# Light Absorption by Charge Transfer Complexes in Brown Carbon Aerosols

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Ⓢ *Supporting Information*

ABSTRACT: Recently, it has become apparent that a fraction of the organic species in ambient aerosols absorbs ultraviolet–visible light with a potential impact on climate. It is believed that this light-absorbing, sometimes called "brown", carbon originates from biomass and biofuel burning and could be formed through secondary processes in particles or clouds. Here, we identify for the first time charge transfer (CT) complexes as a significant source of light absorption by organic compounds in aerosols. A dense manifold of these complexes, formed from interactions between alcohol and carbonyl moieties, accounts for approximately 50% of the absorption (300–600 nm) observed for water-extracted ambient particulate matter collected in Athens, GA. Corresponding fluorescence emission spectra with broad, overlapping long-wavelength tails are consistent with efficient energy transfer among a near continuum of such coupled excited states. We postulate that a wide variety of CT complexes are formed as a result of a supramolecular association of self-assembling, smaller molecules, just as they are in natural humic substances, and that this gives rise to absorption that extends to red wavelengths. These findings imply that light absorption by organic aerosols is governed by a combination of independent as well as interacting chromophores and that both must be included in an accurate representation of aerosol optical properties.
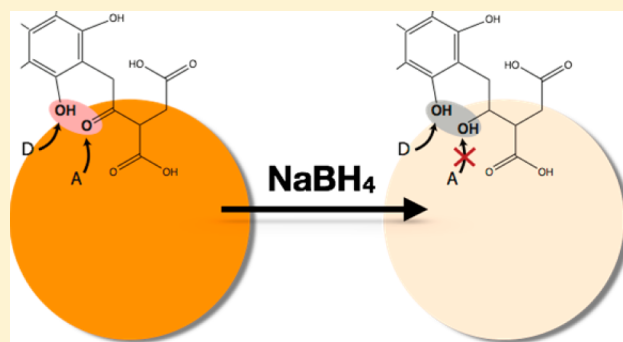
INTRODUCTION

Organic molecules in atmospheric aerosol particles can be significant absorbers of ultraviolet (UV) and visible light.[1,2] Unlike black carbon particles that absorb strongly throughout the UV–visible spectrum, the light-absorbing organic fraction of aerosols has a much more pronounced wavelength dependence that increases exponentially with decreasing wavelength giving rise to the term "brown carbon".[3] Field studies indicate that this brown carbon could be responsible for half or more of light absorption by aerosol particles at UV wavelengths[4] and could alter local gas-phase photochemistry as well as perturb the radiative balance in the atmosphere.[5] While black carbon particles are known to originate from high-temperature combustion of diesel and other fuels,[6] brown carbon particles can be formed both directly from low-temperature and incomplete combustion of biomass and fuels[4,7] and indirectly from combustion sources and biogenic organic compounds.[2,8–13]

The chemical characterization of brown carbon has proven to be difficult and remains incomplete.[14] The organic aerosol fraction comprises hundreds of different species, and identifying specific chromophores responsible for the absorption exhibited by brown carbon has been challenging. Jacobson suggested that nitro-aromatic species in aerosols could absorb light,[15] and several groups have since detected them[16–18] and been able to attribute as much as 4% of observed brown carbon absorption to them as a class.[17,18] Others have demonstrated that

condensation reactions involving ammonia, amines or amino acids, and various aldehydes produce products that could be responsible for as much as 10% of brown carbon UV–visible absorption.[13,19] However, each of these types of chromophores exhibits little to no absorption at wavelengths longer than 450 nm,[13,17–19] whereas brown carbon absorption extends to at least 600 nm.[1,2] Thus, the molecular origin of how brown carbon absorbs light is an outstanding area of interest.

Here, we demonstrate for the first time that charge transfer (CT) complexes are responsible for much of the observed absorption by the water-soluble fraction of ambient particulate matter. This fraction has been found to constitute approximately 20–50% of the total (methanol-extracted) BrC absorption depending on wavelength.[17] These CT complexes, which are formed from weak associations between molecules or separate parts of a single molecule, give rise to electronic transitions in the UV–visible spectrum that cannot be attributed to individual, isolated chromophores. Through a transfer of charge from a donor group, such as the hydroxyl of a hydroxy-aromatic, to an acceptor group, such as the carbonyl of a ketone or aldehyde (Figure 1), these complexes lead to optical transitions with energies lower than those of the
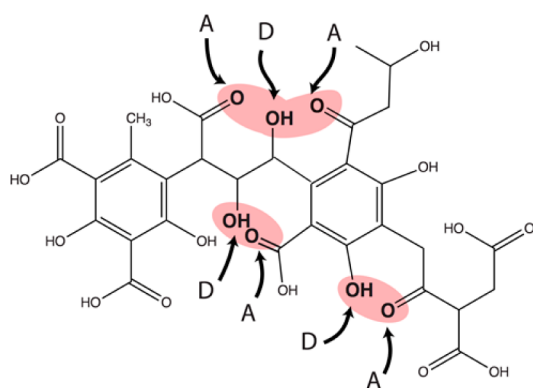
Figure 1. Hypothetical structure for a representative humic acid molecule or fragment. Charge transfer complexes formed from interactions between donor (D) and acceptor (A) groups are denoted by the red shaded regions.

transitions of the individual constituent groups. Consequently, they contribute to the long-wavelength tail of the absorption spectrum that defines brown carbon.

MATERIALS AND METHODS

Aerosol Collection. Ambient aerosols were collected out of a window in the Chemistry Building at the University of Georgia (∼20 m above ground level) in Athens, GA (33.9488°N, 83.3747°W) from January 2014 to March 2014. A total of 10 samples were collected on polytetrafluoroethylene (PTFE, Teflon) filters (0.2 μm pore size, Sterlitech) at a rate of 16.7 L/min for 10 separate 24 h (±1 h) periods. A very sharp cut cyclone inlet (BGI, Inc.) was employed to size select for particles with diameters of <2.5 μm. Water-soluble organic species were then extracted in a manner similar to that described by Hecobian et al.[2] by sonication of the filter for 20 min in 10 mL of Milli-Q water (<18.2 MΩ cm). Extracted solutions were filtered using a 0.45 μm PTFE disposable syringe filter and adjusted to pH 7 with NaOH because the magnitude of the absorption spectra was pH-dependent (Figure S1 of the Supporting Information). More details about the samples collected, including calculated back trajectories, are included in Table S1 of the Supporting Information.

Reduction. Reductions were adapted from the protocol detailed by Ma et al.[20] Extracted aerosol solutions and 50 mg/L aqueous Suwannee River fulvic acid (SRFA) (International Humic Substances Society) solutions were reduced in a 1 cm quartz cuvette (3 mL) by adding approximately 5 mg of solid $NaBH_4$ and dissolving it by stirring. Reduction proceeded until no further change in absorbance was noticed (25 min). Because of an excess of $NaBH_4$, the pH of the solution increased to 10. The solution was readjusted to pH 7 with HCl before optical absorption spectra were recorded on a Cary 60 spectrophotometer (Agilent) over a range of 200−800 nm. Fluorescence spectra were recorded on a FluoroLog 2 fluorometer (Horiba) over an excitation range of 280−450 nm scanned in 10 nm steps.

RESULTS AND DISCUSSION

Absorption Loss Accompanies Removal of Charge Transfer Complexes. While CT complexes have never before been identified in ambient aerosols, they have been suggested to be responsible for the absorption observed in a model aerosol system[21] as well as in aquatic and terrestrial humic

substances.[22,23] In particular, Blough and co-workers have used a variety of methods to confirm the presence of CT complexes in aquatic humic substances, including chemical reduction to eliminate them[20] and excitation−emission matrix (EEM) fluorescence spectroscopy to learn more about the CT states.[20,22,24] Here, we use these same methods with ambient aerosol extracts.

We used $NaBH_4$ to reduce carbonyl functional groups in ketones and aldehydes, likely electron acceptors in CT complexes, to the corresponding alcohols. Importantly, $NaBH_4$ does not reduce other moieties that have been proposed to be responsible for absorption of visible light, including extended aromatic or highly conjugated systems as well as heteroaromatic structures.[20] Absorption spectra of a typical aqueous extract of ambient particulate matter before and after reduction are shown in Figure 2a, with the absorbance loss
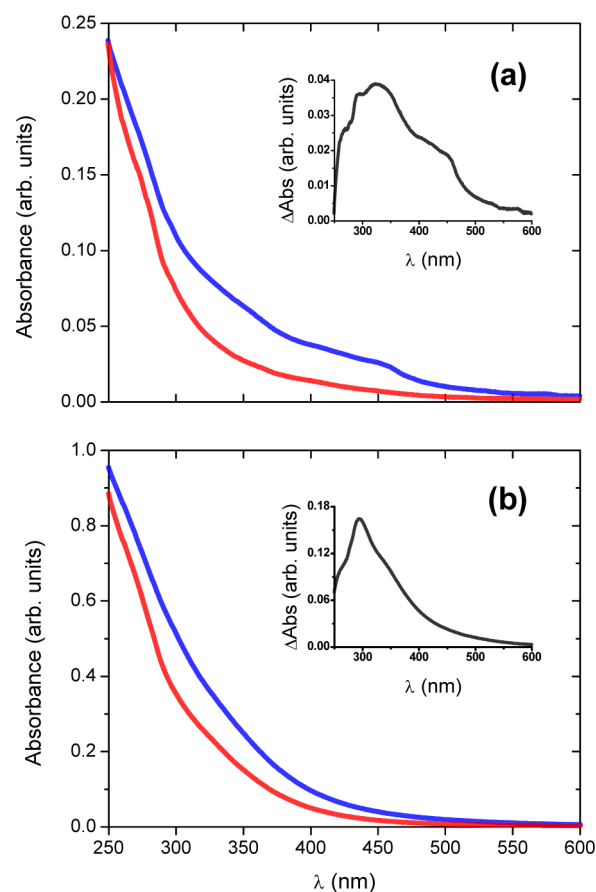

Figure 2. Absorption spectra of aqueous solutions of (a) an ambient aerosol extract collected over a 24 h period from February 6, 2014, to February 7, 2014, in Athens, GA, and (b) Suwannee River fulvic acid prior to (blue) and after (red) reduction by $NaBH_4$. Insets show absorption loss after reduction as a function of wavelength.

in the inset representing the collective absorption spectrum of the CT complexes removed upon reduction. For comparison, we performed the same reduction on Suwannee River fulvic acid (SRFA), a standard commonly used to represent natural humic substances (Figure 2b). The similarities in the near-exponential shapes of the spectra and the absorbance losses after reduction suggest that these two different types of substances, one atmospheric and one aquatic, could share a

common chemical explanation for light absorption, i.e., CT complex formation.

Figure 3 shows the average percent absorption loss spectrum for ambient aerosol samples collected on 10 different days over
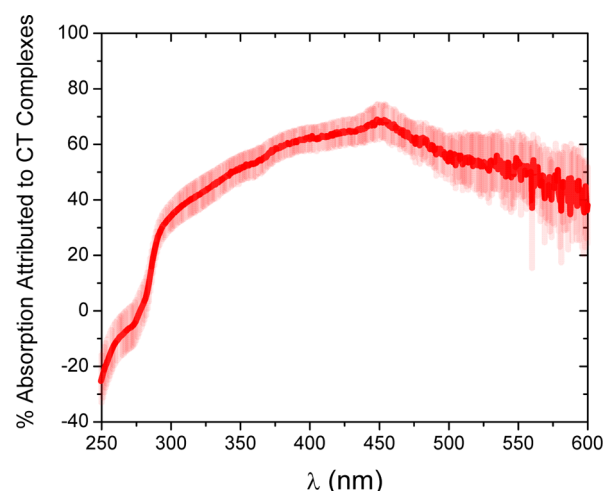

Figure 3. Average percentage absorption loss of 10 ambient aerosol extracts after reduction by NaBH$_4$. The light red area represents the uncertainty as ± the standard error of the mean.

7 weeks showing that absorption loss starts abruptly at ∼275 nm, increases to ∼65% at 450 nm, and then decreases to 40% at 600 nm. Despite the small absorption at wavelengths above 500 nm, a sizable fractional loss due to reduction is observed. Over the 300−600 nm region of the spectrum, there is an average loss of 53% of the absorption by water-soluble ambient particulate matter that can be attributed to CT complexes. We postulate that there is a near continuum of such CT states that gives rise to the observed monotonically decreasing absorption spectra extending to the red wavelengths, just as Blough and co-workers have suggested for natural humic substances.[20,22,24]

Fluorescence Spectra Indicate a Large Number of Coupled Excited States. We also recorded EEM fluorescence spectra of the ambient samples and SRFA (Figure 4). In each case, we observed broad, unstructured emission with substantial Stokes shifts of ∼100 nm. Also of note is the fact that the long-wavelength tails of the emission spectra all fall within a single envelope independent of excitation wavelength, λ_{exc}, which is evident in the insets of Figure 4. Such overlap suggests that there is a dense set of excited (fluorescing) states that are coupled to each other,[21,22] allowing the lower-energy excited states to be reached by excitation of a variety of higher-energy excited states followed by energy transfer.

It is also interesting to note that the peak emission wavelength, λ_{em}^{max}, is nearly constant (430 nm for the ambient sample, 450 nm for SRFA) for short-wavelength excitation and then increases at longer-wavelength excitation ($\lambda_{exc} > 330$ nm for the ambient sample and $\lambda_{exc} > 350$ nm for SRFA). These two regions are represented by the arrows in the EEM plots of Figure 4. The correlation between λ_{em}^{max} and λ_{exc} is unusual because fluorescence generally originates from emission by the lowest-energy excited state, and therefore, the wavelength of emission is not determined by the wavelength of excitation as long as $\lambda_{em} \geq \lambda_{exc}$. The continuous red shift of λ_{em}^{max} indicates the existence of a large number of fluorescing states with an increasingly smaller subset of states accessible as λ_{exc} increases. We interpret this near continuum of states as likely to consist of
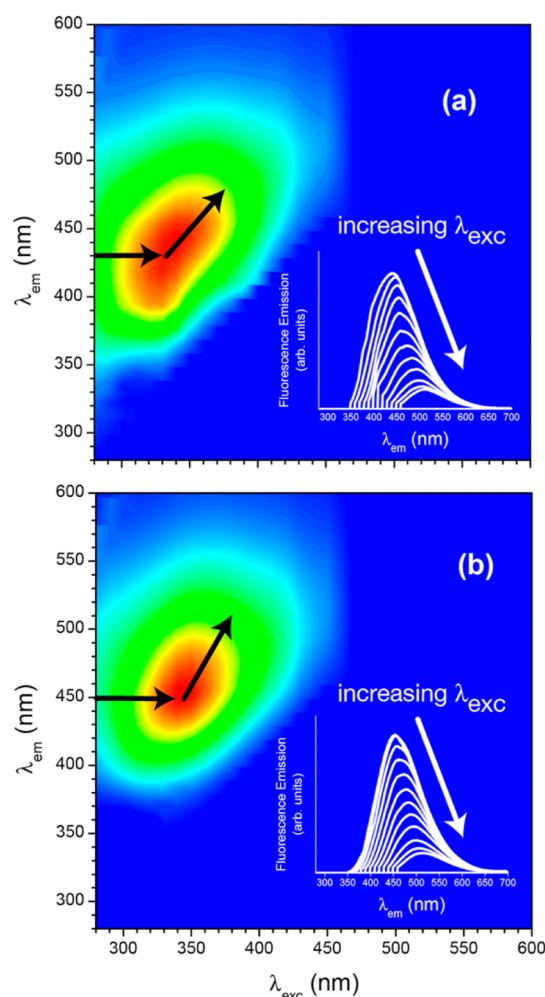

Figure 4. Fluorescence excitation−emission matrix (EEM) spectra of (a) an aqueous ambient aerosol extract collected over a 24 h period from February 6, 2014, to February 7, 2014, in Athens, GA, and (b) an aqueous solution of Suwannee River fulvic acid. Arrows indicate the trends of constant and then increasing λ_{em}^{max} with increasing λ_{exc}. Insets show fluorescence spectra with λ_{exc} values of 340−450 nm (every 10 nm).

a variety of excited CT complexes just as Blough and co-workers did in their studies of SRFA and other natural humic substances.[22]

CT Model for Atmospheric Aerosol Absorption. Given the observed similarities between ambient aerosol extracts and SRFA, it seems reasonable that they would share a common origin of light absorption. Furthermore, the ubiquitous nature of humic-like substances in aerosols[25,26] and the prevalence of functional groups (carbonyls and alcohols) responsible for CT complex formation in them suggest that the CT model put forth by Blough and co-workers to explain humic substance absorption[22] could also apply to aerosols. This model consists of independent chromophores that are coupled to a dense manifold of CT complexes (Figure 5).

At shorter wavelengths, absorption and fluorescence are dominated by the independent chromophores that may, but do not necessarily include, the donor and acceptor species that form the CT complexes. Coupling to the dense manifold of CT complexes gives rise to the long-wavelength tails in the fluorescence emission spectra. At longer wavelengths, these CT complexes can be excited directly, too, and the maximal
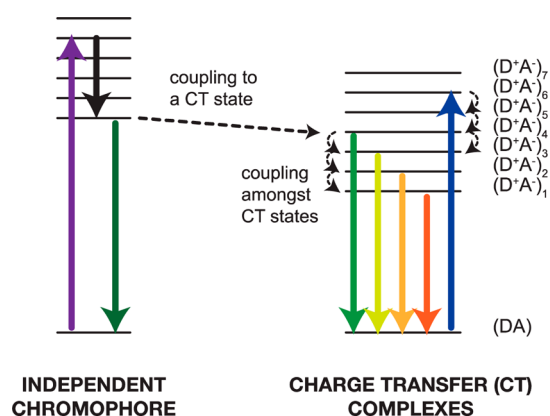
Figure 5. Energy level schematic showing the absorption and fluorescence of independent chromophores (left) and charge transfer (CT) complexes (right). A near continuum of CT states gives rise to the observed monotonic wavelength dependence in the absorption spectrum. Coupling between the chromophores and the CT complexes and among the CT complexes (dashed arrows) leads to the common emission tail at longer wavelengths observed in the fluorescence spectra.

fluorescence emission shifts to longer and longer wavelengths as the lower-energy CT states are preferentially populated. This model is consistent with the $NaBH_4$ reduction results, as well, because the carbonyl groups are reduced to alcohols, thereby eliminating the CT complexes and decreasing the long-wavelength absorption attributed to them. The fact that not all absorption is removed upon reduction, however, indicates that chromophores other than CT complexes are also present.

Certainly other chromophores exist in ambient aerosols, but none seems to be as consistent with all of the observations as CT complexes are. As mentioned previously, possible chromophores such as extended aromatic or highly conjugated systems will not be reduced by $NaBH_4$ and therefore cannot explain the decreased absorption. Incorporation of carbonyl groups into those systems would make them susceptible to reaction with $NaBH_4$, but such species are still not likely or are not consistent with observations. For example, extended conjugated systems containing carbonyl groups in resonance could absorb into the visible region of the spectrum, but as mentioned by others,[16] extended conjugated systems are unlikely to be present in appreciable amounts in ambient aerosols because ozone reacts with the double bonds. Systems containing quinoid groups could be responsible for some absorption at UV and blue wavelengths; however, in general, they do not absorb red wavelengths,[20] and though they are reduced by $NaBH_4$, that reaction is reversible in the presence of O_2,[27] as is the case in our experiments. Extended aromatic systems containing conjugated carbonyls could also contribute to absorption and would be reactive toward $NaBH_4$, but an unlikely and coincidental superposition of many different such systems would be necessary to reproduce the absorption spectra (Figure 2) and the observed continuous red shift in peak fluorescence wavelength and the overlapping "tails" (Figure 4). Furthermore, the fluorescence quantum yields for our ambient samples [~0.02 (Supporting Information)] are much lower than those typical of extended aromatics; for example, the quantum yield for anthracene ($C_{14}H_{10}$) is 0.22−0.33 (depending on solvent), while it is 0.87−0.89 for perylene ($C_{20}H_{12}$), an even larger polyaromatic species.[28]

The existence of CT complexes in ambient aerosols could have implications for how brown carbon particles are studied and understood. Beyond the fact that these complexes determine the brown color of these particles to a large extent, they also influence the wavelength dependence of the aerosol absorption spectrum that is often used to infer properties and sources. For example, the absorption Ångström exponent (AAE), the exponent in a power law fit to the absorption spectrum absorbance $\propto \lambda^{-AAE}$, is used to summarize wavelength dependence with a value of 1 for particles dominated by freshly emitted black carbon and values substantially larger than 1 indicating the contribution from BrC.[1,29] These values have also been used to differentiate sources such as motor vehicles from biomass smoke.[1,4] The steep wavelength dependence of the CT complex absorption spectrum (Figure 2a, inset) could, therefore, contribute to making overall AAE values larger than 1 and may even indicate a link to biomass smoke.

The wavelength dependence has also been noted to be remarkably different depending on whether particles are extracted in water or methanol,[17] and it seems likely that solvent-dependent CT complex formation might be, in part, responsible. In analogy to humic substances, these complexes may form from the aggregation of smaller units that could be affected by the nature of the solvent. The link between CT complex formation and aggregation might also explain why it has proven difficult to identify specific chromophores in ambient aerosols; for example, even relatively gentle techniques such as electrospray ionization (ESI) mass spectrometry may dissociate the aggregates,[30] leaving no evidence of the CT complexes responsible for absorption. The weak forces holding these complexes together suggest that particular attention must be paid to solvent properties such as polarity, pH, and temperature when extracting and analyzing particulate matter and that it may be difficult to compare the optical properties of samples extracted in different solvents.

While the extent to which CT complexes are formed in ambient aerosols is not known, in general, the necessary components, namely, ketones or aldehydes and alcohols, can originate from oxidation and low-temperature combustion of biogenic species including lignin.[31] Perhaps, then, these complexes provide a link between biomass burning and the formation of BrC. Our findings also intimate that these complexes could be responsible for a significant fraction of aerosol direct radiative forcing. For example, recent measurements by Liu et al.[14] indicate that BrC constitutes 25% of aerosol absorption (at 365 nm), half of which could originate from CT complexes if we assume that our findings for water-soluble BrC represent the total BrC. Clearly, that assumption needs to be validated, and correlations between CT complex formation and specific sources need to be explored to determine how prevalent they are.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

pH dependence of ambient particulate matter absorption spectra and a table of samples collected. This material is available free of charge via the Internet at http://pubs.acs.org.

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dx.doi.org/10.1021/ez500263j | *Environ. Sci. Technol. Lett.* 2014, 1, 382−386