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Role of Vibrational Dynamics on Excited-State Electronic Coherence in a Binuclear Platinum Complex

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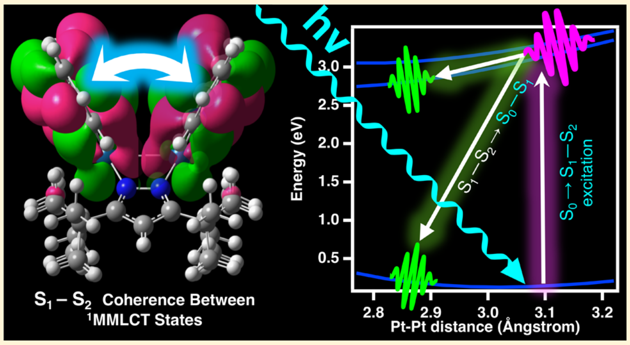
Supporting Information

ABSTRACT: Long-lived quantum coherence between excited electronic states can enable highly efficient energy and charge transport processes in chemical systems. Recent pump−probe experiments on binuclear platinum complexes identified persistent, periodic beating of transient absorption anisotropy signals, indicating long excited-state coherence lifetimes. Our previous simulations of the electronic dynamics of these complexes indicate that coherence lifetimes are sensitive to the balance between competitive electronic couplings. The complexes with shorter Pt−Pt distances underwent no appreciable dephasing in the limit of static nuclei, motivating the inclusion of nuclear motion into our simulations. The *tert*-butyl-substituted complex is studied in this work using the Ehrenfest method for mixed quantum−classical dynamics to investigate the role of vibrational dynamics on a complex shown to support long coherence lifetimes. Results indicate that the inclusion of excited-state vibrations drives a rapid collapse of the two-state coherence prior to the experimentally determined intersystem crossing. This further suggests singlet excited-state coherences may not be prerequisites for long-lived triplet coherences.



■ INTRODUCTION

The role of quantum-coherent excited-state electronic processes in efficient energy and charge transport has become a prominent question in the study of photophysical processes in complex condensed-phase materials.[1−5] Understanding how the electronic structure and geometric parameters of molecules affect the persistence of coherence in molecular chromophores may inform the design of functional materials supporting long-lived quantum coherent states. Coherences between excited states result ubiquitously from the interaction of matter with electromagnetic radiation. However, dephasing typically occurs on time scales characteristic of the vibrational modes of the system or interactions with surrounding media.

In recent years, time-resolved nonlinear optical spectroscopy experiments in the pump−probe architecture carried out on the binuclear platinum complex $[(\mathrm{ppy})\mathrm{Pt}(\mu\text{-}^t\mathrm{Bu}_2\mathrm{pz})]_2$ (ppy = 2-phenylpyridine, $^t\mathrm{Bu}_2\mathrm{pz}$ = 3,5-di-*tert*-butylpyrazolate) have shown signatures of excited-state electronic coherence upon impulsive excitation of the weakly split metal−metal to ligand charge transfer (MMLCT) states. The characteristic beating in the anisotropy of the transient absorption intensity attributed to the electronic coherence persists for picoseconds after excitation.[6−11] On very long time scales, the rotational diffusion of the chromophores in solution may render this technique insensitive to the coherent electronic evolution, so this impressive coherence time may even be regarded as a lower bound.

Recent theoretical work from the authors,[12] relying on the time-dependent density functional theory (TD-DFT)[13−15] for both electronic dynamics simulations and calculation of the charge-localized states and their electronic couplings, demonstrated that the necessary conditions for long-lived coherence in the singlet metal−metal to ligand charge transfer (^{1}MMLCT) states of binuclear platinum complexes can be satisfied through structural modifications of the bridging pyrazolate ligands that sterically enforce certain interplatinum distances. A series of binuclear platinum complexes with different bridging and cyclometalating ligands have been synthesized, forming a full library of bichromophoric metal complexes with subtly different electronic structure.[16−18] The interplatinum separation length correlates strongly with the electronic couplings between excitons localized on either half of the bichromophoric system, resulting in long dephasing times for these coherent two-state

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superpositions in complexes showing short Pt−Pt separation distances at their crystal structure geometries.

This earlier work sought to answer the question of whether effective two-state electronic coherences suspected to underlie the experimentally observed quantum beating can be maintained, in the absence of any nuclear vibrations, in a complex many-electron system where other states can couple into the effective two-state electronic evolution to bring about its decoherence. The study ultimately suggested that the two-state superposition maintains its strict phase relationship beyond the experimentally resolved time scale of the intersystem crossing to the triplet manifold in the absence of any nuclear motion. Molecular vibrations excited in response to the electronic excitation—especially those that modulate the Pt−Pt separation distances—may strongly impact the evolution of the excited electronic wavepacket relative to the simulations at a fixed nuclear configuration.

In this report, the ability of vibrational motions to bring about the dephasing of an impulsively excited superposition of MMLCT states takes center stage. The open question now is how, or indeed whether, an initial coherent MMLCT superposition generated in the ultrafast pump−probe experiment can be responsible for the observed long-lived coherent two-level superposition in the triplet manifold. Does the coherence "survive" through the intersystem crossing, or does the initial superposition in the singlet manifold dephase prior to the intersystem crossing?

■ METHOD

To provide the ^{1}MMLCT-state energies and transition dipole moments to the ground state along the nuclear trajectory, time-dependent density functional theory (TDDFT) in the "linear response" formulation[19−22] was employed. All calculations were carried out using the development version of the Gaussian suite of quantum chemistry programs.[23] The CAM-B3LYP range separated hybrid functional was employed for all DFT calculations. The LANL2DZ effective core potentials and associated double-ζ basis were used for Pt atoms, while the main-group atoms utilize the double-ζ D95V basis set.

To explicitly model the combined electron−nuclear evolution of the system initialized in the MMLCT superposition, mixed quantum−classical dynamics simulations were performed in the Ehrenfest formalism.[24−27] Under this approach, nuclei are regarded as classical particles that evolve according to the expectation value of the forces evaluated for the propagated electronic superposition state. Classical treatment of the nuclear dynamics of light elements is not expected to appreciably affect the electronic evolution in this case, because the light atoms' motions do not strongly affect the ^{1}MMLCT splitting and the S_1−S_2 energy gap is nonresonant with vibrational transitions in these electronic states (see Supporting Information for details.) While other mixed quantum−classical formalisms (i.e., the surface hopping,[28,29] multiple spawning,[30] path integrals,[31] etc.) are the more accurate nonadiabatic dynamics methods for treating electronic dynamics in the incoherent charge-hopping regime, the Ehrenfest scheme has been shown suitable for treating the electronic decoherence.[32,33] The nuclear equation of motion was integrated via the velocity Verlet algorithm with a 1.0 fs time step, while electronic degrees of freedom were propagated by numerical integration of the time-dependent Kohn−Sham equations ("real-time" (RT) TDDFT) via a modified midpoint unitary transformation approach with 0.001 fs time step.[26,27] Total energy was conserved to within 10^{-4} kJ/mol. Nuclear positions—and therefore electron−nuclear attraction terms in the Kohn−Sham Hamiltonian—were updated during the RT-TDDFT electronic dynamics by assuming constant forces on the nuclei between Verlet steps. RT-TDDFT and its application to mean-field electron−nuclear dynamics are becoming increasingly well-adopted approaches for the study of ultrafast chemical dynamics.[34−37]

The initial electronic density for the dynamics was prepared to mimic the impulsively excited system as a linear combination of the MMLCT states. As demonstrated in the authors' earlier work on this system (and confirmed here) the lower/higher energy ^{1}MMLCT excitations are dominated by the HOMO → LUMO/LUMO+1 transitions (Figure 1) These calculations were performed strictly in the nonrelativistic limit. Real-time dynamics calculations incorporating spin−orbit coupling for systems of this size currently remain elusive due to their intractably large cost. While the nonrelativistic, spin-unrestricted Kohn−Sham Hamiltonian does not couple states of differing spin, the dynamics of the singlet coherent state still provide insights into the excited-state processes that precede the intersystem crossing, which are the focus of this report.

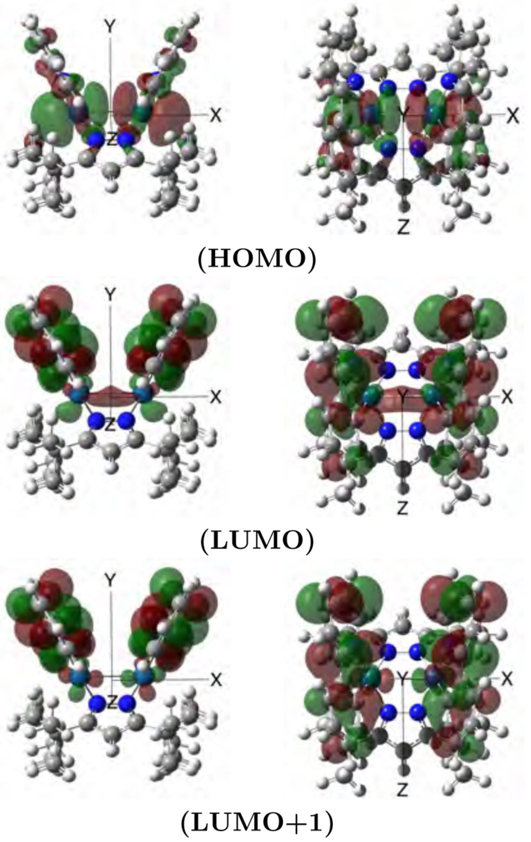

Figure 1. Isosurfaces of the (canonical) HOMO, LUMO, and LUMO+1 for $[(ppy)Pt(\mu\text{-}^tBu_2pz)]_2$ complexes at the ground-state equilibrium geometry.

Vibrational degrees of freedom were initialized at the Franck−Condon geometry with zero initial momentum. Only those vibrational modes displaced from their equilibrium positions in the excited state are excited in this simulation by the vertical excitation of the system at its ground-state equilibrium geometry. The purpose of this choice of initial conditions is to isolate the dephasing due to vibrations intrinsic to the excitation from any dephasing resulting from vibrations in electronic ground state prior to photoexcitation. If the coherent electronic wavepacket is dephased by the nuclear motions induced by the change of electronic state, with initially stationary nuclei at the equilibrium geometry, then certainly a proper accounting of the ground-state nuclear motions would only hasten this process. These simulations may therefore be regarded as providing a lower bound for the potential dephasing strength of the vibrations on the electronic superposition.

Tracking the coherence of the superposition will require information about the populations of the MMLCT states as the electronic degrees of freedom evolve in time. The efficiency of the RT-TDDFT approach results from integrating the time-dependent Kohn–Sham equations directly in the atomic orbital basis, so the population of a given state is not evaluated along the trajectory. However, the population of electronic states can still be accessed indirectly through the dipole–dipole (auto)-correlation function, $C_{\mu\mu}(t)$, which can be expressed in the energy eigenbasis as in eq 1.

$$C^{i}_{\mu\mu}(t) = \sum_{n} p_n \langle \Psi_n | \mu_i(0)\, \mu_i(t) | \Psi_n \rangle \tag{1}$$

where p_n is the population of the nth enegy eigenstate, Ψ_n, and i represents a Cartesian coordinate in the lab frame. Resolving the identity and Fourier transforming to the frequency domain exposes the linear relationship between the frequency domain dipole autocorrelation function intensity and the eigenstate population (eq 2).

$$\tilde{C}^{i}_{\mu\mu}(\omega) = \sum_{n,m} p_n |\langle \Psi_m | \mu_i | \Psi_n \rangle|^2 \delta(\omega - \omega_{mn}) \tag{2}$$

Here, ω_{mn} represents the energy difference between states m and n. The expectation value of the electric dipole is calculated at each step in the numerical integration of the electronic equation of motion.

The frequency-domain dipole autocorrelation function was then calculated over short-time (17.5 fs) windows translating in time with 1 fs steps via discrete Fourier transformation. The length of the translating window was chosen to maximize the resolution in the frequency domain while still retaining sufficient time-resolution to follow the MMLCT population dynamics (which evolve on this characteristic time scale). The resolution in the frequency domain (inversely related to the length of the window) is limited to ∼0.2 eV for this window size, very close to the splitting in the two MMLCT states. Fittingly, though, the translating short-time Fourier transform approximation to $\tilde{C}_{\mu\mu}(\omega)$ is still sensitive to the population dynamics for the very same reason that the coherence can be monitored through the transient absorption anisotropy experiment—the near orthogonality of the transition dipole vectors between the two states in superposition and some third state. Here, it is the alignment of the transition dipole vectors between the two ^{1}MMLCT states and the ground state that permit the population dynamics to be tracked during the dynamics.

■ RESULTS AND DISCUSSION

Figure 2 shows the evolution of certain key structural parameters during the Ehrenfest dynamics trajectory. The lowest-frequency Pt–Pt stretch in the ground-state structure (S_0) is calculated as 106 cm^{-1}, corresponding to a vibrational period of 316 fs. Upon excitation of the coherent ^{1}MMLCT superposition, the Pt–Pt bond elongates slightly followed by a contraction, as shown in Figure 2. The ppy ligands, however, begin contracting immediately and then quickly equilibrate to a new average value on the effective excited-state potential energy surface. Excited-state vibrational frequency calculations[38] show that the lowest frequency associated with the Pt–Pt stretching is between 140 cm^{-1} in S_1 and 127 cm^{-1} in S_2, which corresponds to a period between 238 and 278 fs for a coherent mix of S_1 and S_2 states. This suggests that the simulation performed here covers slightly more than one-half of the vibrational period of the slowest excited-state stretching mode in the system as well as the full range of bond lengths of Pt–Pt during the vibration in this superposition of excited states. This is important, since the Pt–Pt distance coordinate was shown in previous work to correlate strongly with changes in the electronic couplings between the low-lying singlet states across a series of binuclear platinum complexes.[12]

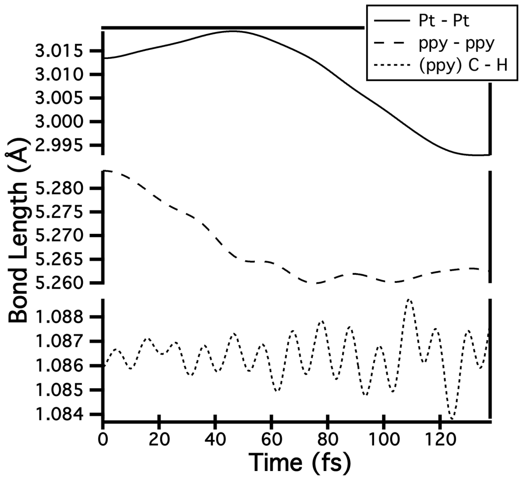

Figure 2. Evolution of the Pt–Pt distance (top panel), ppy–ppy distance (averaged over each atom pair, middle panel), and a C–H distance from the ppy ligand (bottom panel) along the Ehrenfest trajectory.

The ^{1}MMLCT states' energies and transition dipole moment vectors to the ground state were calculated via LR-TDDFT at regular intervals along the nuclear trajectory and are collected in Table 1 and Table 2, respectively. The S_1–S_2 (i.e., ^{1}MMLCT) splitting varies by less than 16 meV over the course of the dynamics for these mild vibrational initial

Table 1. LR-TDDFT Splittings of the Two ^{1}MMLCT States Evaluated along the Classical Nuclear Trajectory

		energy (eV)		
time (fs)	$R_{\mathrm{Pt}}(t)$ (Å)	$\omega(S_0{\to}S_1)$	$\omega(S_0{\to}S_2)$	$\omega(S_1{\to}S_2)$
0	3.01343	3.0778	3.3061	0.2283
20	3.01583	3.0344	3.2718	0.2374
40	3.01879	3.0390	3.2780	0.2390
60	3.01723	3.0247	3.2498	0.2251
80	3.01100	3.0208	3.2443	0.2235
100	3.00259	3.0572	3.2861	0.2289
120	2.99460	3.0076	3.2377	0.2301
140	3.01879	3.0017	3.2339	0.2322

Table 2. (Unsigned) Transition Electric Dipole Vector Components between the Ground State and ^{1}MMLCT States Evaluated via LR-TDDFT (Tamm–Dancoff Approximation Utilized for Transition Dipole between Excited States)

	$S_0 \rightarrow S_1$			$S_0 \rightarrow S_2$			$S_1 \rightarrow S_2$		
time (fs)	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z
0	0.9683	0.0001	0.0001	0.0000	0.0439	0.2546	3.5151	0.0002	0.0001
20	0.9876	0.0001	0.0006	0.0019	0.0520	0.2804	3.4581	0.0009	0.0004
40	0.9786	0.0014	0.0035	0.0108	0.0743	0.2699	3.4651	0.0055	0.0102
60	0.9473	0.0006	0.0014	0.0031	0.0746	0.2557	3.4908	0.0016	0.0065
80	0.9763	0.0021	0.0050	0.0148	0.0753	0.2775	3.4810	0.0089	0.0158
100	0.9820	0.0025	0.0068	0.0184	0.0559	0.2687	3.5217	0.0093	0.0193
120	0.9812	0.0030	0.0065	0.0186	0.0534	0.2541	3.5478	0.0138	0.0180
140	1.0007	0.0031	0.0070	0.0233	0.0542	0.2692	3.5428	0.0158	0.0042

conditions. In the lab frame (Figure 1), the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations lie predominantly along the *x*- and *z*-directions throughout the trajectory (Table 2). Therefore, one must separately investigate these two spatial components of $C_{\mu\mu}(t)$ to observe the population dynamics for the ^{1}MMLCT states.

Figure 3 shows the time evolution of the relevant components of the dipole expectation value. In the very early time of the simulation (first ~20 fs) the coherent evolution of the ^{1}MMLCT-state superposition is clearly indicated by the regular oscillations of the dipole *x*-component with a period equal to that of the S_1–S_2 energy gap. On this time scale, only the fastest-evolving vibrational coordinates will have deviated appreciably from their initial positions (Figure 2).

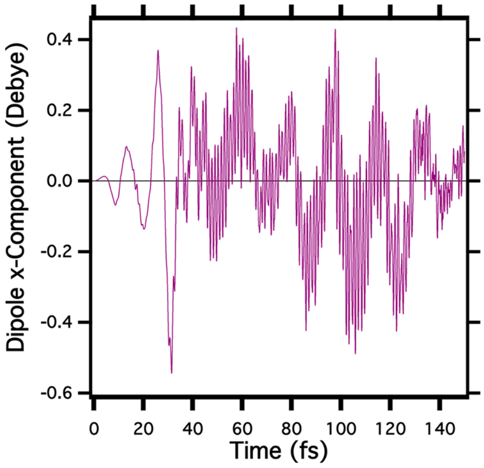

Figure 3. Electric dipole expectation value (*x*-component) during the Ehrenfest trajectory. From Table 2, the early time (first ~20 fs) oscillation in the *x*-component confirms the initially prepared density as S_1–S_2 coherence, and higher frequency oscillations at times >20 fs show the onset of mixing of other states into the superposition.

Figure 4 shows the dipole–dipole autocorrelation functions evaluated via Fourier transformation of the dipole expectation values from Figure 3 over a translating time window. On the basis of the analyses in Table 1 and Table 2, the S_1–S_2 coherence will result in a peak in $\tilde{C}^x_{\mu\mu}(\omega)$ at the ~0.2 eV energy gap between the S_1 and S_2 states. While this peak is present in the very early time, it resides in the region of molecular vibrational signals and therefore cannot be easily isolated as the nuclear motions begin to develop. Instead, we will track the evolution of the ^{1}MMLCT-state populations through their oscillations with the ground state.

The important features in $\tilde{C}_{\mu\mu}(\omega)$ can be found between 3.0 and 3.3 eV as this is the region that reports on the populations of the S_1 and S_2 states over the 17.5 fs discrete Fourier transformation window. The changing intensities in the 3.0–3.3 eV region of $\tilde{C}^z_{\mu\mu}(\omega)$ and $\tilde{C}^x_{\mu\mu}(\omega)$ can be regarded as reporting on the rise and fall of populations of the S_2 and S_1 states, respectively.

As the vibrational dynamics proceed, the temporal behavior of the electronic degrees of freedom quickly deviates from the coherent evolution observed for the same S_1–S_2 wavepacket with nuclei held fixed at the crystal structure geometry.[12] For pure two-state coherence, the populations of participating states should exhibit out-of-phase oscillations with a frequency given by the energy difference between the two states. However, after the first period of coherent evolution of the S_2 to S_1 populations, this behavior can no longer be appreciated in $\tilde{C}_{\mu\mu}(\omega)$. Furthermore, the S_1 population grows in on a time scale that is not consistent with pure two-state ^{1}MMLCT superposition. The pure two-state coherent oscillation behavior is compromised within the first 20 fs following excitation, consistent with the time evolving dipole (*x*-component) starting to exhibit higher frequency Fourier components on the same time scale. Since nonadiabatic transitions are not favorable under these low vibrational energy conditions, the loss of coherence can only be attributed to the modulation of

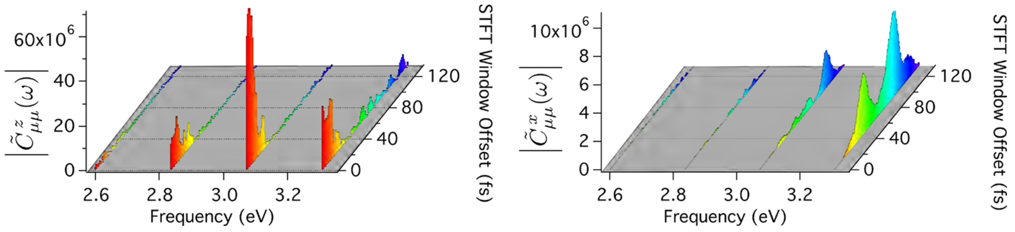

Figure 4. Fencepost plots of the short-time (17.5 fs window), discrete Fourier transformed dipole autocorrelation function. Left panel plots the *z*-component, $\tilde{C}^z_{\mu\mu}(\omega)$, and the right panel plots $\tilde{C}^x_{\mu\mu}(\omega)$. The lack of regular oscillations in the intensity between $\tilde{C}^z_{\mu\mu}(\omega)$ and $\tilde{C}^x_{\mu\mu}(\omega)$ in the ~3 eV region indicates the loss of two-state coherence as the nuclear motions develop in the excited electronic state.

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electronic coupling strength by the low-amplitude vibrational motions. The loss of intensity overall in this region of $\tilde{C}_{\mu\mu}(\omega)$ is consistent with population transfer from the ^{1}MMLCT subsystem and into other excited states outside the energy region considered here, quite possibly with low, or even zero transition dipole strength (i.e., "dark") to the ground state. The role of vibration in the cascading of coherence can be considered dissipative in the way that population of coherent S_1−S_2 state is spread over multiple states,[39,40] including to the coherent S_0−S_1 state.

■ CONCLUSION

In this work, we have carried out *ab initio* Ehrenfest dynamics of a binuclear Pt(II) complex following a photoexcitation that creates a coherent ^{1}MMLCT state. Results show that the inclusion of vibrational motions in the coupled electron−nuclear dynamics—even with the mildest vibrational initial conditions conceivable—serves to dephase the initial coherent ^{1}MMLCT superposition on an ultrafast time scale (i.e., less than the Pt−Pt stretching vibrational period). Note that such a pure dephasing mechanism represents the fundamental upper bound to the coherence time in the absence of inhomogeneous broadening.

These population dynamics illustrate that the coherent superposition of ^{1}MMLCT states resulting from impulsive excitation of the system in the pump−probe experiment very likely dephases prior to the experimentally reported intersystem crossing approximately 150 fs after photoexcitation.[6] The dephasing time from the simulation suggests that initial ^{1}MMLCT coherence is not a necessary condition to observe the two-state coherence in the triplet manifold following the intersystem crossing. However, this is not to say that the ultrashort optical pulse does not play an indirect (e.g., nonelectronic) role in facilitating the excited-state processes. The cascading excited-state pathway from singlet to triplet manifolds may be facilitated by the ultrashort optical pulse via an excitation of a coherent superposition of vibrational excited states along the reaction coordinate through impulsively stimulated Raman processes.

While semiclassical methods have been formulated to treat vibrationally induced electronic dephasing phenomenologically, the fully atomistic, first-principles description of the cascading of excited-state coherence featured in this work is very challenging for semiclassical approaches. The results of this study can serve as a potential benchmark for analytical methods to satisfactorily treat excited-state dephasing via time-dependent couplings associated with specific (potentially anharmonic) vibrational motions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Excited-state vibrational analysis (PDF)

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‡Authors contribute equally

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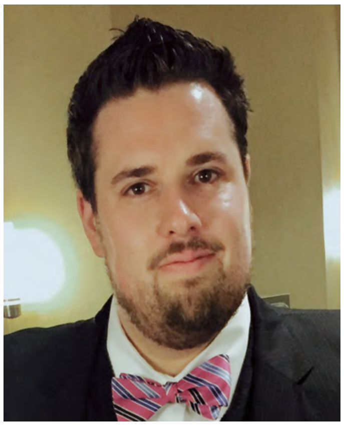
The authors declare no competing financial interest.

Biographies



Joseph J. Radler is currently a third-year graduate student working towards a Ph.D. in the Xiaosong Li research group at the University of Washington. His research focuses on the development and application of mixed quantum−classical dynamical simulation methods as well as both *ab initio* and semiempirical time-dependent electronic structure theories for investigating excited-state chemical and photophysical processes. Radler completed his undergraduate studies in 2012 at Purdue University in West Lafayette, Indiana, followed by three years working as a laboratory technician at the Purdue Rare Isotope Measurement (PRIME) Laboratory. He began a Ph.D. program at the University of Washington in 2015, joined the Li research group in early 2016, and earned his MS degree in 2017.

David B. Lingerfelt is a postdoctoral researcher in the group of Xiaosong Li in the chemistry department at the University of Washington. His research is focused on the dynamics of molecular and condensed phase systems in excited electronic states. His work ranges from applying mixed quantum−classical methods for large systems to fully quantum mechanical treatment of systems containing light elements. David did his undergraduate studies at the University of North Carolina Asheville, where he performed computational research on heterogeneous catalysis with Dr. Sally Wasileski. His undergraduate research naturally lead him to pursue a Ph.D. with Xiaosong Li, focusing on the development nonadiabatic molecular dynamics techniques.

Felix (Phil) N. Castellano earned a B.A. in Chemistry from Clark University in 1991 and a Ph.D. in Chemistry from Johns Hopkins University in 1996. Following an NIH Postdoctoral Fellowship at the University of Maryland, School of Medicine, he accepted a position as Assistant Professor at Bowling Green State University in 1998. He was promoted to Associate Professor in 2004 and to Professor in 2006 and was appointed Director of the Center for Photochemical Sciences in 2011. In 2013, he moved his research program to North Carolina State University where he is currently the Goodnight Innovation Distinguished Chair. He was appointed as a Fellow of the Royal Society of Chemistry (FRSC) in 2015. His current research focuses on metal−organic chromophore photophysics and energy transfer, photochemical upconversion phenomena, solar fuels photocatalysis, energy transduction at semiconductor/molecular interfaces, and excited-state electron transfer processes.

Lin X. Chen is a Professor of Chemistry in Northwestern University and a Senior Chemist in Argonne National Laboratory. She received her Ph.D. from the University of Chicago. After her postdoctoral research at UC Berkeley, she joined Argonne as a staff scientist. In 2007, she joined Northwestern University where she has four research foci: (1) excited-state molecular structural dynamics in photochemical processes using ultrafast optical and X-ray spectroscopy and X-ray scattering, (2) electronic processes in organic materials using ultrafast laser spectroscopy, theoretical modeling and GIWAXS/GISAXS, (3) understanding roles of ultrafast and coherent electronic and atomic motions in in photochemical reactions, and (4) transient structures of metalloproteins on multiple spatial and temporal scales during their functions. She has >200 publications and over 180 invited lectures. She has been a member of the Research Council for the Chemical, Biological and Geological Sciences Division, Basic Energy Science, US Department of Energy, a member of the Advisory Editorial Boards of *The Journal of Physical Chemistry* and *Chemical Physics Letters*, a Senior Editor of *ACS Energy Letters*, and a member of the International Science Advisory Committee for π-Functional Materials. She is an AAAS Fellow and has won the distinguished performance award at Argonne.

Xiaosong Li is the Harry and Catherine Jaynne Boand Endowed Professor of Chemistry at the University of Washington. His research focuses on developing and applying time-dependent relativistic and nonrelativistic electronic structure theories for studying excited-state chemical processes that underpin energy conversion, photocatalysis, and ultrafast spectroscopies. After completing his undergraduate studies at the University of Science and Technology of China in 1999, Li attended graduate school and received his Ph.D. in 2003 from the Wayne State University where he worked with Professor Bernhard Schlegel. He pursued his postdoctoral work at the Yale University with Prof. John C. Tully on nonadiabatic electron−nuclear dynamics. Li joined the University of Washington as Assistant Professor in the fall of 2005 and was promoted to Associate Professor in 2011 and to Full Professor in 2015. He has received awards that include the Sloan Research Fellowship, NSF CAREER Award, and ACS Open-Eye Outstanding Junior Faculty Award.

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