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# Ab Initio Transient Vibrational Spectral Analysis

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ABSTRACT: Pump probe spectroscopy techniques have enabled the direct observation of a variety of transient molecular species in both ground and excited electronic states. Timeresolved vibrational spectroscopy is becoming an indispensable tool for investigating photoinduced nuclear dynamics of chemical systems of all kinds. On the other hand, a complete picture of the chemical dynamics encoded in these spectra cannot be achieved without a full temporal description of the structural relaxation, including the explicit timedependence of vibrational coordinates that are substantially displaced from equilibrium by electronic excitation. Here we present a transient vibrational analysis protocol combining ab initio direct molecular dynamics and time-integrated normal modes introduced in this work, relying on the recent development of analytic time-dependent density functional theory (TDDFT) second derivatives for excited states. Prototypical molecules will be used as test cases, showing the evolution of the vibrational signatures that follow electronic excitation. This protocol provides a direct route to assigning the vibrations implicated in the (photo)dynamics of several (photoactive) systems.



Advances in ultrafast pulsed laser technology have made it possible to probe chemical processes on the fundamental time scale of molecular motions, revealing the underlying driving forces behind reaction dynamics.<sup>1-4</sup> In particular, timeresolved vibrational spectroscopies (IR and Raman) have become increasingly important in modern day chemical, materials, and biological research because of their unique capability to investigate nonequilibrium structural dynamics of ultrafast chemical phenomena.<sup>5–10</sup> For instance, transient vibrational spectroscopies following resonant UV pump pulses can be used to investigate important molecular motions that may drive charge transfer, polaron formation, exciton dissociation, or nonradiative transitions in the short lifetime of the photoexcited species.<sup>11–15</sup>

Interpretation of these multiphoton spectroscopic signals is made challenging by the complex interplay among many degrees of freedom and their ultrafast nature. In some cases where only a few degrees of freedom are important, semiclassical perturbative approaches are sufficient and have been very successful.<sup>16-32</sup> Nevertheless, full ab initio tools that are not subject to any preassumed model Hamiltonian can be very useful in identifying the key molecular degrees of freedom involved in important chemical processes.

The most popular approach to analyze vibrational spectra is based on harmonic normal modes computed at the equilibrium structure.<sup>33</sup> Nowadays, ab initio calculations of harmonic normal modes on the ground electronic state can be routinely done using many well-established electronic structure methods. The change in the dipole moment along these modes can be evaluated, providing both the spectrum and a molecular interpretation of the experimental signal. It is also possible to include anharmonic corrections,  $^{34-36}$  although their *ab initio* analytical treatment is only available on the ground state and at increased computational cost relative to simple harmonic analysis. A critical limitation of such static approaches is that they cannot be directly applied to studying vibrational phenomena far from equilibrium, or their corresponding time-resolved signals.

Another route to simulate vibrational spectra is through the Fourier transform of the dipole moment time correlation function extracted from ab initio molecular dynamics simulations.<sup>37-41</sup> As a dynamical method, this approach can address phenomena far from equilibrium, and can also predict chromatic spectral shifts due to solvation effects. 39,42-45 However, it generally still requires access to equilibrium normal mode information to establish a molecular view of the vibration. There have been several attempts to extend the ab initio dynamical approach to enable some time resolution in the vibrational analysis by, for example, expressing the molecular dynamics in generalized<sup>39,46,47</sup> and instantaneous<sup>48-51</sup> normal modes, and by application of wavelet analysis.<sup>52,53</sup> However, these approaches still have their own limitations mainly due to the fact that transient normal modes for vibrational analysis are not well-defined and molecular level understanding of vibrational evolution is still very difficult to obtain.

In this work, we develop a transient vibrational analysis protocol combining ab initio direct molecular dynamics and transient analytical excited state Hessian 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 spectroscopic signals in terms of the evolution of molecular degrees of freedom.

Received: October 5, 2016 Accepted: October 27, 2016 Published: October 27, 2016 Given a molecular structure, the mass-weighted Hessian **H** of the energy with respect to nuclear coordinates  $\mathbf{R} = \{R_1, R_2, R_3, ...\}$  can be evaluated,

$$H_{ij} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 E}{\partial R_i \partial R_j} \tag{1}$$

where  $m_i$  is the mass of nucleus *i*. As a real Hermitian matrix, its eigenvalues  $\lambda = \{\lambda_{11}, \lambda_{22}, \lambda_{33}, ...\}$  and eigenvectors  $\mathbf{U} = \{\mathbf{U}_{1j}, \mathbf{U}_{2j}, \mathbf{U}_{3j}, ...\}$  can be obtained via a diagonalization procedure:

$$\mathbf{U}^T \mathbf{H} \mathbf{U} = \boldsymbol{\lambda} \tag{2}$$

If the nuclear coordinates **R** correspond to a molecular equilibrium geometry (i.e., a local minimum), **U** is the transformation matrix from the Cartesian to the normal vibrational coordinates or modes, in which the potential energy surface for each independent mode is a purely quadratic function of the normal coordinate.<sup>33</sup> Their harmonic vibrational frequencies can be computed from the eigenvalues of **H** as  $\nu_i = \frac{\sqrt{\lambda_{ii}}}{2\pi}$ .

Although the mathematical procedure in eq 2 is still applicable, for a nonequilibrium molecular structure, the coordinates U's become ill-defined because the potential energy can not be expressed as a simple quadratic function of the coordinates. This is because the energy's first derivative, or force, for a nonequilibrium molecular structure is nonzero. For near equilibrium processes, the force is small. In such a situation, the coordinates U can be approximately used as vibrational normal modes, which are often termed as instantaneous normal modes to be differentiated from the classical definition of vibrational modes.<sup>51,54,55</sup> However, for chemical processes far away from equilibrium, such as those occurring in the excited state immediately following photoexcitation, the instantaneous normal modes are inadequate. It is the goal of this work to develop a transient (time-dependent) normal-mode analysis that can be applied to far-fromequilibrium molecular processes.

At any given time t, the potential energy can be written as a Taylor series expanded about the current position,  $\mathbf{R}(t)$ :

$$V(\Delta \mathbf{R}, t) = V(\mathbf{R}(t)) + \mathbf{g}(t)^T \Delta \mathbf{R} + \frac{1}{2} \Delta \mathbf{R}^T \mathbf{H}(t) \Delta \mathbf{R} + O(\Delta \mathbf{R})^3$$
(3)

Equation 3 can be integrated and normalized over a fixed time window T centered at time *t*,

$$\overline{V}(\Delta \mathbf{R}, t) = \overline{V}(t) + \overline{g}(t)^T \Delta \mathbf{R} + \frac{1}{2} \Delta \mathbf{R}^T \overline{H}(t) \Delta \mathbf{R}$$
(4)

$$\overline{V}(t) = \frac{1}{\mathcal{T}} \int_{t-\mathcal{T}/2}^{t+\mathcal{T}/2} \mathrm{d}t' V(\mathbf{R}(t'))$$
(5)

$$\overline{g}(t) = \frac{1}{\mathcal{T}} \int_{t-\mathcal{T}/2}^{t+\mathcal{T}/2} \mathrm{d}t' \mathbf{g}(t')$$
(6)

$$\bar{H}(t) = \frac{1}{\mathcal{T}} \int_{t-\mathcal{T}/2}^{t+\mathcal{T}/2} \mathrm{d}t' \mathbf{H}(t')$$
(7)

For an ideal quadratic potential with no dissipation, the dynamical system has a periodicity of  $\mathcal{T}_0$  in time, where  $\mathcal{T}_0$  is the fundamental vibrational period. Since after  $\mathcal{T}_0$  the dynamical system returns to the same point in phase space

with no net acceleration, the conservative forces acting on the nuclei ( $\propto$  g) must integrate to zero over this period,

$$\frac{1}{n\mathcal{T}_{0}}\int_{t-n\mathcal{T}_{0}/2}^{t+n\mathcal{T}_{0}/2}\mathrm{d}t'\mathbf{g}(t')=0$$
(8)

where *n* is a positive integer. By choosing  $T = nT_0$  and substituting eq 8 into eq 4, we then obtain a quadratic expression of the integrated potential energy,

$$\overline{V}(\Delta \mathbf{R}, t) = \overline{V}(t) + \frac{1}{2} \Delta \mathbf{R}^{\mathrm{T}} \overline{H}(t) \Delta \mathbf{R} + O(\Delta \mathbf{R})^{3}$$
(9)

From eq 9, it is clear upon integrating over the fundamental period of the vibration, the potential, just like that at the equilibrium geometry, is a simple quadratic function of  $\Delta \mathbf{R}$  (to second order in the series expansion). While eq 9 is only exact when *all* nuclear positions return to their original positions, the normal modes are energetically decoupled from one another to second order, and can be associated (to a good approximation) with independent, one-dimensional potentials. Therefore, one can define transient normal modes by diagonalizing the time-integrated Hessian,

$$\overline{\mathbf{U}}(t)^T \overline{\mathbf{H}}(t) \overline{\mathbf{U}}(t) = \overline{\lambda}(t)$$
(10)

By employing a translating time-window strategy<sup>56</sup> in eq 9, modes expressed in eq 10 become time-resolved transient vibrational modes. The transient IR intensity can be computed as  $^{40,57}$ 

$$\overline{I}_{i}(t) \propto \int_{t-\mathcal{T}/2}^{t+\mathcal{T}/2} \mathrm{d}t' \left(\frac{\partial \mu(t')}{\partial U_{i}(t')}\right)^{2}$$
(11)

In order to define the transient line shape and width, we extend the formulation of Skinner et al.<sup>56</sup> to the time-resolved domain. The time-dependent fluctuation of  $\overline{I}_i(t)$  arises from changes in the dipole magnitude (non-Condon effects) and/or in the angle between the field and the dipole itself. By including the time-integration approach, these effects are minimized, and the line shape at each time is only proportional to the transient distribution of the mass weighted Hessian eigenvalues over the period of the mode ( $\delta(\nu_i(t) - \overline{\nu}_i(t))$ ). In the current work, we used a Gaussian distribution for the line shape, where the width is determined at a given time to be proportional to the standard deviation of the corresponding frequency within the fundamental period:

$$\overline{\sigma}_i^2(t) = \frac{1}{\mathcal{T}} \int_{t-\mathcal{T}/2}^{t+\mathcal{T}/2} \mathrm{d}t' (\nu_i(t') - \overline{\nu}_i(t))^2 \tag{12}$$

If the rotations and non-Condon effects are important, their effects on the line shape can also be explicitly included.<sup>56</sup>

Calculations of time-dependent density functional theory (TDDFT) excited state energy,<sup>58–62</sup> gradient,<sup>63–67</sup> and nonadiabatic coupling<sup>68–75</sup> have become common practice in computational chemistry. However, efficient analytical approaches to the excited state Hessian have only recently been developed (unpublished work and ref 76). In order to obtain quantities to establish the time-integrated normal mode framework defined in eq 10, instantaneous analytical excited state Hessians are evaluated along the direct Born– Oppenheimer molecular dynamics (BOMD),<sup>77–80</sup> using the velocity Verlet algorithm to integrate the Newtonian equation for the nuclear motions. In the direct excited state BOMD, energies and gradients were obtained "on-the-fly" at each time step using the linear response TDDFT formalism<sup>58-62</sup> for excited states. Due to the expensive computational cost for calculating excited state Hessians, the instantaneous Hessian is evaluated less frequently than the Verlet integration steps.

The following benchmark calculations were performed using the development version of the Gaussian software suite.<sup>81</sup> 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.<sup>82,83</sup> 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.

In order to test the robustness of the proposed transient IR protocol and understand some intrinsic characteristics of the method, we choose to analyze transient vibrational spectra of IR active heteronuclear diatomic molecules, NaCl and HF, on the ground state for which both harmonic and anharmonic analyses are readily available (see Table 1).<sup>34–36</sup> The

Table 1. Ground-State Harmonic and Anharmonic Frequencies Computed at the B3LYP/3-21G Level of Theory<sup>a</sup>

	harmonic	anharmonic
NaCl	349	346
HF	3629	3481
<i>a</i>	1 ( -1)	

<sup>*a*</sup>All values are in wavenumbers (cm<sup>-1</sup>).

trajectories were collected for 1 ps with 0.1 fs time step computed at the B3LYP/3-21G level of theory.<sup>84–86</sup> Analytical Hessians were computed every 1 fs for NaCl and 0.2 fs for HF.

Figure 1 compares the ground-state transient IR spectra computed using the instantaneous and time-integrated normalmode analyses for NaCl and HF. The transient IR spectrum using the instantaneous normal mode exhibits oscillatory vibrational frequency behavior even for such simple onedimensional near-harmonic vibrations. As previously discussed, instantaneous normal modes are ill-defined because the potential energy can 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 transient IR spectrum—near-constant vibrational frequency as a function of measurement time.

To gauge the reliability of the protocol developed herein, transient frequencies using different time windows  $\mathcal{T}$  are plotted in Figure 2 for NaCl and HF vibrations. When the integration window  $\mathcal{T}$  deviates from the fundamental period ( $\mathcal{T}_0 = 95$  fs) of the vibration of interest, eq 8 becomes less valid. As a result, the transient frequency becomes unphysically oscillatory when  $\mathcal{T}$  is far away from  $\mathcal{T}_0$ . It is easy to understand that worse case is when  $\mathcal{T} = 0$ , which corresponds to the instantaneous normal mode case.

Figure 2 also shows that the transient IR spectrum using time-integrated normal-mode analysis gives rise to an absorption peak near the vibrational frequency with anharmonic correction. This can be understood from the deviation of the potential energy surface (PES) from the quadratic form. If a PES is perfectly quadratic, the second derivatives are constant. When a PES is anharmonic, the second derivative matrix can be written in terms of cubic (C), quartic (Q), and higher order anharmonic terms.

$$\mathbf{H}(\Delta \mathbf{R}) = \mathbf{H}_0 + \mathbf{C}^T \Delta \mathbf{R} + \Delta \mathbf{R}^T \mathbf{Q} \Delta \mathbf{R} + \dots$$
(13)



**Figure 1.** Top Panel: Transient vibrational spectra of NaCl using (a) time-dependent instantaneous normal mode and (b) time-integrated normal mode ( $T_0 = 95$  fs). Botton Panel: Transient vibrational spectra of HF using (c) time-dependent instantaneous normal mode and (d) time-integrated normal mode ( $T_0 = 9.4$  fs). Gaussian broadening is employed for the time-integrated normal modes, with a fixed HWHM = 2 cm<sup>-1</sup> applied to the instantaneous normal modes.



Figure 2. Time-resolved frequency evolutions for (a) NaCl and (b) HF. Different windows of  $\mathcal{T}$  in eq 7 are applied: 10 fs (~3340 cm<sup>-1</sup>), 95 fs (~350 cm<sup>-1</sup>), and 200 fs (~167 cm<sup>-1</sup>) for NaCl; 5 fs (~6671 cm<sup>-1</sup>), 9.4 fs (~3548 cm<sup>-1</sup>), and 25 fs (~334 cm<sup>-1</sup>) for HF. Corresponding harmonic and anharmonic frequency values obtained at the equilibrium geometry (see Table 1) are plotted as horizontal lines labeled as "H' and 'A", respectively.

It is then easy to see from eq 13 that while time integrating does away with terms that are first-order in the nuclear displacements, it also includes contributions from anharmonic terms.

In the section above, the transient IR protocol presented here has been shown to be able to realistically capture the temporal evolution of a vibrational mode. In this next test case, we compute the transient IR signals following a vertical electronic excitation in a 2-(2'-hydroxyphenyl)-benzothiazole (HBT, Figure 3) molecule. The initial conditions of the HBT system were generated from the corresponding cis-enol minimum ground state conformation. The trajectories were collected for 300 fs with 0.1 fs time step computed at the TD-B3LYP/6-31G(d,p) level of theory on the first excited state ( $S_1$ ) potential energy surface. This choice of simulation length



Figure 3. Ball and sticks representation of the HBT, including enol (top left) and keto (top right) configurations in the cis conformation. Lower panel: Time-evolutions of NH and OH following photoexcitation of the HBT molecule from  $S_0$  to  $S_1$  state.

is both sufficient to observe the proton transfer event and to prevent the system from exploring the subsequent isomerization that would require the inclusion of nonadiabatic couplings to be properly described.<sup>87,88</sup> Previous studies on HBT have shown that TDDFT gives accurate results for proton transfer processes involving  $\pi \rightarrow \pi^*$  excitations.<sup>88–90</sup> Analytical Hessian for the S<sub>1</sub> state is computed for every 1 fs.

Photoexcitation of the HBT molecule gives rise to a spontaneous proton transfer on the excited state  $S_1$  from the enol to the keto configurations<sup>88,91,92</sup> (see Figure 3) that can be studied via transient vibrational spectroscopies. Figure 3 plots the time-evolution of bond distances of OH and NH that are characteristic of a proton transfer event. Excited state proton transfer for this BOMD trajectory is seen to take place at ~100 fs. At  $\sim$  160 fs, there is a recrossing event but the proton transfer is quickly stabilized, leading to the keto form of HBT on the excited state. The transient vibrational spectra of this event are illustrated in Figure 4. We used the time integration windows that correspond to the ground state anharmonic frequencies of OH (in enol configuration) and NH (in keto configuration), respectively. Due to the characteristic change of the transient mode from OH to NH stretching, the analysis is separated into two domains according to the time-evolution of OH (Figure 4a) and NH (Figure 4b) bonds shown in Figure 3. Transient vibrational analysis performed in the first time interval from t = 0 fs to t = 90 fs corresponds to transient spectra of the OH vibration, whereas the second time interval from t = 100 fs on corresponds to transient spectra of the NH stretching. It is obvious from Figure 4 that the OH stretching mode decays quickly followed by an appearance of the NH mode as the proton transfer event takes place on the excited state.

The analysis above has to be carried out in two different time intervals because the characteristic transient normal modes of interest change due to structural reorganization that occurs following photoexcitation. The structural relaxation corresponds to a transition between two minima on the excited state PES associated with the enol and keto tautomers. A complementary approach to indirectly analyze the excited state proton transfer event is to track the transient vibrational spectra of the backbone vibration of the HBT molecule. Figure 4c shows the excited state transient vibrational spectrum at ~1544 cm<sup>-1</sup>. This region is characteristic of the concerted stretching motion of the C=O group and conjugated C=C bonds,

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Figure 4. Transient vibrational spectra of (a) OH, (b) NH, and (c) backbone stretching modes following photoexcitation of the HBT molecule from  $S_0$  to  $S_1$  state. OH:  $\mathcal{T}_0 \sim 11$  fs, corresponding to  $\nu \sim 2960$  cm<sup>-1</sup>. NH:  $\mathcal{T}_0 \sim 10$  fs, corresponding to  $\nu = 3150$  cm<sup>-1</sup>. Backbone stretching:  $\mathcal{T}_0 \sim 21$  fs, corresponding to  $\nu \sim 1544$  cm<sup>-1</sup>.

which has been considered as a signature mode strongly affected by the proton transfer event.<sup>87,91,93,94</sup> Indeed, Figure 4c shows that the intensity of this mode is quenched when the proton is "shared" by N and O between t = 110 fs and t = 170 fs. This particular mode becomes rather bright after the proton transfer event is finished. This is due to the formation of the C=O bond, which gives rise to additional contributions to the conjugated backbone stretching.<sup>87,91,93,94</sup>

Here we demonstrated that the proposed transient IR protocol can capture the time-evolution and temporal progression of a vibrational mode with averaged anharmonic corrections. As the time-integration is mode specific, the spectrum can only be resolved on a mode-by-mode basis. Nevertheless, the presented method is cost-effective, since this protocol requires only the additional evaluation of the instantaneous Hessian's for a given trajectory, and most of the time this quantity is already available due to the type of the integration procedure employed for the equation of motion.

This analysis showed very promising results to study vibrational signatures of transient species, through a careful choice of the modes of interest to obtain the appropriate time windows. The protocol also can be used with any level of theory where energy Hessian's are available, without losing any generality. As the delay time between pump and probe pulses is increased in the experiment, ground-state recovery processes may begin to occur, rendering adiabatic evolution of the nuclei on the excited state potential an incomplete descriptor of the experimentally resolved transient signal. The protocol developed herein can be extended, in that case, to account for the nonadiabatic molecular dynamics associated with nonradiative decay. Benchmark tests, using prototypical molecules, showed the capability of our proposed method to properly describe the time evolution of the vibrational signatures that follow electronic excitation. Applying the proposed method to more relevant systems to investigate the role of vibrations in mediating the (photo)dynamics of several (photoactive) processes will be a central objective of our future work.

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#### Notes

The authors declare no competing financial interest.

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