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INFRARED INVESTIGATIONS OF C_{60} AND C_{70} NANOPARTICLE INTERACTIONS WITH THE AMIDE FUNCTIONALITY IN FORMAMIDE

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ABSTRACT. Fourier transform infrared spectroscopy was used to investigate the interactions between C_{60} and C_{70} nanoparticles and the amide functionality in formamide. Infrared spectra were collected for neat formamide, formamide in a toluene environment, formamide in a C_{60} toluene environment, and formamide in a C_{70} toluene environment. A Digilab FTS 7000 infrared spectrometer and a ZnSe circle cell were used for spectral data collection. Challenges were expected and encountered because of solubility compatibilities of the reagents and special ATR spectral collection issues; however, these challenges helped shape the final form of the study and are addressed in the paper. Shifts of the carbonyl, stretching frequency to higher wavenumbers, were observed when formamide was treated with both the C_{60} and C_{70} indicating nanoparticle interactions with its amide functionality. The spectrum of neat formamide showed a carbonyl absorption near 1665 cm^{-1}; the spectrum of formamide in a toluene environment showed a carbonyl absorption near 1669 cm^{-1}; and the spectra of formamide in a toluene environment with C_{60} and C_{70} showed carbonyl absorptions near 1677 cm^{-1}. Spectral subtraction was used to identify the carbonyl absorptions (near 1690 cm^{-1}) for the nanoparticle (C_{60} and C_{70}) - formamide complexes.

Keywords: infrared spectroscopy, nanoparticles, C60 & C70, fullerenes, fullerene/nanoparticle interactions

INTRODUCTION

Significant interest in the interactions of diverse molecular systems with C_{60} and C_{70} nanoparticles has motivated a variety of studies using a number of analysis methods (Holleman et al. 1999; Kyzyma et al. 2008; Jurow et al. 2012; King et al. 2012; Kyrey et al. 2012; Tropin et al. 2013; Bowles et al. 2014). This paper reports the results of an infrared spectroscopy study of the interactions between C_{60} and C_{70} nanoparticles and the important functionality of amide in formamide using toluene as a solvent environment (Aksenova et al. 2013). The initial plan of the investigation was to prepare solutions of formamide with C_{60} and C_{70} nanoparticles and use infrared spectroscopy to seek shifts in the carbonyl absorption of the formamide resulting from its interactions with the nanoparticles. It is well known that C_{60} and C_{70} nanoparticles dissolve in aromatic solvents such as toluene to form colored solutions; C_{60} in toluene is blue, while C_{70} in toluene is red (Ruoff et al. 1993). Certainly, challenges resulting from solubility compatibilities of the relatively polar formamide and the nonpolar toluene solvent needed for the nanoparticle solubility were expected.

Initial spectral collections gave promising results. The infrared spectrum of formamide in a toluene solution saturated with C_{60} showed a shift in the carbonyl absorption to higher wavenumbers compared to formamide in pure toluene. Confirmation experiments, however, generated confusing results by sometimes showing shifts and sometimes showing no shifts. Spectra were collected at different concentrations of the formamide in the toluene C_{60} solvent system in an attempt to address the confusing results, but the experiments yielded the same results of sometimes showing a shift and sometimes showing no shift. Spectra were collected in a circle cell which is an attenuated total reflectance (ATR) device. Some compounds can bind to the ATR crystal rod forming a coating of compound on its surface, and spectral collection showed that formamide is a compound that binds to the ATR rod used in the study. ATR devices also measure the spectrum of the environment near the ATR crystal surface. Possible contributions to the shift and no shift observations in the repeated experiments could be competitive binding of formamide

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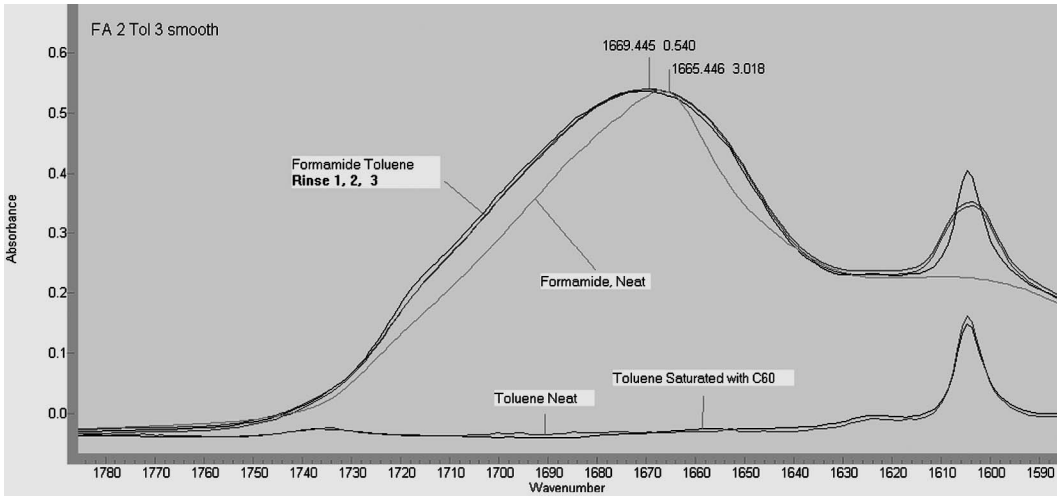

Figure 1.—The spectrum of neat formamide in the circle cell, the spectra of formamide on the circle cell rod after each of three rinses with toluene (the rinse process was over a six hour period of time), the spectrum of toluene, and the spectrum of toluene saturated with nanoparticles (C_{60}). Spectra are auto-scaled to equal intensity along the absorbance axis to clarify shifts or profile changes along the wavenumber axis.

between the ATR rod and nanoparticles along with the thickness of formamide coating on the ATR rod. These notions motivated a new plan of study focusing on nanoparticle interactions with a film of formamide coated on the ATR rod surface.

METHODS AND RESULTS

New experiments with consistent observations.—A Digilab FTS 7000 infrared spectrometer and a circle cell fitted with a ZnSe ATR rod was used to collect spectra for the investigation by averaging 150 scans at a spectral resolution of two wavenumbers. The empty circle cell was used as the background single beam spectrum for spectral collection. The spectrometer was purged with dry air for one hour prior to spectral collection to remove potentially interfering atmospheric water vapor. Figure 1 shows the spectra of neat toluene, toluene saturated with C_{60} nanoparticles, and neat formamide with its carbonyl absorption at 1665 cm^{-1}. The spectra in Fig. 1 show that toluene and toluene saturated with nanoparticles do not exhibit spectral absorptions in the formamide carbonyl spectral region. Next, the neat formamide was emptied from the circle cell, and the circle cell was rinsed with toluene three times with spectra being collected on the toluene in the circle cell during each rinse. Figure 1 shows that formamide remained bound to the ATR rod after each rinse with toluene. The spectra in all Figures are auto-scaled to equal intensity along the Absorbance axis to clarify shifts or profile changes along the wavenumber axis. The rinsing of the circle cell with toluene and the collection of the spectrum of formamide bound to the ATR rod in a toluene environment required about two hours for each spectrum including cell rinsing, spectrometer purge time, and spectral data collection. The multiple rinsing process of the circle cell with toluene and recollections of the spectra of the formamide coated on the ATR rod during each rinse, therefore, were completed over a six hour period of time. Figure 1 shows an observable shift to higher wavenumbers after the first rinse with no further shifts after the second and third rinses. This observation indicates that after two hours of immersion in toluene, a coating of formamide remained bound to the ATR rod and also that the stable coating of formamide was bound to the ATR rod after six hours of immersion in toluene. A reasonable description of the "rinsed circle cell spectra" is formamide bound to or coated on the ATR rod in a toluene environment.

After the cell rinsing process was completed, the toluene in the circle cell was replaced with toluene saturated with C_{60}, and spectra recollected. Spectra of formamide bound to the ATR rod immersed in toluene saturated with C_{60} were collected immediately, three hours,

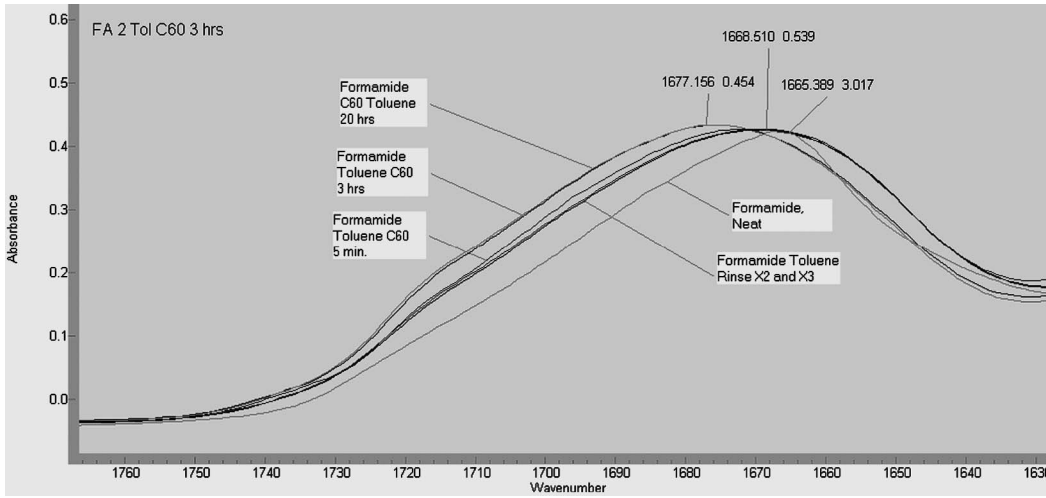

Figure 2.—The spectrum of neat formamide in the circle cell; the spectra of formamide on the circle rod after rinse 2 and 3; and the spectra of formamide on the circle rod in a toluene saturated with C_{60} environment at five minutes, three hours, and twenty hours after the addition of toluene saturated with C_{60}. Spectra are auto-scaled to equal intensity along the absorbance axis to clarify shifts or profile changes along the wavenumber axis.

and twenty hours after the addition of the toluene saturated with C_{60} (Fig. 2). A small but observable shift in the formamide carbonyl absorption to higher wavenumbers occurred immediately after the addition of toluene saturated with C_{60} with a major shift observed three hours after the addition. No further shift in the carbonyl absorption was observed after sitting for twenty hours. The observed shifts immediately, after three hours, and after twenty hours suggest a C_{60} interaction with the formamide coating on the ATR rod in a toluene solvent environment. Similar experiments were performed with formamide and toluene saturated with C_{70}, and shows results similar to the formamide-C_{60} experiments (Fig. 3).

DISCUSSION

The carbonyl infrared absorption in amide functionality is characterized by an absorption peak below 1700 cm^{-1} compared to "normal" carbonyl absorption peaks observed above 1700 cm^{-1}. This observation has been explained by the lone pair electrons on the nitrogen being delocalized into the amide carbon–nitrogen chemical bond generating a minor resonance structure with a carbon–oxygen single bond. This minor resonance structure adds single bond character to the carbonyl bond and contributes to the lower wavenumbers observed for the carbonyl infrared absorption in amide functionality (Avram & Mateescu 1970).

The observed shifts to higher wavenumbers of the carbonyl absorption for formamide interacting with the nanoparticles can be explained by the nitrogen lone pair electrons being donated to the nanoparticles resulting in less delocalization of those electrons into the carbon–nitrogen amide bond, less stability of the carbon–oxygen, single-bond resonance structure, and more stability of the carbon–oxygen, double-bond resonance structure. Many studies suggest that C_{60} and C_{70} are good electron acceptors for molecular systems (Charvet et al. 2012; Schubert et al. 2013; Stranius et al. 2014). Certainly, a reasonable explanation is that the lone pair electrons of formamide donate into the antibonding MO's of the delocalized electrons on the surface of the C_{60} and C_{70} molecules (Feng et al. 2008). A resonance structure model of formamide interacting with nanoparticles and the resulting impact of the nanoparticle bonding on the formamide carbonyl infrared absorption is shown in Fig. 4. So, observed shifts of the formamide carbonyl absorption to higher wavenumbers in both toluene–C_{60} and toluene–C_{70} environments are consistent with formamide bonding to the nanoparticles through the lone pairs of nitrogen in the amide functionality of the formamide.

Analysis enhancement and confirmation through spectral subtraction.—The spectra and obser-

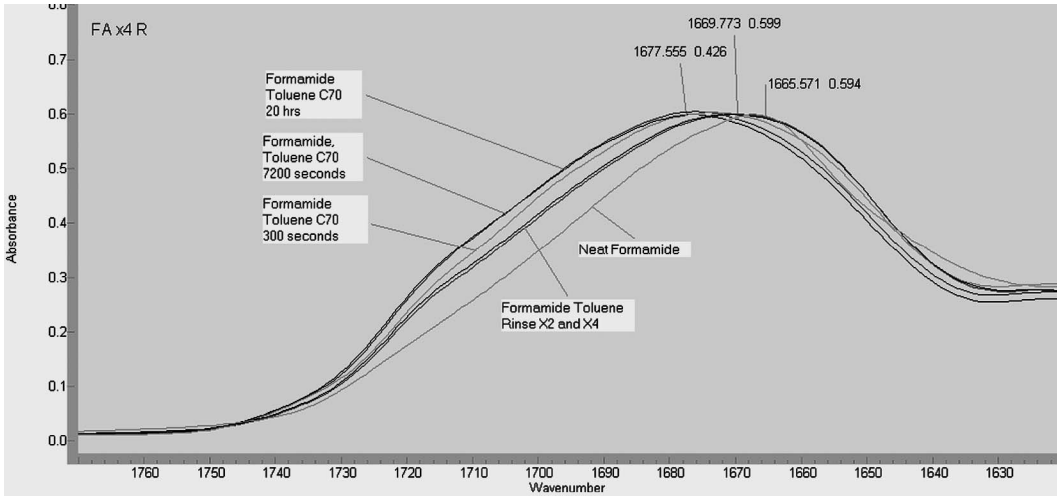

Figure 3.—The spectrum of neat formamide in the circle cell; the spectra of formamide on the circle rod after rinse 2 (three hours) and rinse 4 (six hours); and the spectra of formamide on the circle rod in a toluene saturated with C_{70} environment at five minutes, two hours, and twenty hours after the addition of toluene saturated with C_{70}. Spectra are auto-scaled to equal intensity along the absorbance axis to clarify shifts or profile changes along the wavenumber axis.

vations presented to this point result from "simple" collection of FT IR spectral data. Spectral subtraction has been shown to be a useful tool in the separation of spectral absorptions resulting from mixed absorbing species systems, and it was used in this study to suggest the likely carbonyl absorption of the formamide bound to the nanoparticles. In addition, spectral subtraction was used to address the potential of solvent interference in the spectral analysis (Gillette & Koenig 1984; Honigs et al. 1985; Yang 1994; Siyuan et al. 2010).

The spectra of formamide coated on the ATR rod in toluene saturated with C_{60} (Fig. 2) and in toluene saturated with C_{70} (Fig. 3) are very likely the summations of spectra of an equilibrium mixture of formamide bound and unbound to the nanoparticles. The equilibrium

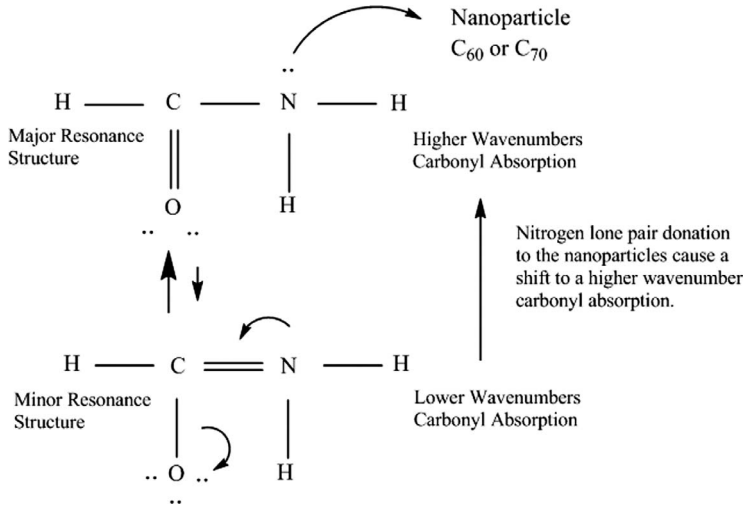

Figure 4.—A resonance structure model suggesting nitrogen, lone pair donation to the nanoparticles (C_{60} and C_{70}) that shifts stability toward the resonance structure with the double bonded carbonyl and supports a shift of the carbonyl absorption to higher wavenumbers.

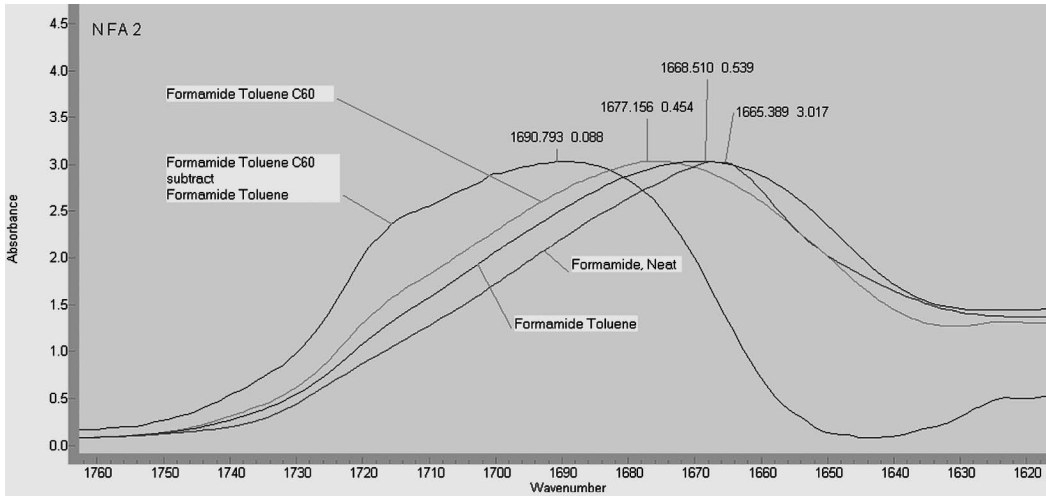

Figure 5.—The spectrum of neat formamide in the circle cell; the spectrum of formamide on the circle rod in a toluene environment; the spectrum formamide on the circle rod in a toluene saturated with C_{60} environment; and the spectrum resulting from spectral subtraction of formamide on the circle cell rod in a toluene saturated with C_{60} environment minus the spectrum of formamide on the circle rod in a toluene environment. The subtraction process yields a carbonyl absorption of formamide interacting with C_{60} in a toluene environment at approximately 1691 cm^{-1}. Spectra are auto-scaled to equal intensity along the absorbance axis to clarify shifts or profile changes along the wavenumber axis.

mixture likely has contributions from chemical bounding character between formamide and nanoparticles, the notion that the interaction takes place on the outer surface of the formamide coating, and the thickness of the formamide coating on the ATR rod. Since the spectra of both the equilibrium mixture along with formamide coated on the ATR rod unbound to

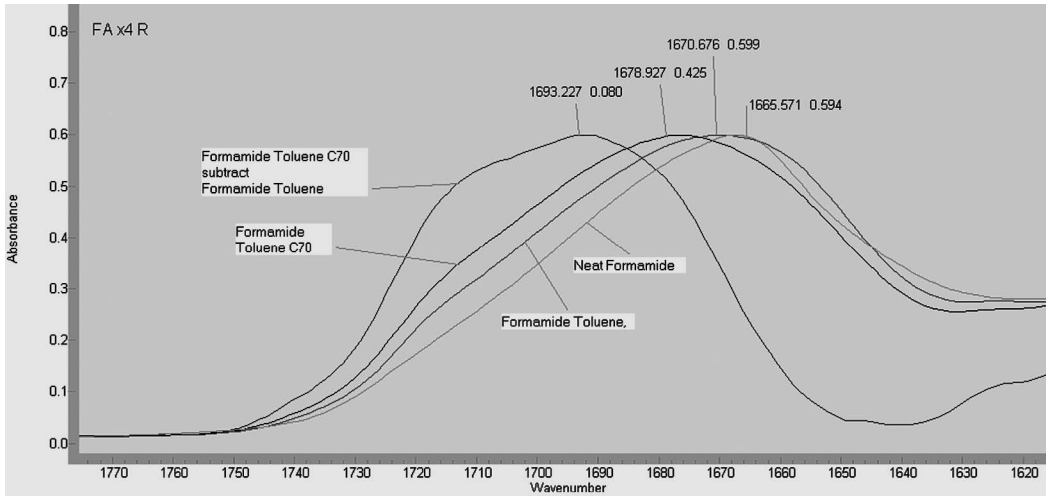

Figure 6.—The spectrum of neat formamide in the circle cell; the spectrum of formamide on the circle rod in a toluene environment; the spectrum of formamide on the circle rod in a toluene saturated with C_{70} environment; and the spectrum resulting from spectral subtraction of formamide on the circle cell rod in a toluene saturated with C_{70} environment minus the spectrum of formamide on the circle rod in a toluene environment. The subtraction process yields a carbonyl absorption of formamide interacting with C_{70} in a toluene environment at approximately 1693 cm^{-1}. Spectra are auto-scaled to equal intensity along the absorbance axis to clarify shifts or profile changes along the wavenumber axis.

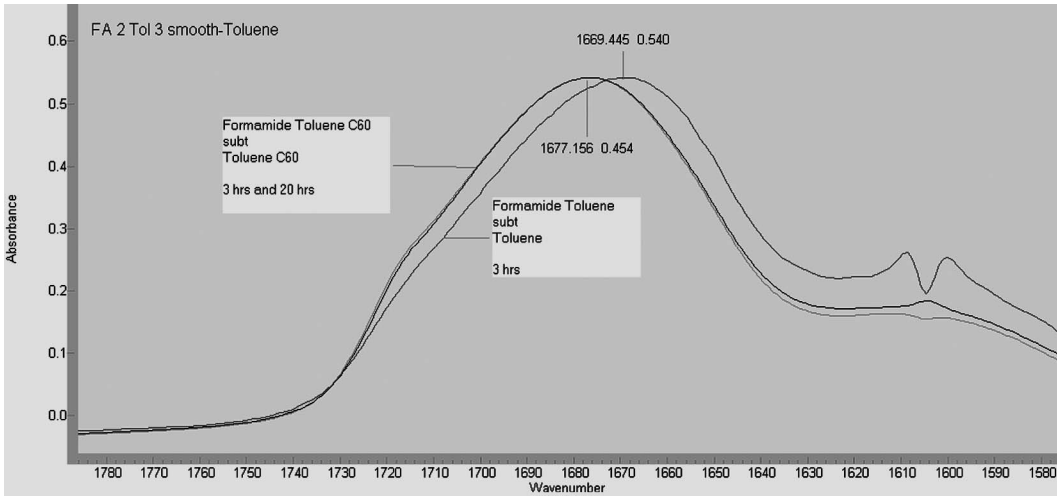

Figure 7.—The spectrum of formamide coated on the circle cell rod in a toluene environment minus the spectrum of toluene in the circle cell and the spectra of formamide coated on the circle cell rod in a toluene with C_{60} environment at three hours and twenty hours minus spectrum of toluene with C_{60} in the circle cell. Spectra are auto-scaled to equal intensity along the absorbance axis to clarify shifts or profile changes along the wavenumber axis.

nanoparticles were measured, the spectra of the formamide coated on the ATR rod bound to the nanoparticles can be obtained by spectral subtraction. Figure 5 shows the result of the spectral subtraction of the spectrum of formamide coated on the ATR rod in a toluene environment saturated with C_{60} minus a subtraction factor times the spectrum of formamide coated on the ATR rod in a toluene environment. Figure 6 shows a similar result for spectral subtraction of the spectrum of formamide coated on the ATR rod in a toluene environment saturated with C_{70} minus a subtraction factor times the spectrum of formamide coated on the ATR rod in a toluene environment.

The subtraction factor that yielded a reasonably good base line leading into and out of the carbonyl absorption for the subtraction process was about 0.6. The spectra resulting from this spectral subtraction process represent the carbonyl absorptions of formamide bound to the ATR rod interacting with C_{60} (Fig. 5) and interacting with C_{70} (Fig. 6). The subtracted spectra show a fairly broad carbonyl absorptions near 1691 cm^{-1} for formamide bound to C_{60} (Fig. 5) and 1693 cm^{-1} for formamide bound to C_{70} (Fig. 6).

Figure 1 shows that the toluene and toluene saturated with C_{60} nanoparticles do not have spectral features that would interfere with spectral interpretation; however, spectral subtraction was used to confirm the lack of interference from the solvent environments. Figure 7 shows the results of the spectral subtraction of the spectrum of formamide coated on the ATR rod in a toluene environment minus a subtraction factor times the spectrum of toluene. Figure 7 also shows the results of spectral subtraction of the spectrum of formamide coated on the ATR rod in a toluene saturated with C_{60} environment minus a subtraction factor times the spectrum of toluene saturated with C_{60}. The subtraction factors yielding good baselines were near 0.9. It is clear from Fig. 7 that the spectra for both formamide coated on the ATR rod interacting with C_{60} and formamide coated on the ATR rod with their respective solvent spectra removed by spectral subtraction show the identical shift observed in Fig. 2, and this analysis supports formamide–nanoparticle interactions in a toluene environment.

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