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A growing body of work has pointed to vibronic mixing as a crucial design principle for efficient energy and charge transfer in natural[1–3] and artificial systems.[4,5] Notable among these studies was the recent observation of vibronically promoted ultrafast energy flow in the major antenna complex of green plants and algae light-harvesting complex II (LHCII)—the most abundant membrane protein on the Earth[6]—via the emerging experimental technique two-dimensional electronic-vibrational (2DEV) spectroscopy.[3] This spectroscopy, which correlates electronic and nuclear degrees-of-freedom, shows promise for providing mechanistic insight into vibronic coupling; however, explicit theoretical input is necessary to extract such a detail. In a separate paper,[7] we have developed a heterodimer model that describes various forms of vibronic coupling—which were speculated to be present in LHCII—resulting from diagonal electron–phonon coupling giving Franck–Condon (FC) activity and the nuclear dependence of the electronic transition dipole moment giving Herzberg–Teller (HT) activity. Here, we draw connections between this theoretical work and recent experimental studies in order to demonstrate how HT activity is leveraged in the function of LHCII.

We simulated the linear absorption and 2DEV spectra using the heterodimer model of Ref. 7 with similar parameters to LHCII for comparison.[8] While the model heterodimer mimics the linear absorption spectrum of LHCII shown in Fig. 1, exhibiting two dominant peaks arising from the excitonic states of the electronically coupled chromophores, the presence of the higher-energy side-band is the most significant similarity. By comparing the FC-active and HT-active models of Figs. 1(a) and 1(b), respectively, it is clear that this feature emerges specifically as a result of HT activity[7]—remaining hidden by the inhomogenous broadening when the system is only vibronically mixed by FC activity through a Huang–Rhys factor similar to those found in LHCII.[9] In the model, this side-band can only be observed when additional vibronic mixing through HT activity is included. This side-band also appeared in the heterodimer 2DEV spectra [highlighted by the black dashed box in Fig. 1(b)] where the vibrational structure specifically replicated the excitonic state with significant electronic character from the higher-energy chromophore (analogous to chlorophyll *b* in LHCII).[7] Remarkably, not only does the experimental 2DEV spectrum of LHCII [Fig. 1(c)] clearly display side-band features, but also the vibrational structure along these bands replicates that of the higher-lying excitonic states composed of mainly chlorophyll *b* (spanning 15 200–15 600 cm^{-1}) as marked by the characteristic ground state bleach signature at 1690 cm^{-1} and predicted by the model. These observations, in agreement with the key features displayed by the model, highlight the potential presence of HT activity in LHCII.

The time evolution of 2DEV spectra also reports on the energy transfer dynamics. A frequency-domain characterization of the complex oscillatory signals is often performed and visualized with a beat map (see Ref. 7 for details of this analysis), which is shown in Fig. 2. These beat maps are calculated at a fixed, local detection mode that serves as a sensitive reporter of the interplay between excitonic states. The beat map from the HT-active model simulations

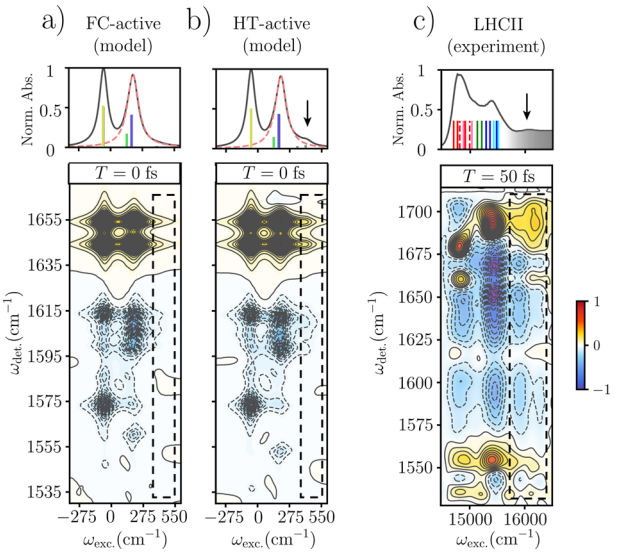

FIG. 1. Electronic linear absorption spectra (top row) and 2DEV spectra (bottom row) for a heterodimer model without (a) and with (b) HT activity and (c) LHCII at 77 K. Vertical lines in the linear absorption spectra denote excitonic states (see Ref. 11 for LHCII). Dashed curves in the top row of (a) and (b) denote Lorentzian fits to the higher-energy peak. The dashed box highlights the higher-excitation frequency portion of the 2DEV spectra where HT-induced vibronic transitions appear. The black arrows indicate higher-energy vibronic states that are promoted by HT activity. Positive features indicate ground state bleaches, and negative features indicate excited state absorptions. (c) has been adapted with permission from Arsenault *et al.*, Nat. Commun. **11**, 1460 (2020). Copyright 2020 Author(s), licensed under a Creative Commons Attribution 4.0 License. (http://creativecommons.org/licenses/by/4.0/).

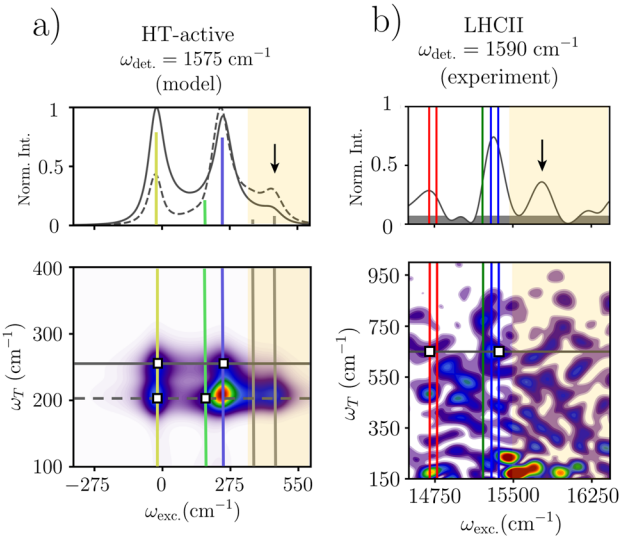

FIG. 2. Beat maps at a fixed detection frequency (bottom row), $\omega_{\text{det.}}$, for the (a) model and (b) experiment (only peaks that survive the noise floor are shown). Vertical lines denote excitonic states (for LHCII, these are based on Ref. 11), and horizontal lines are specific beat frequency slices, which are shown in the top row [gray shading in (b) represents the noise floor]. In (a), the activity of the two beat frequencies is distinguished with a solid vs dashed line. The yellow shaded region and black arrows indicate higher-energy vibronic states that are promoted by HT activity. At a given beat frequency, squares indicate the energetic gap between excitonic states corresponding to that frequency. (b) has been adapted with permission from Arsenault *et al.*, Nat. Commun. **11**, 1460 (2020). Copyright 2020 Author(s), licensed under a Creative Commons Attribution 4.0 License. (http://creativecommons.org/licenses/by/4.0/).

[Fig. 2(a)] displays two distinct dynamical frequencies that report on the two relevant energy gaps and shows contributions from higher-lying excitonic states (shaded regions of Fig. 2) at both dynamical frequencies. This manifests as an additional peak in the map that can be clearly seen at *both* beat frequencies [highlighted by a black arrow in the top panel of Fig. 2(a)], which is a feature specific to HT activity.[7] The experimental measurements [Fig. 2(b)] are considerably more structured due to the many additional excitonic states relative to the model, but the beat map shows a similar distribution of higher-energy vibronic activity across the numerous beat frequencies. One example of the prevalence of the high-energy vibronic states in the observed beat frequencies corresponding to excitonic energy gaps is presented in Fig. 2(b) (see the top panel). Despite the complexity of the experimental beat maps, the observable features from our model analysis elucidate the role of vibronic mixing in promoting additional, ultrafast relaxation pathways in the energy transfer dynamics of LHCII.

More specifically, HT activity was found to be a potential mechanism of energy transfer in the model. Further 2DEV studies on LHCII, featuring excitation well into the green absorption region,[10] have indicated that vibronically induced ultrafast energy flow persists across nearly 3000 cm^{-1} of the electronic linear absorption spectrum of the complex, which in conjunction with the model results suggests that HT activity is also the mechanism responsible for the extension and enhancement of the light-harvesting capabilities of LHCII across the photosynthetically active region.

AUTHORS' CONTRIBUTIONS

E.A.A. and A.J.S. contributed equally to this work.

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DATA AVAILABILITY

The data and codes that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] F. D. Fuller, J. Pan, A. Gelzinis, V. Butkus, S. S. Senlik, D. E. Wilcox, C. F. Yocum, L. Valkunas, D. Abramavicius, and J. P. Ogilvie, "Vibronic coherence in oxygenic photosynthesis," Nat. Chem. **6**, 706–711 (2014).

[2]J. C. Dean, T. Mirkovic, Z. S. D. Toa, D. G. Oblinsky, and G. D. Scholes, "Vibronic enhancement of algae light harvesting," Chem **1**, 858–872 (2016).
[3]E. A. Arsenault, Y. Yoneda, M. Iwai, K. K. Niyogi, and G. R. Fleming, "Vibronic mixing enables ultrafast energy flow in light-harvesting complex II," Nat. Commun. **11**, 1460 (2020).
[4]C. Andrea Rozzi, S. Maria Falke, N. Spallanzani, A. Rubio, E. Molinari, D. Brida, M. Maiuri, G. Cerullo, H. Schramm, J. Christoffers *et al.*, "Quantum coherence controls the charge separation in a prototypical artificial light-harvesting system," Nat. Commun. **4**, 1602 (2013).
[5]S. M. Falke, C. A. Rozzi, D. Brida, M. Maiuri, M. Amato, E. Sommer, A. De Sio, A. Rubio, G. Cerullo, E. Molinari *et al.*, "Coherent ultrafast charge transfer in an organic photovoltaic blend," Science **344**, 1001–1005 (2014).
[6]J. Standfuss, A. C. Terwisscha van Scheltinga, M. Lamborghini, and W. Kühlbrandt, "Mechanisms of photoprotection and nonphotochemical quenching in pea light-harvesting complex at 2.5 Å resolution," EMBO J. **24**, 919–928 (2005).
[7]E. A. Arsenault, A. J. Schile, D. T. Limmer, and G. R. Fleming, "Vibronic coupling in energy transfer dynamics and two-dimensional electronic-vibrational spectra," J. Chem. Phys. **155**, 054201 (2021).
[8]All parameters have been kept the same as in Ref. 7 ($\eta = 0.0$ for FC-active and $\eta = -0.15$ for HT-active) except $S = 0.05$ in this work.
[9]Y. Jia, J. M. Jean, M. M. Werst, C. K. Chan, and G. R. Fleming, "Simulations of the temperature dependence of energy transfer in the PSI core antenna," Biophys. J. **63**, 259–273 (1992).
[10]E. A. Arsenault, Y. Yoneda, M. Iwai, K. K. Niyogi, and G. R. Fleming, "The role of mixed vibronic Q_y-Q_x states in green light absorption of light-harvesting complex II," Nat. Commun. **11**, 6011 (2020).
[11]V. I. Novoderezhkin, M. A. Palacios, H. Van Amerongen, and R. Van Grondelle, "Excitation dynamics in the LHCII complex of higher plants: Modeling based on the 2.72 Å crystal structure," J. Phys. Chem. B **109**, 10493–10504 (2005).