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Ab Initio Excited-State Transient Raman Analysis

Alessio Petrone,[‡] David B. Williams-Young,[‡] David B. Lingerfelt, and Xiaosong Li*

Department of Chemistry, University of Washington, Seattle, Washington 98195, United States

ABSTRACT: Time-resolved Raman spectroscopy has proven useful for studying the formation of polarons in conjugated polymers, verifying the presence of reactive intermediates in photochemical reactions, investigating nonradiative transitions in the short lifetime of the photoexcited species, and resolving electron—phonon coupling strengths and exciton dissociation in crystalline materials. In this paper, we present an excited state transient Raman analysis protocol combining *ab initio* direct molecular dynamics, transient excited state Hessian, and excited state nonresonant Raman activities evaluations. Prototypical molecules are used as test cases, showing the evolution of the transient Raman signatures that follow electronic excitation. This protocol provides a direct route to assigning the vibrations



implicated in the (photo)dynamics of several (photoactive) systems, complementary to the transient infrared analysis.

INTRODUCTION

Time-resolved vibrational spectroscopies, such as infrared (IR) and Raman spectroscopies, have become increasingly important in modern chemical, biological, and materials research. This modern focus is primarily due to their unique capability to investigate nonequilibrium structural dynamics of ultrafast chemical phenomena.¹⁻⁶ Infrared and Raman spectroscopy are complementary tools for obtaining vibrational spectra. Depending on the molecular symmetries, a vibrational mode may contribute a peak to the infrared and/or Raman spectrum. A vibrational mode is IR or Raman active (with non-negligible intensity in the spectrum), if displacement of the nuclei along the vibrational coordinate induces a change in the molecular dipole or polarizability, respectively. While these are the canonical selection rules, in general any monochromatic electromagnetic radiation incident on a molecular system may induce an electric moment in the system through the polarizability tensor. The resulting scattered light can have either the same frequency as the incident light (Rayleigh scattering) or a different one (Raman scattering).⁷⁻⁹ When such a vibrational spectroscopy experiment is carried out as the "probe" pulse in a pump-probe architecture, the nonequilibrium response of the vibrational degrees of freedom to the initial pump pulse may be captured in the vibrational spectra taken at different pump-probe delays.^{1-6,10,11} This type of experiment has proven useful for studying the formation of polarons in conjugated polymers,^{12–14} verifying the presence of reactive intermediates in photochemical reactions,^{15–20} investigating nonradiative transitions in the short lifetime of the photoexcited species 21-23 and resolving electron-phonon coupling strengths and exciton dissociation in crystalline materials²⁴⁻²⁷ when the pump pulse is on-resonance with an electronic transitions.

The *ab initio* prediction of static Raman spectra can be accomplished via two distinctly different directions. The most commonly applied method relies on the calculation of vibrational energy eigenstates (typically within the harmonic approximation) and the transition probabilities between them to resolve the spectrum peak-by-peak.^{28–32} However, the Raman scattering cross-section can also be related to the Fourier transform of time correlation functions of certain observables.^{33–36} However, neither of these approaches are capable of reproducing the nonequilibrium response of the vibrational degrees of freedom to an electronic excitation, and in their basic formulations are therefore insufficient to reproduce time-resolved Raman spectra. In some cases where only a few degrees of freedom are important, semiclassical perturbative approaches are sufficient and have been very successful for computing time-resolved vibrational spectra.^{37–53}

In this work, a computational approach relying on both *ab initio* direct molecular dynamics and transient vibrational analysis is presented to establish a time-dependent density functional theory (TDDFT)-based protocol capable of capturing transient Raman active vibrational phenomena. Due to the success of Kohn–Sham DFT^{54–56} in describing the electronic structure of molecular and condensed phase systems, development of quantum mechanical methods relating to DFT and its analogues has become a high priority in the field of quantum chemistry. Use of DFT in the evaluation of molecular energies, $^{57-59}$ gradients, 60 and higher order properties $^{28-32,61-67}$ has become highly efficient over the years, making its application to ground state calculations of a variety of nontrivial systems quite routine. $^{67-69}$

Via the adiabatic approximation, the description of electronically excited states in DFT is also made possible through the time-dependent density functional theory (TDDFT)^{70,71} method. In relation to its Hartree–Fock counterpart, TDHF, TDDFT represents a large stride forward in accuracy to cost

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ratio. While both methods utilize a multideterminantal description of the excited states, TDDFT better captures the effects of many-body correlation of both the ground and excited states through the inclusion of the exchange-correlation (XC) kernel.⁷¹ As such, for the computational cost of a single reference method, one has the capability to, at least in principle, obtain results of similar accuracy to multiconfigurational methods. Evaluation of TDDFT excited state energies,^{72–75} gradients,^{76–81} and nonadiabatic couplings^{82–89} have become common practice in computational chemistry.^{90–92} However, methods for the evaluation of higher-order TDDFT properties, such as the TDDFT Hessians,^{93–95} have only recently been developed. To the authors' knowledge, no implementation of analytical expressions for TDDFT properties past second order, such as those required in the case of excited state Raman spectroscopy, exists.

METHODOLOGY

TDDFT Excited State Nonresonant Raman Intensity. The excited-state Raman activity expressions derived in this paper are suitable for the off-resonance condition, which can be obtained by one order of numerical differentiation of the analytical TDDFT excited-state Hessian. We defer the development of resonant Raman activities to a future work because it requires an extra order of frequency-dependent perturbation, which adds a great deal of complexity and computational cost.

The intensity of the nonresonant Raman signal of the *n*th electronic excited state is characterized by the differential Raman scattering cross-section, which is proportional to the Raman scattering activity measured directly in suitable experiments, $^{36,96-100}$

$$I_p^n \propto (45(a_p^{n'})^2 + 7(\gamma_p^{n'})^2)$$
(1)

$$a_p^{n'} = \frac{1}{3} \sum_j \frac{\partial \alpha_{jj}^n}{\partial Q_p^n}$$
(2)

$$(\gamma_p^{n'})^2 = \frac{1}{2} \left(3 \sum_{jk} \left(\frac{\partial \alpha_{jk}^n}{\partial Q_p^n} \right)^2 - 9(a_p^{n'})^2 \right)$$
(3)

$$\frac{\partial \alpha_{jk}^n}{\partial Q_p^n} = \sum_{i=1}^{3N} \frac{\partial \alpha_{jk}^n}{\partial R_i} U_{pi}^n \tag{4}$$

where α^n is the rank-2 static polarizability tensor of the *n*th electronic excited state. *j*,*k* indices are the Cartesian components (*x*, *y*, and *z*) of the polarizability tensor. The primed notation refers to differentiation with respect to the *p*th vibrational mode with the normal coordinate Q_p . This quantity can be readily obtained via a coordinate transformation from differentiation in the molecular Cartesian coordinate to the vibrational normal coordinate using eq 4, given the eigenvectors **U** of the Hessian of the *n*th excited state. For calculations of static Raman intensity, the vibrational normal coordinates correspond to the minima on a potential energy surface. However, **U** values become ill-defined at nonstationary points of the potential energy surface.⁹⁴ In the next section, we will introduce a protocol to define time-resolved transient vibrational modes for computing transient Raman intensities.

The excited-state polarizability tensor α^n is defined as second derivatives of the total energy of the *n*th excited state, \mathcal{E}^n , with respect to a static incident field, **E**,

$$\alpha_{ij}^{n} = \frac{\partial^{2} \mathcal{E}^{n}}{\partial E_{i} \partial E_{j}} \tag{5}$$

As a result, the evaluation of the Raman activity involves third derivatives of the excited-state energy with respect to external perturbations in the form of $\frac{\partial^3 \mathcal{E}^n}{\partial R_i \partial E_j \partial E_k}$. Evaluations of this quantity depend explicitly on up to the fourth functional derivative of the XC kernel. While this may or may not present an obvious problem in the evaluation of ground state properties, the *analytical* evaluation of the functional derivatives required for the evaluation of the TDDFT energy derivatives becomes quite challenging and numerically unstable even as early as second order.^{93,94}

In practice, one can use numerical schemes for the evaluation of the energy derivatives required to compute the excited-state Raman intensities. However, a complete *numerical* third derivative evaluation of TDDFT excited-state energy is computationally prohibitive. Given the recent development of analytical TDDFT second derivatives,⁹⁵ $\frac{\partial^3 \mathcal{E}^n}{\partial R_i \partial E_j \partial E_k}$ can be evaluated as a numerical first derivative of the Hessian. Assuming that \mathcal{E}^n is a smooth, analytic function of **R** and **E** over the sampled parameter space, one may freely interchange the order of differentiation in the 3-gradient $(\frac{\partial}{\partial R_i}, \frac{\partial}{\partial E_j}, \frac{\partial}{\partial E_k})$. Considering the 3N degrees of freedom of nuclear Cartesian coordinates **R** and only 3 degrees of freedom of external electric

coordinates **R** and only 3 degrees of freedom of external electric field **E**, it is much more computational efficient to evaluate the TDDFT third derivatives with the expression

$$\frac{\partial^{3} \mathcal{E}^{n}}{\partial R_{i} \partial E_{j} \partial E_{k}} \approx \frac{\Delta}{\Delta E_{j}} \left(\frac{\partial^{2} \mathcal{E}^{n}}{\partial R_{i} \partial E_{k}} \right) = \frac{\Delta}{\Delta E_{j}} \left(\frac{\partial \mu_{k}^{n}}{\partial R_{i}} \right)$$
(6)

where Δ refers to the numerical differentiation procedures, and $\frac{\partial \mu_k^m}{\partial R_i}$ is the *n*th excited-state electric dipole derivative. Equation 6 requires only *m* solutions of the coupled-perturbed TDDFT equations at a given nuclear configuration for the chosen numerical differentiation scheme. In this work, we chose a three-point stencil numerical central differentiation scheme (*m* = 7) to evaluate the third derivative of TDDFT excited-state energy, since it provides the best balance between accuracy and computational cost,

$$\frac{\Delta}{\Delta \mathbf{E}} \left(\frac{\partial \mu_k^n}{\partial R_i} \right) = \frac{1}{2|\Delta \mathbf{E}|} \left(\frac{\partial \mu_k^n}{\partial R_i} \bigg|_{\Delta \mathbf{E}} - \frac{\partial \mu_k^n}{\partial R_i} \bigg|_{-\Delta \mathbf{E}} \right) + O(|\Delta \mathbf{E}|^2)$$
(7)

where ΔE is an electric field displacement, and the *n*th excitedstate electric dipole derivative is evaluated analytically at each displacement point.

Transient Raman Analysis. The discussion above illustrates an efficient strategy to evaluate the instantaneous nonresonant Raman intensities of electronically excited states expressed in terms of the excited-state polarizability derivatives. To obtain transient Raman signals, excited transient state vibrational normal modes must be defined to represent characteristics of excited-state reaction dynamics. In this section, we present a brief review of the theoretical strategy



Figure 1. Top Panel: Transient Raman vibrational spectra of Cl_2 using (a) time-dependent instantaneous normal mode and (b) time-integrated normal mode ($\mathcal{T}_0 = 61$ fs, given the harmonic frequency ~540 cm⁻¹). Gaussian broadening is employed for the lineshapes with a fixed HWHM = 2 cm⁻¹, left, and HWHM = 5 cm⁻¹, right.

used in the case of transient IR spectroscopy⁹⁴ and develop the necessary theory for the extension to transient Raman spectroscopy.

Given a molecular geometry, one may evaluate the massweighted *n*th excited-state energy Hessian, \mathbf{H}^n , with respect to the set of nuclear coordinates, **R**, to obtain a set of real eigenvalues, λ^n , and eigenvectors, \mathbf{U}^n , of \mathbf{H}^n ,

$$H_{ij}^{n} = \frac{1}{\sqrt{m_{i}m_{j}}} \frac{\partial^{2}\mathcal{E}^{n}}{\partial R_{i}\partial R_{j}}$$
(8)

$$\boldsymbol{\lambda}^n = (\mathbf{U}^n)^T \mathbf{H}^n \mathbf{U}^n \tag{9}$$

where m_i is the mass of the nucleus associated with coordinate *i*.

If **R** represents a molecular geometry corresponding to a local energetic minimum where the gradient vanishes, **U**ⁿ represents a linear transformation of **R** from Cartesian coordinates to the *n*th electronic excited-state normal vibrational coordinates or modes with corresponding vibrational frequencies $\nu_p^n = \frac{\sqrt{\lambda_p^n}}{2\pi}$. However, during the dynamical evolution of a molecular system, the gradient $\mathbf{g}^n(t)$ is usually nonzero, and eigenvectors of \mathbf{H}^n (or the instantaneous normal modes) are poor representations of vibrational modes of a reactive system.⁹⁴

Recently, we have introduced a transient vibrational analysis protocol that is based on a time-integrated potential energy surface of excited state, over a fixed time window NT_0 centered at time t_1^{94}

$$\overline{V}^{n}(\Delta \mathbf{R}, t; \mathcal{NT}_{0}) = \overline{V}^{n}(t; \mathcal{NT}_{0}) + \frac{1}{2} \Delta \mathbf{R}^{T} \overline{\mathbf{H}}^{n}(t; \mathcal{NT}_{0}) \Delta \mathbf{R} + O(\Delta \mathbf{R})^{3}$$
(10)

where N is any positive integer, T_0 is the fundamental vibrational period of interest, and we defined several time integrated quantities according to the following definition:

$$\overline{X}(t;\mathcal{T}) = \mathcal{T}^{-1} \int_{t-\mathcal{T}/2}^{t+\mathcal{T}/2} \mathrm{d}t' X(t')$$
(11)

Note that the time-integrated gradient term disappears in eq 10. This is due to the fact that, after time NT_0 , the dynamical system has returned to its original point in phase space with no net acceleration, so the conservative forces acting on the nuclei must integrate to zero over NT_0 . As a result, the timeintegrated potential surface, eq 10, is a simple quadratic function of $\Delta \mathbf{R}$ out to second order in the series expansion, similar to the harmonic expansion around the equilibrium geometry.

While eq 10 is only exact when *all* nuclear coordinates return to their original positions, it is sufficient that only the particular normal mode under consideration return to its initial position at $t = NT_0$ (i.e., not concurrently with all other modes) for eq 10 to be approximately satisfied. Therefore, one can define transient normal modes by diagonalizing the time-integrated Hessian,

$$(\overline{\mathbf{U}}^{n}(t;\mathcal{T}))^{T}\overline{\mathbf{H}}^{n}(t;\mathcal{T})\overline{\mathbf{U}}^{n}(t) = \overline{\lambda}^{n}(t;\mathcal{T})$$
(12)

By employing the translating time-window strategy 94,101 in eq 10, the modes expressed in eq 12 become time-resolved transient vibrational modes.

The transient Raman signals can be computed using eq 1 with the time-resolved transient vibrational modes and polarizabilities,

$$\frac{\partial \alpha_{jk}^{n}(t)}{\partial \bar{Q}_{p}^{n}} = \sum_{i=1}^{3N} \frac{\partial \alpha_{jk}^{n}(t)}{\partial R_{i}} \bar{U}_{pi}^{n}(t; \mathcal{T})$$
(13)

where $\overline{\mathbf{U}}_{p}^{n}$ is the *p*th eigenvector of $\overline{\mathbf{U}}^{n}$.

RESULTS AND DISCUSSION

The following benchmark calculations were performed using a locally modified development version of the Gaussian software suite.¹⁰² The proposed protocol requires the calculation of the instantaneous excited-state Hessian and the numerical evaluations of the Raman activities for the nuclear configurations collected by molecular dynamics at different time steps to establish the time-integrated normal mode framework and perform the excited-state transient Raman analysis, outlined in eq 12 and eq 13. A direct Born–Oppenheimer molecular dynamics (BOMD)^{103–106} trajectory was carried out for each test case, using the velocity Verlet algorithm to integrate Newton's equations for the nuclear motion. Throughout the direct excited-state BOMD trajectory, TDDFT energies and energy gradients were evaluated "on-the-fly" at each time step. $^{70,71,73-75}$ Due to the computational cost for calculating excited-state Hessians and numerical evaluations of the Raman intensities, these terms are evaluated less frequently than the Verlet nuclear integration steps. The transient Raman spectra are obtained by reporting the transient Raman activity as a function of the corresponding transient frequency both obtained by applying the time-window procedure explained in the Methodology section, for a given transient normal mode of choice. In the current work, a Gaussian broadening (HWHM = 5 cm^{-1} , fixed in time) is used to obtain the lineshapes of the transient signals, although different approaches may be also used for modeling lineshapes.⁹⁴ The initial conditions for each trajectory were generated to simulate a Boltzmann ensemble at room temperature (298 K) in the ground state. Given a Boltzmann-sampled vibrational energy in a specific normal mode in the ground state structure, the initial phase (nuclear

positions and momenta) was chosen randomly and classically within the harmonic oscillator approximation.^{107,108} Since the real potential energy surface is not strictly harmonic, the initial vibrational coordinates generated by this procedure were scaled to correct for the anharmonicity. In this work, we discuss only the results of a single trajectory since the focus of the current work is to gauge the reliability of the developed transient vibrational analysis protocol rather than to perform the exhaustive sampling of the phase space needed to compare with experiments.

Ground State Transient Raman. In order to test the robustness of the proposed transient Raman protocol and to understand some intrinsic characteristics of the method, we choose to analyze the ground state transient vibrational spectra of a Raman active (IR inactive) homonuclear diatomic molecule, Cl₂. A trajectory with 0.1 fs nuclear time step and 500 fs in duration was computed at the B3LYP/cc-pVTZ level of theory.¹⁰⁹⁻¹¹¹ Analytical evaluations of the energy Hessians and numerical evaluations of the required 3-gradient terms were performed every 1.0 fs. Figure 1 compares the ground state transient Raman spectra computed using the instantaneous and time-integrated normal-mode analyses. The transient Raman spectrum using the instantaneous normal modes exhibits oscillatory vibrational frequency behavior even for such simple one-dimensional near-harmonic vibrations. As previously discussed, vibrational frequencies for the instantaneous normal modes are ill-defined because the potential energy may not be simply expressed as a quadratic function of the nuclear degrees of freedom. By contrast, the time-integrated normal-mode analyses display the correct behavior of a steadystate Raman spectrum-a near constant vibrational frequency as a function of measurement time. When the integration window $\mathcal T$ deviates from the fundamental period of the vibration of interest, the assumption that the gradient term integrates to zero, as in eq 10, becomes less valid.⁹⁴ As a result, the transient frequency becomes unphysically oscillatory when \mathcal{T} is far away from \mathcal{T}_0 . This is easily reconciled with the fact that the choice $\mathcal{T} = 0$ coincides with the limiting case of instantaneous normal modes.

Excited-State Transient Raman. To demonstrate the capability of the transient Raman protocol presented here to realistically capture the temporal evolution of a vibrational mode, we have computed the transient nonresonant Raman signals following a vertical electronic excitation in the *trans*-stilbene (Figure 2) molecule, which has been extensively studied from both the experimental and theoretical vantage.^{112–118}

Photoexcitation of the *trans*-stilbene molecule gives rise to a spontaneous trans-cis isomerization on the excited state $S_1^{116-118}$ around the $\langle C-C=C-C \rangle$ dihedral angle (see Figure 2) that can be monitored via transient vibrational spectros-



Figure 2. Ball and sticks representation of the *trans*-stilbene. Left: vibrational mode corresponding to the *trans*-*cis* isomerization. Right: characteristic C=C stretching mode sensitive to the change of potential energy surfaces.

copies. We focused on the effects of the ultrafast dynamics and molecular rearrangements on the vibrational features immediately after the photoexcitation. There is an experimentally observed ultrafast decreasing of the intensity of the resonant Raman signal at short time after the photoexcitation, while no significant decay of trans-stilbene excited-state population is observed on this time scale (<0.5 ps) either by transient absorption or time-resolved fluorescence.^{119,120} Although experiments on this system were carried out in the resonant Raman condition, the nonresonant Raman computational work presented herein probes the same underlying physical characteristics but with a different intensity profile of the signal. Note that experiment in the off-resonance condition was carried out on a much longer time scale.¹²¹ Experimental evidence has shown that the nonradiative relaxation to the ground state that terminates the isomerization process occurs for the trans conformation on longer time scales (~30 ps).^{116,117} The initial conditions for the BOMD nuclear dynamics of this system were generated from the minimum energy ground state trans-conformation. The trajectories were collected for 500 fs with 0.1 fs time step computed at the TD-B3LYP/6-311++G(d,p) level of theory on the first excited state (S_1) potential energy surface. Analytic evaluations of the excited-state energy Hessians and numerical evaluations of the required 3-gradient terms were performed every 1.0 fs. This level of theory has been shown to be accurate for both the electronic and vibrational analysis of this system.¹¹⁴ The S₁ state is a $\pi \to \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), both of which are highly localized in the ethylenic region.

Figure 3 plots both the time-evolution of the $\langle C-C=C-C \rangle$ dihedral angle and the calculated transient vibrational spectra of trans-stilbene following photoexcitation to track the progress of the photoisomerization. Specifically, the transient Raman activity for a characteristic composite C=C backbone stretching mode (see Figure 2) at ~1685 cm⁻¹ is computed during the reaction dynamics. This mode has a high Raman intensity with large contributions from the C=C stretch, and has been shown to be very sensitive to the bond elongation and ring stretching mixing.¹¹⁴ Figure 3 also shows that this mode is mostly IR inactive, exhibiting weak transient IR signal during the reaction dynamics. This transient Raman signal of the C= C backbone stretching is highly correlated to the $\langle C-C=C-$ C dihedral dynamics, showing a frequency red shift when the systems deviates from planarity (~180°) along with a significant decrease in intensity. The computed spectrum exhibits an oscillatory decay in the intensity, in contrast to a monotonic decay as observed in the experiment.¹¹⁶ This discrepancy is likely due to the limited time-resolution in experiment and the single molecular nature in simulation.

Although we can not make a direct comparison of the signal profile of the nonresonant transient Raman calculated here to those obtained in the resonant Raman experiments, we can make an informative rationale to understand the experimentally observed decreasing of the intensity at the ultrafast time scale probed by resonant Raman experiments.^{116–118} The nonresonant transient analysis presented here suggests that the observed intensity decreasing arises as the system diverges from the planar region, showing the capability of the proposed protocol to provide a molecular interpretation of the transient features in the spectrum.



Figure 3. Time-evolution of $\langle C-C=C-C \rangle$ dihedral angle following the photoexcitation of the *trans*-stilbene molecule from S₀ to S₁ state (top panel). Transient vibrational spectra of the composite C=C backbone stretching mode following photoexcitation of the *trans*-stilbene molecule from S₀ to S₁ state (bottom left: Raman; bottom right: IR). A Gaussian broadening (HWHM = 5 cm⁻¹) is employed for the lineshapes. $T_0 \sim 19$ fs, corresponding to $\nu \sim 1685$ cm⁻¹, which is the unscaled frequency computed at the ground state *trans*-stilbene energy minimum.

CONCLUSION

In this work, we have developed a transient Raman analysis protocol suitable for both ground and excited states, supported and calibrated by benchmark tests. This technique combines *ab initio* direct molecular dynamics with transient excited-state Hessian and Raman activities evaluations, thereby establishing an *ab initio* time-resolved approach that is capable of capturing the time evolution of transient phenomena and providing an interpretation for transient Raman spectroscopic signals in terms of the evolution of molecular degrees of freedom.

AUTHOR INFORMATION

Corresponding Author

*E-mail: xsli@uw.edu.

ORCID 0

Alessio Petrone: 0000-0003-2232-9934 Xiaosong Li: 0000-0001-7341-6240

Author Contributions

[‡]Authors contributed equally

Notes

The authors declare no competing financial interest.

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