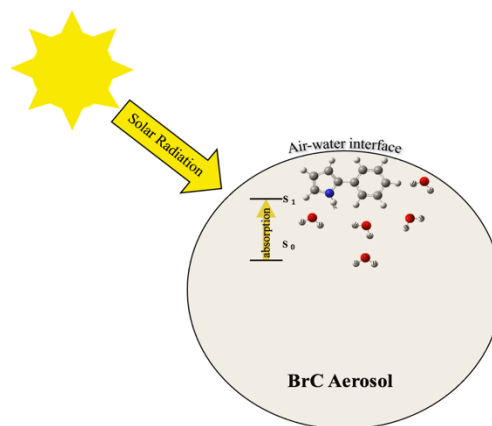


Figure 1: Schematic of absorption of chromophores in a prototypical Brown Carbon (BrC) aerosol.

atmosphere.⁴ Radiative forcing is defined as the difference between the incoming electromagnetic radiation from the sun and the infrared radiation that is emitted from the Earth's atmosphere; it is essentially a measure of how much solar radiation the atmosphere absorbs and emits.⁵ Notably, radiative forcing due to aerosols is not well determined, and

further studies are required to more accurately refine that uncertainty.⁴ The uncertainty in aerosol radiative forcing has wide-reaching implications for the creation of models that more accurately predict global climate, so performing further observational and experimental studies of aerosols is vital for building a realistic model to predict the future of our global climate.⁶

Previously, black carbon (often referred to as soot) was thought to be the only type of light absorbing carbonaceous aerosol, and therefore has been the main focus of research studies.⁷ Black carbon does strongly absorb solar radiation, and therefore has a significant effect on global climate. In reality, however, carbonaceous compounds exist on a spectrum based on their imaginary refractive index, which is proportional to how much solar radiation these compounds absorb.³

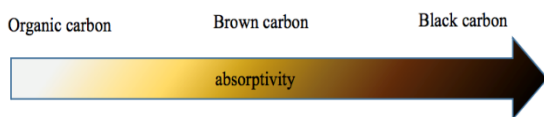


Figure 2: *Spectrum of carbonaceous compounds.*

Black carbon (BC), which absorbs strongly in the visible and infrared regions of the electromagnetic spectrum, has an overall warming effect on the earth's atmosphere. Aerosols that contain black carbon compounds have a relatively long atmospheric lifetimes.⁸ On the opposite side of the spectrum is organic carbon (OC), which primarily absorbs at UV wavelengths.⁷ Organic carbon is generally thought to have a cooling effect on the atmosphere.⁹

However, the discovery of so-called "brown carbon" (BrC) compounds introduced an intermediary between these two extremes.⁷ BrC absorption is wavelength dependent; absorption is strongest at ultraviolet wavelengths, with decreasing absorption intensity into visible wavelengths.³ This rapid

increase in absorption at shorter wavelengths gives aerosols with BrC compounds their brown or yellow color.⁷

Chromophores are the individual light absorbing molecules present within an aerosol, so a BrC aerosol is an aerosol that contains BrC chromophores. A previous study indicated that including BrC aerosols in atmospheric models can drastically change the predicted radiative forcing effects.¹⁰ Past models that did not include BrC aerosols predicted that there would be an overall cooling effect from atmospheric aerosols, but accounting for BrC absorption in the model resulted in an overall warming effect on the atmosphere. In addition, the researchers found that BrC contributes approximately 19 percent to the radiative forcing from anthropogenic sources.¹⁰

BrC aerosols originate from a variety of different sources, including natural biomass burnings, such as forest fires; biological sources; man-made sources, such as the burning of fossil fuels and wood; and reactions in the atmosphere.³ The man-made sources of BrC aerosols are of particular interest because studying the structure and absorption of BrC aerosols can have important implications for building a more accurate understanding of humanity's impact on climate change.

However, despite the significant effects that BrC aerosols have on radiative forcing and overall atmospheric absorption, the structure and photophysical properties of BrC chromophores are not well defined.³ The adoption and photophysical behavior of BrC aerosols is highly dependent on the properties of the individual chromophores present within the aerosol.¹¹ In fact, the inadequacy in global modeling of BrC aerosols impact on atmospheric absorption is partially due to the lack of sufficient characterization about the optical properties of BrC chromophores.

Highly conjugated molecules have $\pi \rightarrow \pi^*$ transitions available and are known to absorb at ultraviolet and visible wavelengths. Thus, highly conjugated molecules have been

found to be good candidates as BrC chromophores.⁹ Nitrogen-containing compounds, especially nitrogen-heterocyclic molecules, are prime examples of such molecules. Nitrogen-heterocycles can form in a variety of ways, including atmospheric reactions that involve glyoxal and ammonia.¹¹ Nitrogen-heterocyclic compounds are also significant due to the many pathways that follow absorption of solar radiation.¹¹ In addition, nitrogen-heterocyclic molecules have significant overlap with the solar flux, further reinforcing their status as important light absorbing molecules.¹² The focus of this paper is on the photophysical properties of 2-phenylpyrrole (2PhPy), because it is a nitrogen-heterocyclic compound that is likely to be present in BrC aerosols.

Aerosols are principally comprised of an aqueous environment because, in addition to the chromophores, there are water molecules and other organics present within the aerosol. This aqueous environment may lead to water-mediated interactions that affect how the BrC aerosol chromophores absorb solar radiation.¹² Purely aqueous phase investigations of aerosols have been performed extensively, but these studies tell only a portion of the story. Since aerosols are so small, there is a significant number of molecules at the aerosol interface between the air and internal solvation environment. Chromophores residing in the middle of the aerosol are more solvated, but the chromophores around the air-water interface of the aerosol are only partially solvated. The chromophores at the aerosol interface are particularly important in absorption studies, because they are the first molecules to encounter the incoming solar radiation. The sequential addition of single water molecules to a gas-phase chromophore simulates this partial solvation environment at the aerosol interface.¹¹ The interactions between the chromophore and water also may lead to intramolecular charge transfer, that can further

contribute to the solar absorption properties of the aerosol.¹²

Therefore, in this study we aim to bridge the gap in the literature between purely gas phase and the purely aqueous phase investigations of prototypical BrC chromophores in order to more closely mimic the interfacial environment where these chromophores would be absorbing light.

Experimental Methods

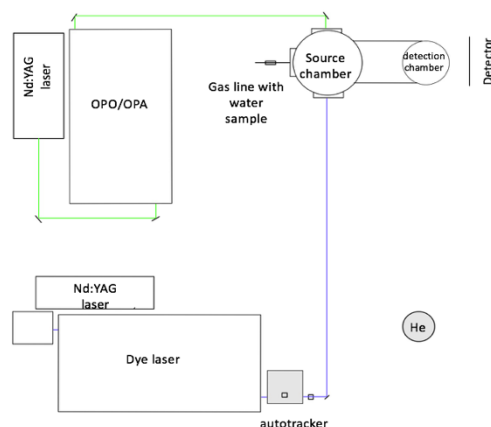


Figure 3: Schematic of laboratory setup

As illustrated in **Figure 3**, the experimental set up consists of a custom-built mass spectrometer that operates under high vacuum conditions. A small amount of 2PhPy sample was placed in glass wool within a sample holder. The sample holder was attached to the helium gas line on the inside of the source chamber, located before a pulse valve (0.5 mm orifice, Parker General Valve, Series 9). A heat rope was placed around the sample holder to heat the 2PhPy sample to its melting point (135°C). A skimmer (2mm, Beam Dynamics) was placed after the pulse valve to select the coldest 2PhPy and water complexes (2PhPy:nH₂O) using a method known as supersonic jet expansion (SJE). SJE was utilized in order to vibrationally and rotationally cool the molecules or complexes to their lowest vibrational levels ($v=0$) in the ground electronic state. This method also ensured that the molecules/complexes occupy

fewer vibrational and rotational levels, thus simplifying the spectral interpretation. When the 2PhPy molecules or 2PhPy:n H₂O complexes are pulsed through the pulse valve nozzle, the sample entrained in He carrier gas is carried from an area of high pressure to an area of very low pressure. Because the pulse valve opening is larger than the mean free path of the molecules, the sample molecules collide with the He carrier gas, thus creating a directional mass flow. Since the molecules are now moving faster and in a more uniform way, the velocity distribution is narrower and shifted towards higher velocities, which means that the overall temperature has decreased. Because the expansion is isentropic at the center, the increased translational energy from collisions leads to rotational and vibrational cooling.¹³ Therefore, all of the molecules/complexes at the center of the expansion, moving toward the detector will be collisionally cooled to their lowest rotational and vibrational states. SJE allows for the internal degrees of freedom to be cooled while keeping a sample in the gas phase.¹⁴

To create the 2PhPy:nH₂O complexes, a sample container with a few drops of water on cotton was attached to the helium gas line outside of the source chamber. Heat rope was also placed along the gas line and water sample (located outside of the chamber) to entrain a small percentage of water in the gas flow. The helium carrier gas carries the water into the sample chamber, where upon supersonic jet expansion in the vacuum chamber, 2PhPy:nH₂O complexes are generated.

Following supersonic jet expansion, a UV laser excites and ionizes the molecules/complexes. In order to shuttle these ions from the pulse valve to the detection chamber, an electric field was established across charged metal plates. The plate located closest to the pulse valve (placed immediately after the skimmer) is known as the repeller plate. The repeller plate has the highest voltage and the subsequent metal plates, known as

extractor plates, decrease in voltage towards the detection chamber. Laser induced photoionization and/or excitation occurs between the repeller and extractor plates. Vacuum pumps were used to reduce the source chamber pressure to vacuum conditions, namely 10⁻⁹Torr.

Mass selection was achieved through the use of a linear time of flight mass spectrometry (TOF MS). This technique separates the molecules/complexes based on their velocities. A voltage is applied across the ion gates, which propels all of the molecules forward with the same kinetic energy. Because $KE = 1/2mv^2$, molecules with larger mass will travel slower and molecules with lower mass will travel faster. The lightest molecules will hit the detector first, and the heaviest molecules will hit the detector later. In this way, the specific molecule or complex can be isolated with mass resolution. Backtracking from the mass of the molecule/complex (m_2), and the known time of flight (T_1) of a molecule of mass m_1 , the time of flight of the molecule/complex in question can be predicted using equation (1).

$$(1) T_1 = \left(\frac{m_1}{m_2}\right) T_2$$

In the experimental studies described below, the mass channel of the target molecule/complex was monitored. This method ensures that only the molecule or complex of interest is being interrogated. Following mass selection, the molecules/complexes are detected by a dual multichannel plate/phosphor screen detector.

A technique known as resonant-two photon ionization (R2PI) was used to record a vibrationally-resolved UV spectrum of 2PhPy and 2PhPy:nH₂O. To generate tunable UV light, a pulsed dye laser (Radiant Dyes NarrowScan K) pumped by a Nd:YAG laser was used. A mixture of Rhodamine B and DCM dyes were used in the dye laser to access the relevant resonant wavelengths. Tunable UV radiation was made with an Inrad Autotracker III, equipped with a beta barium borate (BBO)

crystal, which can be tuned to generate a range of wavelengths. This laser was used as the “probe” laser, to interrogate the supersonically cooled molecules. R2PI is a two-photon experiment, in which the first photon from the laser electronically excites the molecule/complex to its upper electronic state (S_1), allowing for interrogation of the excited state photophysics. The second photon from the laser ionizes the molecule/complex, which then goes through the ion optics and is mass selected in the TOF mass spectrometer. The spectrum generated using R2PI includes all conformations of the molecule and can be a linear combination of the spectra for the individual conformations of the molecules.¹⁵

A double-resonance technique known as ultraviolet hole burning (UV HB) was used to discern the number of unique conformational isomers of a target molecule/complex. This technique can also determine which peaks in the R2PI spectrum originate from certain conformational isomers. UV HB is a two-laser experiment that involves a UV holeburn laser and a UV laser called the probe laser (which is the same one utilized in the R2PI experiments above). The probe laser is a Nd:YAG (Continuum Surelite II-10) pumped dye laser (Radiant Dyes, NarrowScan). The UV holeburn laser and UV probe laser are spatially overlapped and counterpropagating in the source chamber. The holeburn laser precedes the probe laser in time by approximately 50ns. The UV holeburn laser is fixed on an observed vibronic transition in the R2PI spectrum, and since that peak belongs to a specific conformational isomer, the holeburn laser will excite a sizable fraction of the molecules/complexes with that conformation. Thus, the holeburn laser removes ground state population from the target conformational isomer, depleting the available population that can be excited by the probe laser. As the UV probe laser is scanned and becomes resonant on a transition with the same zero-point level as the holeburn laser, a depletion spectrum is

recorded. A difference spectrum is made by active baseline subtraction. If no depletion is seen, then the R2PI peak in question belongs to a different conformational isomer. In this way, a conformationally specific spectrum is generated, and the number of conformational isomers can be determined.

Infrared holeburning (IR HB) experiment is another double-resonance method utilized to create a conformationally specific spectrum. This method is similar to UV HB, but the main difference is that the holeburn laser emits infrared radiation from a Nd:YAG (Continuum Surelite II-10) pumped optical parametric oscillator/amplifier (OPO/OPA) IR laser. This IR holeburn laser has a fixed infrared frequency, causing any molecule/complex with a vibration with that same frequency to be vibrationally excited. The IR holeburn laser is fixed on a vibrational frequency from a specific conformational isomer from the R2PI spectrum. This vibrational excitation removes some population from the ground vibrational state for any molecules with that conformation, reducing the population available for electronic excitation by the UV probe laser. The UV probe laser is delayed in time and scans the region of interest. When the UV probe laser is resonant on an electronic transition, one photon will excite the available ground state population to excited state, and the second will ionize it.

Finally, a technique known as resonant ion-dip infrared spectroscopy (RIDIRS) was used to create a conformationally specific IR spectrum, because it yields a mass-resolved IR spectrum of a single conformer in the ground electronic state. This experimental setup consists of a UV probe laser and an IR pump laser. In this case, the probe laser is fixed on a known electronic transition for the molecule/complex, and the IR pump laser (akin to the holeburn laser in IR HB setup described above) is scanning across a given range of wavelengths. The IR pump laser precedes the

UV probe laser in time. When the IR pump laser is resonant on a vibrational transition for the molecule, it removes population from the ground vibronic state of one conformation, the UV laser is fixed on an electronic transition that originates from a specific peak in the R2PI spectrum. The signal depletion is monitored as a function of the IR wavelength. For the purpose of these investigations the region from 2900-4000 cm^{-1} was scanned.

Non resonant ion-dip IR spectroscopy is essentially the same as the RIDIRS spectroscopy, but it is not conformationally specific, because the UV laser is not resonant on a UV transition from the R2PI spectrum. That is to say, the spectrum includes the IR (vibrational) transitions from all of the conformational isomers of the molecule. Non-resonant IR is acceptable for the purposes of these studies because it has been determined that only one conformational isomer is present for the 2PhPy:nH₂O complex.

Computational Methods

The ABC (artificial bee colony) calculations were performed in order to find the lowest energy structures of the complexes/clusters, thus creating preliminary estimates of the structure of 2PhPy:nH₂O clusters.

In addition, ground state and excited state geometry optimization and vibrational frequency calculations were performed using Gaussian16 software. The vertical excitation calculations were done using density function

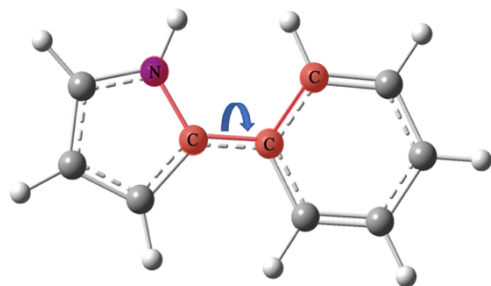


Figure 4: Potential energy surfaces were generated by rotation around 2PhPy NC-CC bond

theory, with a ω B97XD/6-311++G(d,p) level of theory for ground state calculations and TD-SCF ω B97XD/6-311++G(d,p) level of theory for excited state calculations. These calculations were used in order to estimate where the nearby excited electronic states are and to visualize the molecular orbitals that take part in excitation.

Finally, conformational searches of 2PhPy were performed. In these theoretical predictions, the potential energy is modeled as the molecule is rotated around NC-CC bond (see **Figure 4**) to develop a PES along that structural coordinate.

Results and Discussion

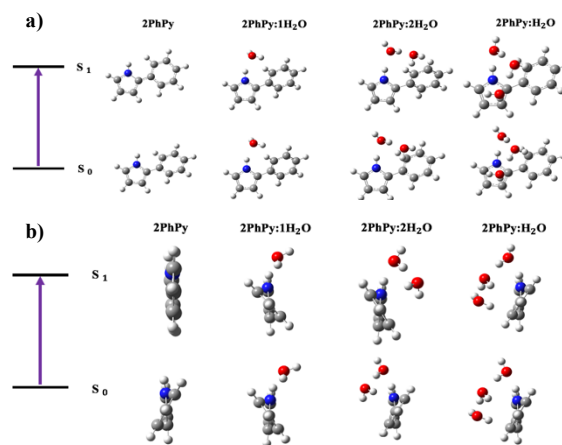


Figure 5: Optimized geometries for the ground electronic state (S_0) and the excited electronic state (S_1) using density functional theory. **a)** shows a view of the molecules/complexes in-plane with the pyrrole ring **b)** shows a view of the molecules/complexes perpendicular to the pyrrole ring

Predictions using DFT theory calculations were performed to determine the lowest energy structures for the ground and excited state of the bare chromophore and the complex. In **Figure 5**, the lowest energy structures are shown in the ground state (S_0) and the excited state (S_1) for increasing number of water molecules in the complex. These calculations show the effects of the water molecules on the

orientation of the molecule, particularly how twisted the phenyl ring is in relation to the pyrrole ring. The ground state of the bare chromophore has a NC-CC dihedral angle of -29.97° , whereas the excited state bare chromophore NC-CC dihedral angle of -2.37° . Since a dihedral angle of 0 degrees would indicate a completely planar orientation of the pyrrole ring in relation to the phenyl ring, the excited bare molecule is in a nearly planar orientation. Upon excitation of the bare chromophore the molecule becomes more planar than it is in the ground state. Therefore, there is a significant difference in the of the ground state and the excited state geometries for the bare chromophore.

The ground state of the 2PhPy:1 H₂O complex has a NC-CC dihedral angle of 36.82° and the excited state has NC-CC dihedral angle of 36.98° . The ground state of the 2PhPy:2H₂O complex has a NC-CC dihedral angle of -33.49° and the excited has 33.49° . The ground state of the 2PhPy: 2H₂O has a NC-CC dihedral angle of -28.95° and the excited has -30.27° . Therefore, there is very little change in planarity upon excitation of the the 2PhPy:1H₂O, 2PhPy:2H₂O, and 2PhPy:3H₂O complexes. The minimal change in geometry

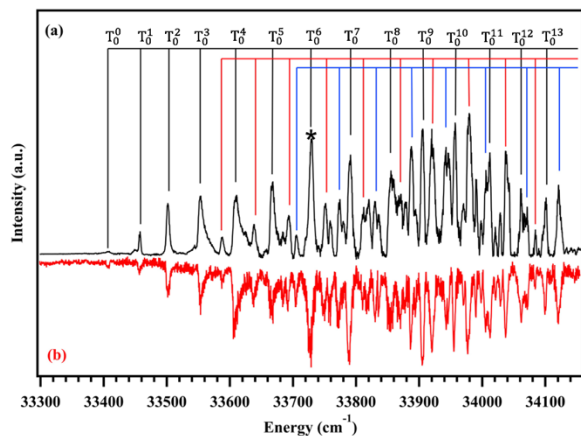


Figure 6: (a) R2PI spectra of the bare 2PhPy molecule. The black trace represents the torsional mode progression (T_0^n). The red trace is from a combination mode, $A_0^n T_0^n$. The blue trace is from a combination mode, $B_0^n T_0^n$. The black asterisks indicate the vibronic transition that was interrogated in the (b) UV HB spectrum.

between the ground and excited states may be due to the additional water molecules serving as proton acceptors from the N-H bond on the pyrrole ring, helping to stabilize the structures.¹⁵

Figure 6 and **7** build upon data previously collected, but further analysis is provided.¹⁵ **Figure 6(a)** shows the R2PI spectrum of the bare chromophore, in which three progressions have been identified. The electronic origin band is seen at 33406 cm^{-1} . The progression indicated by the black trace is proposed to represent the torsional mode progression T_0^n . This assignment was made because the difference between adjacent peaks in this progression agrees with calculated vibration energy for a torsional mode of 53 cm^{-1} . In accordance with this predicted value, the T_0^1 peak is located approximately 50 cm^{-1} from the electronic origin band (T_0^0), with each subsequent quanta of energy ($T_0^2, T_0^3, T_0^4, \text{etc.}$) adding approximately 50 cm^{-1} of energy.

In addition, information about the change in geometry between the molecule's ground and excited state can be gleaned from the intensities of the torsional mode transitions. The intensity of the vibronic transition on the torsional mode for the bare chromophore increases as more quanta are added, indicating large Franck Condon factors, and thus an offset between the ground and excited state geometries. This increase in intensity corroborates the calculated prediction that there is an offset in the geometry between the ground electronic state and the excited electronic state (**Figure 5**).

The red and blue progressions seen in **Figure 6** are identified as $A_0^n T_0^n$ and $B_0^n T_0^n$ respectively. The $A_0^n T_0^n$ progression begins approximately 180 cm^{-1} away from the electronic origin band. $A_0^n T_0^n$ indicates a combination mode resulting from the coupling between a torsion-like vibrational mode (A) with the torsional mode (T). Subsequent peaks in the $A_0^n T_0^n$ progression are from additional quanta added to the torsional mode, because the

peaks are separated by approximately 50cm^{-1} . The $B_0^n T_0^n$ progression is approximately 300cm^{-1} away from the electronic origin, and is attributed to another, higher energy vibrational mode (B) coupling with the torsional mode. In order for these A and B modes to couple with the torsional mode, the vibrations need to sufficiently resemble the torsional mode and be symmetry allowed.

The UV holeburning spectrum of 2PhPy is shown in **Figure 6(b)** in red below the R2PI spectrum. The probe laser was fixed on a vibronic transition indicated by the starred peak. Because every peak in the R2PI spectrum is accounted for by depletion in the holeburn spectrum, the UV HB spectrum shows that there is only one possible conformational isomer for the 2PhPy molecule.

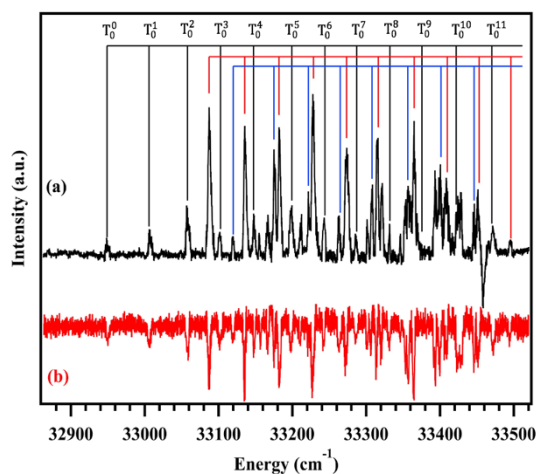


Figure 7: (a) R2PI spectrum of the 2PhPy+1H₂O complex. (b) is the IR hole burning spectrum of the complex.

The R2PI spectrum of the 2PhPy:1H₂O spectrum is shown in **Figure 7(a)**. The addition of one water molecule more closely resembles the *in situ* absorption of the chromophore in the local solvation environment that would be observed at the aerosol interface. The electronic origin band is observed at 32950cm^{-1} , and is 450cm^{-1} lower in energy than the electronic origin band of the bare chromophore, indicating that the addition of water molecules causes a red shift. The black

progression represents the torsional mode progression. The fact that the intensities of the torsional mode transitions do not increase in intensity past three additional quanta (T_0^3) as increasing number of quanta are added, agrees with the theoretical predictions that there is little to no geometry change between the ground and the excited state in the one water complex. For the 2PhPy:1H₂O complex, the torsional mode progression is lower in intensity relative to the other progressions. These other progressions, shown in red and blue in **Figure 7(a)**, are proposed to be due to water migration modes, where the H₂O moves from the pyrrole ring to the phenyl ring. These water migration modes have a larger transition intensity than the torsional mode. The large relative intensity of these water migration progression can be attributed due to their large dipole moment, originating from the large amplitude motion of the water migration from the pyrrole ring to the phenyl unit.

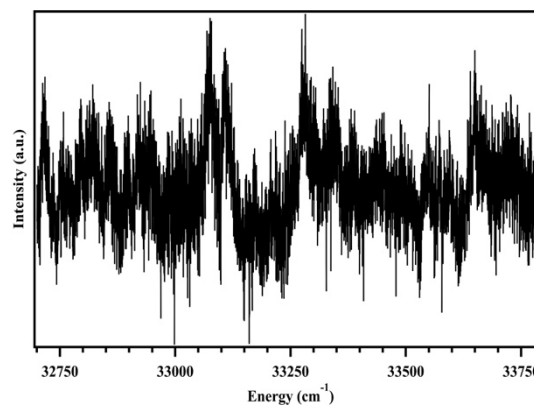


Figure 8: R2PI spectrum of 2PhPy+2H₂O complex.

The R2PI spectrum for the 2PhPy:2H₂O (**Figure 8**) was obtained. Similar to the spectra for the bare chromophore and 2PhPy:1H₂O complex, consistent energy differences between peaks are observed, indicating vibrational progressions. Considering the 450cm^{-1} redshift of the 2PhPy:1H₂O complex's electronic origin band relative to that of the bare chromophore, the electronic origin band for the 2PhPy:2H₂O complex

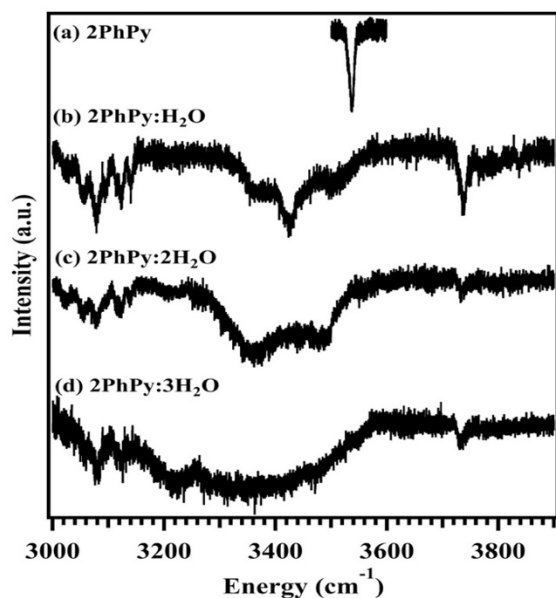


Figure 9: Resonant Ion Dip IR spectrum for a) 2PhPy and non-Resonant Ion Dip IR spectra for b) 2PhPy:1H₂O c) 2PhPy:2H₂O d) 2PhPy:3H₂O

would be expected to be at lower energy than was interrogated in this study. Further averages are required to improve the signal-to-noise ratio and to assign transitions to specific vibrational modes.

In addition, the IR spectra for the bare molecule and for the 2PhPy:1 H₂ O, 2PhPy:2 H₂ O, and 2PhPy:3 H₂ O complexes were obtained (see **Figure 9**). The NH stretch was observed in the IR for the bare molecule. In the one water, two water, and three water complexes were scanned from 3000 to 3900cm⁻¹ is shown in figure. Both the bare chromophore and 2PhPy:1 H₂ O traces were carried out using RIDIR spectroscopy, whereas the other complexes were carried out with non-resonant RIDIR spectroscopy. nRIDIRS still yields a representation of the IR spectrum, but it is not conformationally specific. Non-conformationally specific spectroscopy is permissible because, as seen in **Figures 6 and 7** only one conformer is observed in the bare molecule and 1 water clusters of 2PhPy. Therefore, a resonant IR spectrum is not required, as it is not necessary to distinguish between multiple conformers.

As more water molecules are added to the complex, increasing broadening is seen in the central, hydrogen bonded OH and NH regions of the spectrum. The NH stretch broadens with increasing number of water molecules added, making the NH stretch blend into the hydrogen bonded OH stretch region. In accordance with the IR simulations, as soon as 3 water molecules are added, the NH stretch has a huge coupling constant to water bending modes. This large coupling constant is due to the anharmonic coupling between different oscillators and is consistent with the broad NH stretch region that is observed. In addition, a small red shift is observed in the NH stretch as water molecules are added, likely due to the addition of water molecules. Hydrogen bonding or other weak intermolecular interactions (such as Coulombic interaction) between the H₂O and the NH stretch would reduce the energy, causing a redshift in the spectrum.

Next Steps

Further averages for the R2PI spectrum of the 2PhPy:2H₂O complex are required to increase the signal to noise ratio. The techniques used in these investigations can be extended to other prototypical BrC chromophores.

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