Response to Comment on “Engineering coherence among excited states in synthetic heterodimer systems”

Dugan Hayes, Graham B. Griffin, Gregory S. Engel*

Halpin, Johnson, and Miller contest our assignment of quantum beating signals observed in the two-dimensional electronic spectra of a series of fluorescein heterodimers to electronic coherences. Here, we present resonance Raman spectra, statistical analysis on multiple data sets, and an explanation of differences between the family of molecules described in our Report and the homodimer examined by the commenters. We contend that these results all support our assignment of the beating signals to electronic coherences.

In our paper, we identify quantum beating signals observed in the two-dimensional (2D) electronic spectra of a series of fluorescein heterodimers that are “consistent with the presence of persistent electronic coherences” (1). We distinguish electronic coherences from vibrational coherences by identifying quantum beating signals in the heterodimer spectra that move in a prescribed manner, using small chemical modifications to modify the electronic energy levels across the series of heterodimers. We then verify that these signals do not appear in control experiments performed on unlinked monomers. This approach to identifying electronic coherences is intended as a straightforward means to demonstrate the presence of electronic coherences to Science’s broad audience. In their Comment, Halpin, Johnson, and Miller (2) call for a more detailed and technical analysis of the quantum beating signals measured, citing “major issues with both the collection and the analysis of the four-wave mixing signals,” and find our assignment of certain beating features to electronic coherences “unconvincing.” Here, we present additional control data and more detailed analysis of the observed quantum beating signals, ultimately strengthening our assignment of these signals to electronic coherences. We also clarify several aspects of the original paper that have caused some confusion in the Comment and associated discussion.

The two monomers in our fluorescein heterodimers are linked by dual piperazine bridges. This rigid, bidentate linking strategy holds the two chromophores at a fixed relative orientation ~10 Å apart, a molecular arrangement inspired by photosynthetic pigment protein complexes. In the absence of π-stacking (which is known in fluorescein but forbidden in our dimers by the rigid linkers), we expect our heterodimers to reside in the weak-coupling regime. In this picture, the lowest-lying excitations of the heterodimer should remain well localized on the two monomer chromophores. That said, we do not mean to “infer that the rigidity of the molecules plays an essential role in suppressing dephasing,” as stated in the Comment. We make no claim to have proven that such a design principle is required for coherences to persist. Support for the weak-coupling picture was recently published by Akimov and Prezhdo (3). They calculate the electronic states of our series of fluorescein heterodimers in a realistic solvent environment by combining molecular dynamics simulations with configuration interaction calculations that use the semiempirical ZINDO (Zener’s intermediate neglect of differential overlap) Hamiltonian. Figure 3 of (3) shows that the electron density in the molecular orbitals nearest the optical gap is well localized on single monomers within the dimer, indicating that coupling between these electronic states is not strong enough to mix the states substantially. They also calculate electronic energy gaps and electronic coherence lifetimes and conclude that their results are consistent with our measurements.

Another important design aspect is the selection of heterodimeric compounds instead of homodimers. With a heterodimer, we establish control over spectral separation of the monomer-localized energy levels independent of the coupling strength. The energy gap is partially determined by electrostatic effects of the chemical substituents, making the energy gap less sensitive to conformational changes that might drive dephasing. With a homodimer, coupling controls the energy gap completely and leads to strong mixing—i.e., delocalization of the states across both monomers. As shown by Chen and Silbey, such a situation will naturally lead to rapid dephasing in the presence of any noise affecting the off-diagonal element of the Hamiltonian (4). This effect can be exacerbated by disorder (static or dynamic) in the configuration of the linker. In this regard, our piperazine-linked heterodimers are fundamentally different from the butyl-linked homodimers examined by Halpin, Johnson, Miller, and co-workers (5, 6).

Comparison of the room-temperature absorption spectra of the monomers, shown in figure S1 of our original paper (1), with absorption spectra of the dimers taken at 77 K, confirms the weak electronic-coupling picture. As shown in fig. S1 of this Response, the 77-K absorption spectrum of the dimer AB can be fit to a sum of four Gaussians. The position of the two lowest-energy Gaussians gives an energy spacing of 522 cm⁻¹ between the two low-lying electronic excited states predicted to participate in the measured coherence. The fits of the room-temperature monomer spectra shown in figure S1 of (1) predict an energy gap between the uncoupled monomers of 503 cm⁻¹. The energy gap predicted by the monomer spectra is indistinguishable from the energy gap observed in the dimer, given that the resolution of the absorption spectra is ~0.5 nm, corresponding to ~20 cm⁻¹ at 530 nm. Temperature-dependent hypsochromic shifts of the peaks in the 77-K dimer spectrum relative to the room-temperature monomer spectra should not affect the coupling. We therefore conclude that electronic coupling in the dimer AB is not more than a few tens of wave numbers. Similar analysis supports the same conclusion for dimer AC. For dimer BC, this upper limit to the coupling strength cannot be experimentally verified because the features of the 77-K absorption spectrum cannot be resolved. However, given the similarity of the molecules, it is reasonable to expect similar coupling strength. We are unable to discern directly from our data the degree of vibronic mixing, but our observations are consistent with interpretation within the Born-Oppenheimer approximation.

Halpin, Johnson, and Miller question our choice to present analysis of unphased or, in their words, “homodyne-detected” 2D spectra. Of course, the spectra are in fact heterodyne detected according to the methods of Brixner et al. (7), but the commenters’ meaning is clear. In figures 3 and S2 of (1), we present “absolute-value 2D spectra”—i.e., the square modulus of the measured, complex field. As acquired, the complex data contains a global phase rotation that can be removed through a procedure called “phasering,” as described in detail by Brixner et al. (7), permitting analysis of the more well-resolved real part of the signal field. However, errors in the phasing procedure can introduce oscillatory artifacts that are particularly problematic in the type of analysis presented in (1). We chose to analyze the absolute-value data to avoid the possibility of introducing such artifacts. Rather than try to spectroscopically resolve signals from electronic and vibrational coherences, we assume that both will be present in the integrated region of our spectrum and employ chemical modifications to identify electronic features. Halpin, Johnson, and Miller dispute that the beating signals we assign to electronic coherences.
Fig. 1. Comparison of beating spectra and resonance Raman spectra of dimers. Beating spectra (top panels), measured by taking the magnitude of the Fourier transform of waiting-time traces from 2D electronic spectrometry measurements of fluorescein heterodimers, compared with resonance Raman spectra of the same compounds (bottom panels). For the beating spectra, both the frequency-space data points measured (dots) and Fourier interpolations (solid black curves) are shown. Multiple data sets for dimers AB (eight data sets) and BC (four data sets) were averaged. Error bars shown for the measured points represent ±1 SDM, while the 1-SDM confidence intervals in the interpolated beating spectra are shown as solid gray regions. The dimer AC spectrum is from one representative data set (see fig. S4 for a comparison of both data sets acquired.) Peaks assigned to Raman modes are shown as vertical dashed lines. Peaks assigned to electronic coherences are shown as solid vertical colored lines.

can be classified as “long-lived.” In their analysis, they direct attention toward the absolute lifetime of the coherence, and they are correct that these electronic coherences have an e-folding time of at most a few beat periods. However, our data shows that these coherences between excited states survive substantially longer than coherences between those same excited states and the ground electronic state. The lifetimes of these latter coherences can be extracted from the same data when it is presented in coherence time and rephasing frequency space rather than in frequency-frequency space. As described in (J), these lifetimes were calculated to be approximately 15 fs at a waiting time of \( T = 20 \) fs. When we characterize coherences between excited states as “persistent,” we are concerned with this internally calibrated metric. Similarly “persistent” electronic coherences identified in photosynthetic pigment protein complexes provided the primary motivation for our work.

Halpin, Johnson, and Miller also question the amplitude of low-frequency oscillations in the waiting-time trace for dimer BC, presented in figures 3 and S2 of (J), stating that 200 cm\(^{-1}\) oscillations should have an amplitude “at least an order of magnitude” larger than those of the other frequencies present at very early times. This analysis presumes that the detected linewidths differ substantially between vibrational and electronic peaks in our data, which we do not observe. All peaks in the beating spectra shown in Fig. 1 have comparable linewidths, demonstrating that the amplitudes of the oscillations at \( T > 40 \) fs are consistent with the spectrum calculated directly by transforming the waiting-time trace.

Halpin, Johnson, and Miller contend that the beating spectra presented in figures 4, S3, and S4 of (J) contain “numerous ambiguities” and that resonance Raman spectroscopy measurements are necessary to assign the features in these spectra to vibrational and/or electronic coherences. This is an excellent suggestion (although we recognize that selection rules will differ), and we present resonance Raman spectra of our compounds in Fig. 1, fig. S2, and table S1. We have assigned frequencies to the peaks in each monomer and dimer resonance Raman spectrum between 150 and 800 cm\(^{-1}\), and we have also correlated the frequencies of the peaks in the dimer Raman spectra with those from the component monomers. This analysis strategy for identifying vibrational modes provides improved resolution compared to the approach that we took in the original paper, and we thank Halpin, Johnson, and Miller for the suggestion.

As Halpin, Johnson, and Miller state, it is possible for new Raman modes of the dimer to exist in this frequency range that do not appear in the monomer Raman spectra. However, we find only one such peak in the dimer spectra, appearing at 780 cm\(^{-1}\) in the Raman spectrum of dimer AB. Furthermore, although Halpin, Johnson, and Miller characterize as ambiguous the absence in monomer \( \alpha' \) of vibrational modes that appear near 600 and 750 cm\(^{-1}\) in monomers B\(^{\prime}\) and C\(^{\prime}\), the resonance Raman results confirm that the ~750 cm\(^{-1}\) mode is present in monomers B\(^{\prime}\) (740 cm\(^{-1}\)) and C\(^{\prime}\) (750 cm\(^{-1}\)) but absent in monomer A\(^{\prime}\). Resonance Raman peaks near 600 cm\(^{-1}\) are present in all monomer spectra (575 cm\(^{-1}\) for monomers B\(^{\prime}\) and C\(^{\prime}\), 580 cm\(^{-1}\) for monomer A\(^{\prime}\)). The feature in the monomer A\(^{\prime}\) Raman spectrum may not have been observed in the original experiment because it has a much lower relative intensity than those found in the monomer B\(^{\prime}\) and C\(^{\prime}\) spectra.

Overall, nine of the eleven peaks assigned in the original control experiments are verified by the resonance Raman data (peak positions are within 34 cm\(^{-1}\), the resolution of the beating spectra in the original experiment) and are shown with much higher resolution and signal-to-noise in the resonance Raman spectra. Two vibrational modes identified in the original paper have no corresponding feature in the resonance Raman spectra: a 410-cm\(^{-1}\) peak in monomer \( \alpha' \) and a 414-cm\(^{-1}\) peak in monomer B\(^{\prime}\). We note that resonance Raman experiments cannot capture oscillations arising from nuclear coherences on the excited state, which could account for the presence of these weak features in the beating spectra from the 2D measurements. Regardless, the existence of these modes does not affect our conclusions.

Halpin, Johnson, and Miller also note the appearance of a mode at ~700 cm\(^{-1}\) in the beating spectrum of the mixture of monomers B\(^{\prime}\) and C\(^{\prime}\), shown in figure S4 of (J), which we did not assign to a vibration and which has no corresponding feature in the beating spectra of the individual monomers shown in figure S3 of (J). The resonance Raman data confirm that there is no mode in this region for either the individual monomers or the mixtures of monomers.

Comparing the resonance Raman spectra to the Fourier transforms of the waiting-time traces from the dimer 2D experiments, we find strong support for our assignment of specific peaks to electronic coherences, as shown in Fig. 1 (see the supplementary materials for a complete discussion of the data analysis methods). Peaks corresponding to the Raman modes assigned for each dimer (vertical dashed lines in Fig. 1) appear in the dimer beating spectra, as expected. The Raman spectra show only ground-state vibrational modes and cannot capture coherences among electronic states, allowing us to identify beating signals in
the dimers that are consistent with electronic coherence. In our 2D electronic spectra, we find a beating signal in dimer AB at 522 cm\(^{-1}\) (indicated by a solid vertical cyan line) that is absent from the dimer Raman spectrum. The peak is separately resolved from the neighboring Raman modes at 485 and 585 cm\(^{-1}\) that appear in the dimer beating spectrum. The peak at 700 cm\(^{-1}\) in the beating spectrum of dimer AC (indicated by a solid vertical orange line) is also absent from the corresponding Raman spectrum and well resolved from the nearest Raman peak. The peak at 200 cm\(^{-1}\) in dimer BC (shown by a solid vertical magenta line) overlaps with a peak in the Raman spectrum, preventing us from clearly distinguishing electronic and nuclear contributions to this feature. However, the assignments of electronic features in the other two dimers are clear.

Halpin, Johnson, and Miller state that the “variability and congestion in the measured power spectra” make individual peak assignments “unconvincing.” In (1), we presented traces and beating spectra from representative data sets for each dimer, being satisfied with the reproducibility of our data. This presentation has led some readers to conclude that we are analyzing only a single, noisy data set for each dimer, rather than reproducible oscillating signals. We apologize for not presenting a more detailed statistical analysis. Here, we present spectra generated from all data sets without apodization to demonstrate the reproducibility of our data and the statistical confidence on which our conclusions are based. Averaged power spectra are shown with error bars in Fig. 1 for dimers AB and BC. The error bars represent ±1 standard deviation of the mean (SDM) for each data point in the power spectra. Confidence intervals (1 SDM) are shown for the Fourier interpolation between points as a gray-shaded area. Because we only acquired two data sets for dimer AC, the spectrum from a single representative data set is shown in Fig. 1, and a comparison of the spectra from both runs is shown in fig. S4.

The amplitude of the peak at 522 cm\(^{-1}\) in the dimer AB beating spectrum is greater than 40% of the global maximum of the spectrum and 6 SDs above the baseline. Similarly, the amplitude of the peak at 200 cm\(^{-1}\) in the dimer BC spectrum is greater than 40% of the global maximum and 3.5 SDs above the baseline. For dimer AC, the amplitude of the peak at 700 cm\(^{-1}\) is greater than 75% of the global maximum. We also performed a similar statistical analysis on the waiting-time traces for each dimer, as shown in fig. S3.

We have presented resonance Raman data at the suggestion of Halpin, Johnson, and Miller. We find that these data improve our assignment of vibrational modes while strengthening our assignment of quantum beating signals to electronic coherences for dimers AB and AC. The assignment of quantum beating signals to electronic coherences in dimer BC remains less clear, as the feature observed in the beating spectrum derived from the 2D electronic spectra overlaps with an observed vibrational mode as indicated in (1). We also explain in more detail our data analysis strategy and our molecular design strategy in comparison with the molecules examined by Halpin, Johnson, Miller, and co-workers. Finally, we present an analysis of our data sets showing that the features we observe are statistically significant. We remain confident in our original interpretation of the data, assigning quantum beating signals to electronic coherences.

REFERENCES AND NOTES

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SUPPLEMENTARY MATERIALS
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Supplementary Text
Figs. S1 to S4
Table S1
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