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Charge-Transfer-to-Solvent Spectrum of Thiocyanate at the Air/Water Interface Measured by Broadband Deep Ultraviolet Electronic Sum Frequency Generation Spectroscopy

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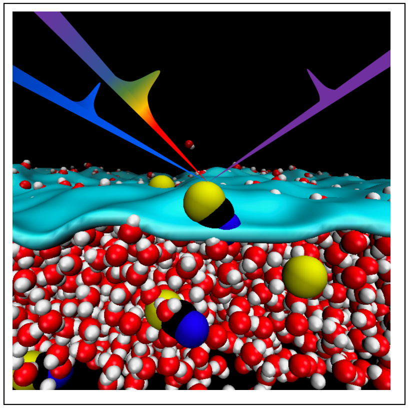
Abstract

Measurement of interfacial electronic spectra is a powerful tool for characterizing the properties of ions in physical, biological, environmental, and industrial systems. Here, we describe measurement of the complete charge-transfer-to-solvent (CTTS) spectrum of thiocyanate at the air/water interface using our recently-developed femtosecond broadband deep ultraviolet electronic sum frequency generation technique. We find that the lower energy CTTS band characterized in bulk thiocyanate spectra is not observed in the $|\chi^{(2)}|^2$-power spectrum of the air/water interface, likely reflecting the different solvation environments, altering of the charge distribution of the ion, and possible ion-ion effects, and that sodium and potassium salts yield identical spectra. Additional experiments and comparison with theoretical calculations are necessary to extract the interesting chemical details responsible for these salient spectral differences.

Graphical TOC Entry



Keywords

ion adsorption, SCN-, nonlinear spectroscopy, aqueous interfaces

Understanding the detailed nature of aqueous interfaces has become a quest of profound significance, as it underlies urgently needed advances in water purification, desalination, and reclamation technologies,[1] and is the key to central processes in electrochemistry,[2] atmospheric chemistry,[3] and biochemistry.[4] Of particular interest is the behavior of *ions* at interfaces ranging from air/water and polymer/water to metal/water. Recent advances in experiment and theory have revealed mechanistic details of the adsorption of the prototypical thiocyanate ion to air/water,[5,6] dodecanol/water,[7] and graphene/water[8] interfaces, focusing on thermodynamic properties (viz. adsorption free energy, enthalpy, and entropy). To further advance our understanding of these systems, additional interfacial properties must be similarly characterized. Towards that end, measuring and interpreting electronic *spectra* of interfacial ions is of much interest. To address this issue, Rizzuto et al. have recently developed femtosecond broadband deep ultraviolet electronic sum frequency generation (DUV-ESFG) spectroscopy.[9] We report the further extension of the detection capability of the broadband DUV-ESFG system to wavelengths below 195 nm. Compared to previous measurements with resonant electronic second harmonic generation (ESHG) spectroscopy[5–7,10,11] that yield incomplete interfacial spectra characterized by time-consuming and error-prone pointwise measurements, broadband DUV-ESFG allows us to obtain a broad, continuous interfacial $|\chi^{(2)}|^2$-spectrum in a single measurement with improved signal-to-noise, thus facilitating a more quantitative analysis of peak positions, linewidths, and relative intensities that can be compared with theoretical calculations to yield additional insights into the nature of ions at complex interfaces. Here, we present the first complete interfacial charge-transfer-to-solvent (CTTS) spectrum of thiocyanate at the air/water interface, measured with broadband DUV-ESFG spectroscopy.

Thiocyanate is a highly surface-active ion and one of the most chaotropic anions in the Hofmeister series.[12,13] The asymmetric solvation shell of SCN^-, a linear triatomic ion, differs from those of halides and other ions (e.g. I^-, NO_3^-, CO_3^{2-}) that possess symmetric structures and charge distributions. Additionally, thiocyanate possesses a significant dipole moment that likely drives the ion to favorable orientations at interfaces and influences its unique chemical properties. Previous experiments that probed the C-N stretch of thiocyanate by vibrational SFG spectroscopy predicted an average tilt angle of 45° with respect to the surface normal at the air/water interface, although the absolute orientation was not determined.[14,15] A recent molecular dynamics study predicted that the sulfur has a greater affinity for the interface than does nitrogen, yielding an average tilt angle of 45° in the outermost surface layer.[16] Here, we probe the CTTS spectrum, which comprise broad, intense, and typically featureless bands in the deep UV (<250 nm), engendering the transfer of an electron from the anion to its surrounding solvent molecules.[17] Because the initial ground state of the anion and the excited CTTS states are defined by both the ion and its corresponding neutral species, as well as the surrounding solvent molecules, CTTS spectra are highly sensitive to the details of the chemical environment, making them powerful tools for elucidating complex chemical interfaces.

The bulk CTTS spectrum of 100 µM sodium thiocyanate is shown in Figure 1(a). Fox et al. measured the absorption spectrum of aqueous tetramethylammonium thiocyanate and assigned two bands in the deep UV, viz. a higher energy band centered at 187 nm and a lower energy band centered at 216 nm, with no observed cation dependence at these low concentrations.[18] Solvent and temperature dependence properties were used to assign the lower energy band as a CTTS feature.[19] The higher energy band resembles similar higher energy bands observed in CTTS spectra of halides.[20] Thus, the higher energy band is proposed to originate from higher energy solvated electron states or higher states of the corresponding thiocyanate radical.[18] Upon irradiation with UV wavelengths, two competing photochemical pathways depending on the wavelength of light are proposed:

$$\mathrm{SCN^-}(aq) \xrightarrow{\lambda < 240\mathrm{nm}} \left[\mathrm{SCN^-}(aq)\right]^* \longrightarrow \mathrm{SCN}(aq) + \mathrm{e^-}(aq)$$

$$\mathrm{SCN^-}(aq) \xrightarrow{\lambda > 240\mathrm{nm}} \mathrm{CN^-}(aq) + \mathrm{S}\,(aq)$$

wherein first is an *external* CTTS transition and the latter is an intramolecular transition.[21]

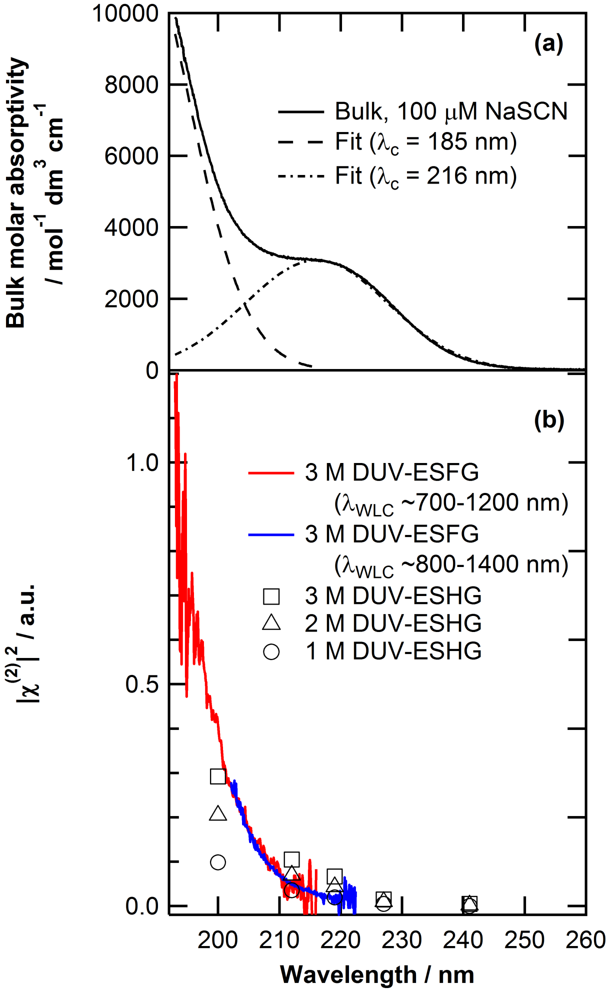


Figure 1. (a) Bulk CTTS spectrum of 100 μM aqueous sodium thiocyanate at 298 K. Dotted black lines indicate Gaussian fits centered at 185 nm and 216 nm. (b) Interfacial $|\chi^{(2)}|^2$-spectra of aqueous thiocyanate CTTS transition measured by resonant ESHG at 200 nm, 212 nm, 219 nm, 227 nm, and 241 nm (1-3 M, black markers)[6] and broadband DUV-ESFG (3 M, red and blue lines). The red and blue solid lines indicate ESFG spectra taken at different temporal overlap of the two input pulses corresponding to different spectral overlap due to the positive chirp of the white light continuum pulse.

To probe *interfacial* spectra, second-order ($\chi^{(2)}$) spectroscopy techniques are commonly used.[22,23] Under the electric dipole approximation, second harmonic generation (SHG) and sum frequency generation (SFG) are surface-sensitive techniques due to symmetry constraints, with probe depths of ca. 1 nm that correspond to the topmost few molecular layers.[22–24]

In femtosecond broadband DUV-ESFG spectroscopy, a spectrally narrow pulse (266 nm, FWHM 2 nm) and a white light continuum pulse (~600-1400 nm) are spatially and temporally overlapped at the surface, generating coherent sum frequency radiation in reflection geometry at the phase-matched angle. When the sum frequency of the input photons is resonant, e.g. with a strong CTTS transition, the detected SF signal is strongly enhanced.[25] The optical design is shown in Figure S1 of the Supporting Information.

The broadband DUV-ESFG spectrum of 3 M NaSCN (Figure 2a) was measured with a ppp-polarization scheme (p-polarized SFG, p-polarized 266 nm, and p-polarized white light continuum). Because of the positive chirp in the white light continuum generation process,[26] we can obtain spectral overlap with shorter or longer wavelength components of the white light continuum by changing the time delay (±60 fs) between the two input pulses. Sodium and potassium thiocyanate salts produced identical spectra; therefore, only sodium thiocyanate results are explicitly reported here. The background (i.e. scattered light, CCD readout, and dark charge noise) has been subtracted and baseline correction has been performed. The background spectra were measured with a time delay of ~2 ps between the two incident pulses, since there would be no SFG contribution without temporal overlap. The raw thiocyanate ESFG spectrum (Figure 2a) is normalized by the SFG spectrum of gallium arsenide (GaAs) shown in Figure 2b to correct for the distortion in the raw thiocyanate ESFG spectrum due to the spectral intensity and positive temporal chirp of the white light continuum pulse[26] and the spectral sensitivities of the optics and CCD detector. GaAs was used as the nonresonant reference sample since it has a large $\chi^{(2)}$ value and has no known resonances at the wavelengths of the incident and sum

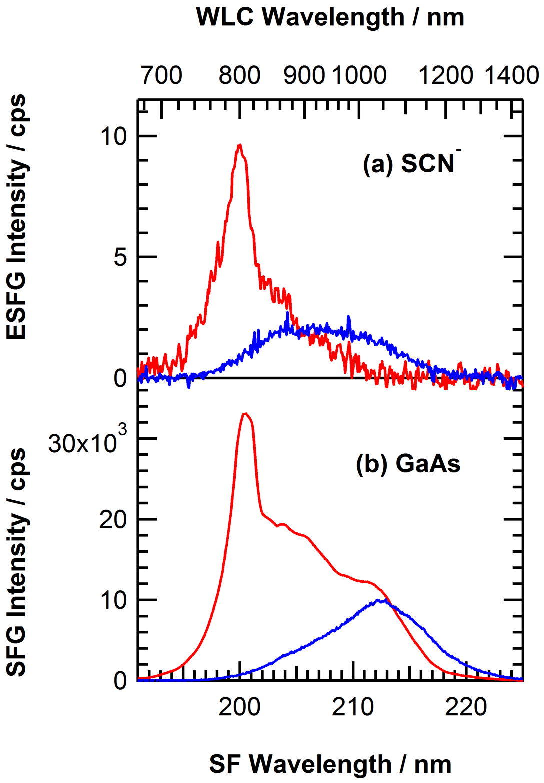


Figure 2. (a) Unnormalized ESFG spectrum of 3 M NaSCN at 298 K. (b) Non-resonant SFG spectrum of gallium arsenide (GaAs). Red (λ_{WLC}=700-1200 nm) and blue (λ_{WLC}=800-1400 nm) lines indicate experiments performed with different temporal overlap of the two incident pulses corresponding to different spectral overlap due to the positive chirp of the white light continuum pulse. The top axis corresponds to the wavelength of the white light continuum pulse mixing with the narrowband 266 nm pulse to generate the sum frequency at the wavelength on the bottom axis.

frequency pulses. The spectra of GaAs and aqueous NaSCN were acquired under the same experimental conditions.

Under the two-photon on-resonance, one-photon off-resonance condition of broadband DUV-ESFG employed here, the normalized DUV-ESFG intensity shown in Figure 1(b) can be expressed as

$$I_{\text{ESFG}} \propto |\chi^{(2)}|^2 \propto \sum_n \frac{|\mu_{0n}(\alpha_{0n})_{\text{TPA}}|^2}{(\omega_{\text{CTTS}} - \omega_{\text{SFG}})^2 + \Gamma_{\text{CTTS}}^2}$$

where $\chi^{(2)}$ is the second-order nonlinear susceptibility, μ_{0n} is the transition dipole matrix element and $(\alpha_{0n})_{\text{TPA}}$ is the two-photon absorption polarizability tensor element connecting the ground state and CTTS excited state n, Γ_{CTTS} is the linewidth of the CTTS transition, ω_{CTTS} is the transition energy between the ground state and CTTS state, and ω_{SFG} is the sum frequency of the incident photons.[27,28] By plotting $|\chi^{(2)}|^2$ vs. ω_{SFG}, the interfacial electronic $|\chi^{(2)}|^2$-power spectrum is obtained. The nonresonant background signal from the solvent is assumed to be negligibly weak, since no SFG signal was observed in the absence of thiocyanate (i.e. neat water).

Figure 1 compares the bulk linear absorption spectrum of thiocyanate and the interfacial $|\chi^{(2)}|^2$-spectra obtained by pointwise resonant ESHG[6] and broadband DUV-ESFG. Compared to the pointwise resonant ESHG spectra obtained at five wavelengths at molar concentrations (1-3 M) reported previously,[6] the broadband DUV-ESFG spectrum is consistent and of much higher quality. The most striking difference between the bulk linear absorption spectrum and interfacial $|\chi^{(2)}|^2$-spectrum is that the lower energy CTTS band observed in the bulk spectrum is not observed at the air/water interface.

The interfacial solvation environment of thiocyanate is distinctly different from that in the bulk. In bulk water, neutron diffraction experiments predict an "eggshell"-like solvation shell with 2-3 water molecules hydrogen-bonded to N and weakly correlated to S at concentrations of 1-3 M with no significant dependence on salt concentration.[29] *Ab initio* calculations with DFT-based interaction potentials predict solvation around the

S-terminus to resemble that of iodide and solvation around the N-terminus to be similar to fluoride.[30] As thiocyanate moves from the bulk to the interface, it can lose water molecules from its solvation shell, likely from the S-terminus, altering its solvation environment. Viswanath et al. observed changes in the vibrational SFG spectra of the water OH stretch region (3000-3800 cm^{-1}), indicating perturbation of the interfacial water hydrogen bonding structure upon addition of KSCN at molar concentrations (1-7 M).[14,15] Furthermore, SCN$^-$ is predicted to alter its charge distribution as the ion moves to the interface,[30] which is less likely to be significant in spherically symmetric anions such as iodide. The absence of the lower energy CTTS band in the interfacial spectrum suggests a significantly different solvation environment and/or state of the thiocyanate ion at the air/water interface, as compared to the bulk.

In the microscopic picture, the molecular nonlinear polarizability with the sum frequency being on-resonance with an electronic transition, e.g. CTTS band, is proportional to the direct product of the transition moment (μ_{0n}) and the two-photon absorption polarizability tensor ($(\alpha_{0n})_{\mathrm{TPA}}$).[28] For interfacial thiocyanate, the ground and/or excited state energy levels corresponding to the CTTS transitions may shift due to the different solvation environments and/or the charge distribution of the ion. This could lead to significantly increased Franck-Condon overlap for the higher energy CTTS band and significantly reduced Franck-Condon overlap for the lower energy CTTS band, which would be consistent with the observed interfacial spectrum. The increased inhomogeneity of solvation environments[31] and orientational constraints in the interfacial region[14–16] may also affect the population distribution of the ground and excited states of the thiocyanate ion.

The high salt concentrations used in the present study can also influence the interfacial water structure and electronic states involved in the CTTS transitions. For the bulk concentration (3 M) used in the experiments presented here, the ratio of all ions to water molecules is ca. 1:10, so we might expect some ion-ion effects to be present. However, aqueous potassium thiocyanate (3 M) showed nearly identical interfacial CTTS spectra to that of the sodium salt, so interfacial cation effects appear to be minimal. This is consistent with molecular dynamics simulations by Tesei et al. at high concentrations (5 mol kg^{-1}) which showed cations (Na^+, K^+) to have negligible influence on the interfacial properties of thiocyanate at the air/water interface, even though the bulk properties showed significant differences.[16] In ESHG experiments at the dodecanol/water interface in our group, sodium and potassium thiocyanate salts (0-3 M) exhibited similar Gibbs free energies of adsorption, within experimental error, suggesting that cation effects at the interface for thiocyanate are minimal.[7] On the other hand, Venkateshwaran et al. predicted the occurrence of “water-bridged” configurations at high ion concentrations, wherein a few hydration water molecules are shared by like-charged ions at and near the interface.[32] An ultrafast 2D IR pump-probe study has shown that ion clusters begin to form in bulk solution at concentrations greater than ~10^{-3} M.[33] For 2 M KSCN, Bian et al. report that ~35% of thiocyanate anions in bulk are present in cluster form, with diluted solutions having fewer, smaller, and tighter ion clusters.[33] Additionally, at high salt concentrations, the formation of an electric double layer (EDL) in the interfacial region can induce ordering of water molecules which, in turn, will lead to further altered solvation environments at the interface.[34,35] The presence of “water-bridged” configurations, ion clusters, and the induced ordering of water molecules due to the EDL at the air/water interface at high bulk concentrations may thus strongly influence the interfacial CTTS spectra.

The upper limit of salt concentrations used in broadband DUV-ESFG experiments of thiocyanate is limited by formation of photoproducts leading to turbidity in the solution and concomitant signal interference. Upon UV irradiation of solutions with bulk concentrations greater than 3 M, formation of sulfur oligomers and elemental sulfur have been observed, consistent with the second reaction in the photochemical scheme presented above.[21,36] On the other hand, the lower limit of usable concentration is established by the ESFG signal intensity and acquisition time. Because SFG is a second-order process, the signal is inherently weak and reducing the bulk concentration below 3 M would lower the signal count, leading to decreased signal-to-noise in the spectra. Longer acquisition times would increase the possibility of introducing contaminants from the lab environment (e.g. oils, dust particles) that would affect the ESFG signal from the solution interface.

In light of the results presented here, previously reported results for the thermodynamics of thiocyanate adsorption to aqueous interfaces obtained via pointwise measurements of resonant ESHG signal intensity as a function of concentration and fits to a Langmuir adsorption model[5–8] should be re-examined to determine if the spectral changes observed herein may have affected the interpretation of those data. In resonant ESHG spectroscopy, as developed in our group, the CTTS transition is two-photon resonant with the second harmonic of the input fundamental frequency.[11] The Langmuir adsorption model used assumes that the orientation of surface species and the magnitude of the microscopic nonlinear polarizability remain constant over the concentration range and that multiple adsorbing species do not interact with each other.[6,11] A recent molecular dynamics study by Tesei et al. predicted the tilt angle to be 45° on average in the outermost layer, while in the subsurface region (0.1-0.5 nm), anions were predicted to be oriented perpendicular, on average, to the surface.[16] If there is any concentration dependence on the orientation, it could lead to a breakdown in the assumptions of the Langmuir adsorption model and might change the magnitudes of the previously calculated thermodynamic quantities. Furthermore, as mentioned above, thiocyanate clusters form in bulk solution at moderate to high concentrations (>10^{-3} M), with concentration effects depending on the number, size, and tightness of the clusters.[33] At the interface, differing degrees of cluster formation at different concentrations could result in concentration-dependence in the measured CTTS spectra and a breakdown of the Langmuir adsorption model, suggesting concentration-dependence in the measured free energy, enthalpy, and entropy of ion adsorption at aqueous interfaces. In other words, thiocyanate in very dilute solution may have different thermodynamic driving forces for interfacial adsorption compared to a highly concentrated solution wherein significant ion-ion interactions and perturbations to the water structure are present. To account for this unique behavior at the interface, further adjustments to the parameters and modifications to the Langmuir adsorption model would be necessary to obtain accurate thermodynamic quantities associated with interfacial ion adsorption. We hope that the present work will stimulate further development of simulations and theoretical calculations to elucidate the complex behavior of ions at aqueous interfaces.

The CTTS spectra of anions are highly sensitive to the surrounding solution environment. The results presented here and in other studies suggest that the solvation environment at the air/water interface is indeed significantly different from that of the bulk. In the $|\chi^{(2)}|^2$-spectrum of interfacial thiocyanate, we do not observe the lower energy CTTS band present in bulk linear absorption spectra. The loss of water molecules from its solvation shell, anion cluster formation and other ion-ion effects, and the different solvent environment at the air/water interface, combined with changes in the charge distribution and preferential orientations at the interface, could have significant influence on the electronic energy levels involved in the CTTS transitions. The exact physical origins of the differences observed in the interfacial CTTS spectrum are not yet clear. Further experiments and associated theoretical studies will be necessary to extract the interesting chemical details responsible for these salient observations.

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Supporting Information

- Complete materials and methods section (PDF)

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