Supporting Information

Substrate influence on the interlayer electron-phonon couplings in fullerene films probed with doubly-resonant SFG spectroscopy†

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Supporting Information Provided:

S1. Delay Dependence: Early in our investigation, we saw evidence of a non-resonant (NR) background signal from the C_{60} films which were manifested in the DR-SFG spectra. Since the fullerene is known to exhibit semiconductor behavior and because we tuned our visible energy above the molecular electronic band gap in our doubly-resonant experiments, the nonlinear (NR) response (possibly resulting from surface free-electrons) was unsurprising. The NR background was observed on all three substrates which confirmed that it was obtained from the fullerene film and not from the substrates. While this the NR component in nonlinear spectroscopy can yield interesting information, we were more focused on elucidating the resonant nonlinear responses from the fullerene films. The resonant responses from laser pulses are generally longer-lived compared to that of non-resonant responses. With this in mind, we simply increased the time-delay of the incident visible pulses with respect to the IR pulses. We were able to reduce the signal intensity of the NR background while not significantly altering the appearance of the resonant vibrational modes. Fig. S1 shows NR background suppression as a function of incident Vis pulse time-delay for C_{60} on gold at 532 nm Vis. The background was shorter lived using the green to blue lasers so the time-delay used was approximately 600 fs at these wavelengths. A rather longer delay was needed for the yellow to red lasers because the NR background appeared to persist longer. The various lifetimes of these resonance present an interesting aspect to be studied in more detail in the future.

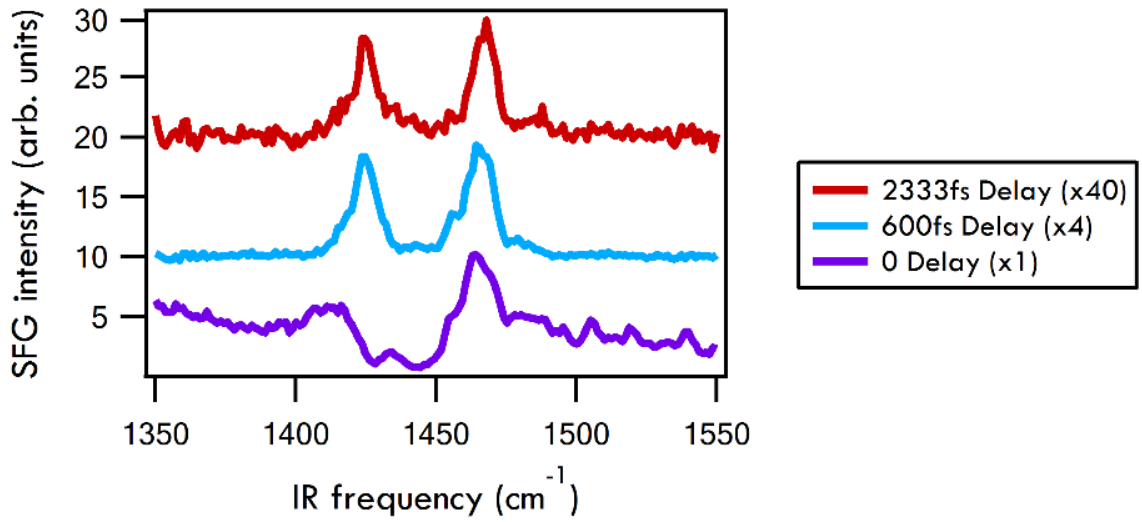

Fig. S1. DR-SFG for a C60/Au film as a function of the delay between the Vis and IR pulses.

S2. Power Dependence: The accompanying figure shows the visible pulse power influence on the spectral line-shapes for the C_{60} fullerene at 650 nm Vis. The orange lines were acquired using a low power visible pulse (~125 nJ/pulse) and the purple lines were acquired using a relatively high power visible pulse (~60 μJ/pulse) after irradiating the same spot on the film for approximately twenty minutes. This experiment accomplished two primary objectives. We first established that the low power spectra obtained matched the spectra obtained during our main experiments and discussion identically. Second, we established that exposing the fullerene films to relatively high powers altered the SFG spectra obtained. The A_g mode was red-shifted and the band at 1440 cm^{-1} saw an increase in intensity. This experiment was repeated using a 532 nm Vis pulse and similar results were obtained.

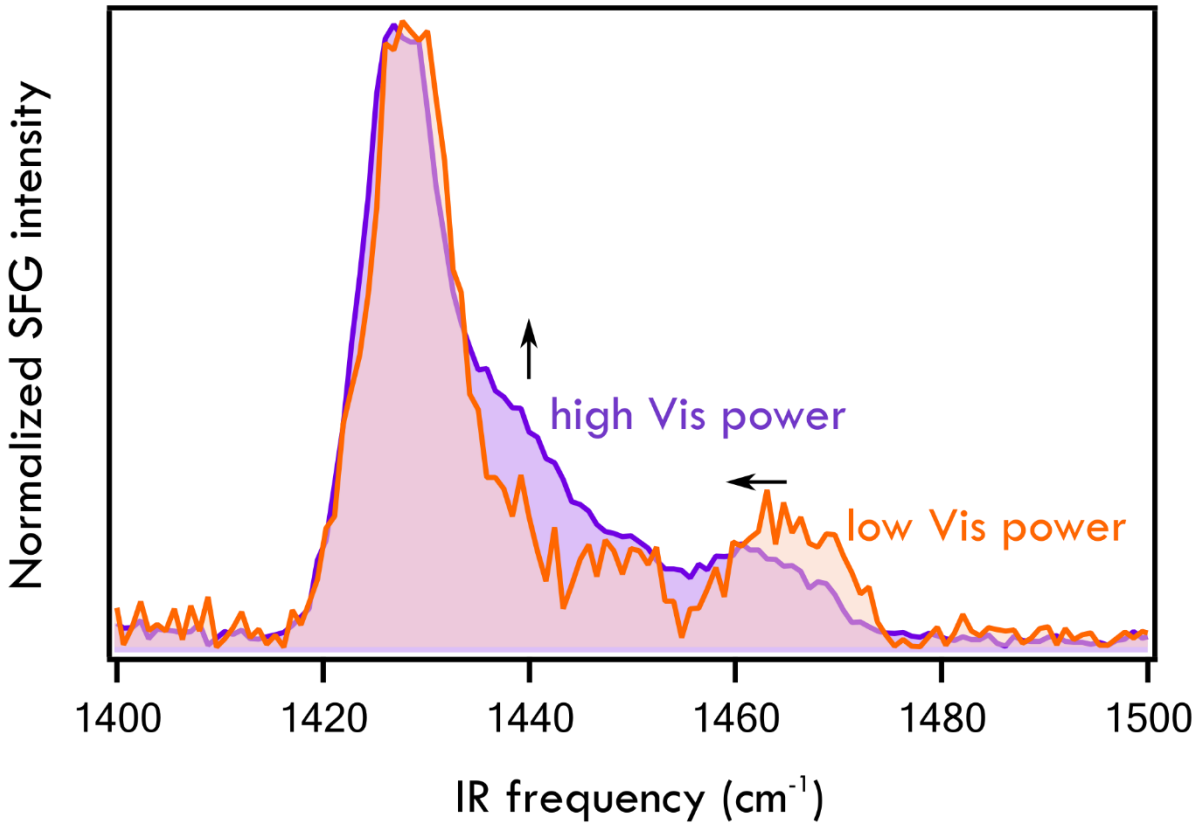

Fig. S2. Power dependence of fullerene film on gold substrate at 650 nm Vis excitation. Orange shows ~125 µJ power. Purple shows ~60.0 mJ power after 20 min. irradiation.