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Wavelet Transforms for Determining Time-Dependent Vibrational Frequencies

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Abstract: Fourier transforms of autocorrelation functions are typically used to calculate spectra and transport properties, but they require oscillations periodic in time (a stationary time series). The time-scale relation revealed by a wavelet transform (WT), on the other hand, gives a relation between time and pseudo-frequency that is used here to calculate vibrational frequencies for HONO and to detect the molecule's trans–cis conformational change in ab initio molecular dynamics simulations. Thus, the WT shows potential for giving new insights into nonstationary time series frequently encountered in chemistry and physics.

The Fourier transform (FT) is ubiquitous in chemistry for extracting the frequency components of a system's response to a time-dependent perturbation.[1,2] In computational chemistry, for example, spectra and transport properties are typically accessed by computing the FT of a time correlation function, $C(t)$:[3,4]

$$F(\omega) = \int C(t)\, e^{-i\omega t}\, dt \qquad (1)$$

where $e^{-i\omega t}$ is the Fourier basis function with frequency (ω) and time (t). Examples of important time correlation functions include the van Hove, dipole density, magnetization, and current–current correlation functions, whose FTs are related to the structure factor, infrared line shape, NMR line shape, and frequency-dependent conductivity, respectively.[3,4] Despite its enormous power, the traditional FT suffers several strict requirements, including the assumption of a stationary

time series.[5,6] A powerful alternative to the traditional FT, the wavelet transform (WT), was recently developed and has potential for resolving frequency- *and* time-dependent properties[6,7] of nonstationary time series. Wavelet analysis was used to study energy transport in OCS,[8] for many-body dynamics[9] and intramolecular energy transfer.[10] The current contribution illustrates the method's power for resolving time-dependent spectral or transport properties by describing the use of WTs to calculate the vibrational spectrum of HONO in its most stable trans conformation and to detect HONO's trans–cis conformational change during ab initio molecular dynamics simulations.

Wavelet analysis has been used extensively in signal and image processing over the past decade[6,7] and has enjoyed increasing use in computational chemistry.[11–14] To understand the wavelet transform, consider replacing the Fourier basis function in eq 1 with a wavelet $\psi_{a,b}(t)$, where the WT can be written as

$$W(a,b) = \int C(t)\, \psi_{a,b}(t)\, dt \qquad (2)$$

The wavelet $\psi_{a,b}(t)$ can be defined by dilation and translation of a "mother wavelet" $\psi(t)$, that is,

$$\psi_{a,b}(t) = |a|^{-1/2} \psi\!\left(\frac{t-b}{a}\right) \qquad (a,b \in R;\ a \neq 0) \qquad (3)$$

where a is the scale (dilation) and b is the position (translation) parameter. In the discrete form, one can rewrite eq 3 as

$$\psi_{m,n}(t) = a_0^{-m/2} \psi(a_0^{-m}t - nb_0) \qquad (4)$$

where $a_0^m = a$ and $nb_0 a_0^m = b$ ($m,n \in Z;\ a_0 \neq 0$). Generally, $a_0 = 2$ and $b_0 = 1$ are used. Now, if one assumes a center frequency (ω_c) associated with a wavelet, then a pseudo-frequency (ω) can be obtained by using the relation

$$\omega = \omega_c / a \cdot \Delta \qquad (5)$$

where Δ is the sampling period and indicates the interval between two data points and a is a unitless scale parameter.[15] The lower scale (a) indicates a higher pseudo-frequency and vice versa. The frequency at the maximum of the mother wavelet's FT is the center frequency (ω_c). For applications envisioned here, pseudo-frequencies are found from the WT of an autocorrelation function.

Compared to the FT (eq 1), where sines and cosines are the analyzing functions, the WT (eq 2) uses a family of analyzing functions called wavelets, derived from the mother

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Table 1. Comparisons of Pseudo-Frequencies Calculated for Scales with Maximum Values of Wavelet Coefficients with Harmonic ab initio Frequencies Determined from Fourier Transformation and Experimental Frequencies[19]

pseudo-freqency (cm^{-1})	scale	ab initio frequency (cm^{-1})	FT frequency (cm^{-1})	exptl. IR frequency (cm^{-1})
		trans		
602	45	599	550, 610	544
796	34	790	750	596
1083	25	1099	990, 1050, 1070	790
1504	18	1514	1600	1263
2082	13	2043	2020	1700
3868	7	4082	3615, 3645, 4200	3591

wavelet $\psi(t)$ (eqs 3 and 4).[6,7] Wavelets are characterized by two parameters, the scale and position in time, so that pseudo-frequencies derived from the WT give a unique time-frequency relation for stationary *or* nonstationary time series that is inaccessible by FT. Here, the trans−cis isomerization of HONO renders the time series of atomic positions and velocities nonstationary, thereby producing two sets of vibrational frequencies, separated in time by a conformational change.

Figure 1a and b show the FT and WT, respectively, of a velocity autocorrelation function from a representative ab initio molecular dynamics trajectory of HONO. (The procedure for generating HONO trajectories is described in the references.[16]) In the Fourier spectrum, bands of frequencies appear near the frequency of each vibrational fundamental. In contrast, Figure 1b shows the wavelet coefficients, $W(a,b)$, for different values of scale, a, and position in time, b (several

different mother wavelets were tested,[7,17,18] but all results reported here used the Morlet wavelet[17]). The scales for which the $W(a,b)$ values are the maximum were chosen, and the corresponding pseudo-frequencies were calculated. Table 1 lists the scales and corresponding pseudo-frequencies, compared with frequencies from ab initio quantum chemical calculations, the FT of the same correlation function, and experimental results.[19] Nearly all the pseudo-frequencies are in better agreement than Fourier frequencies with those frequencies determined by using ab initio quantum chemistry. The lower pseudo-frequencies are in better agreement than
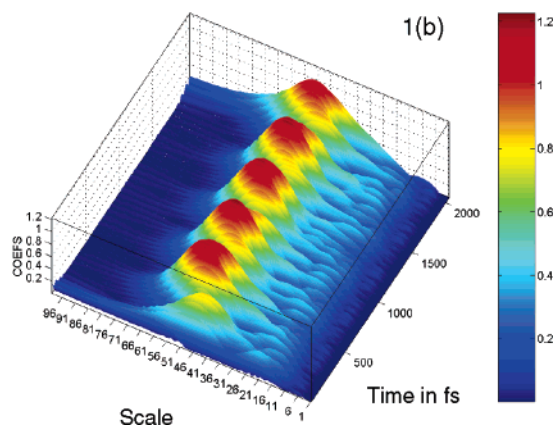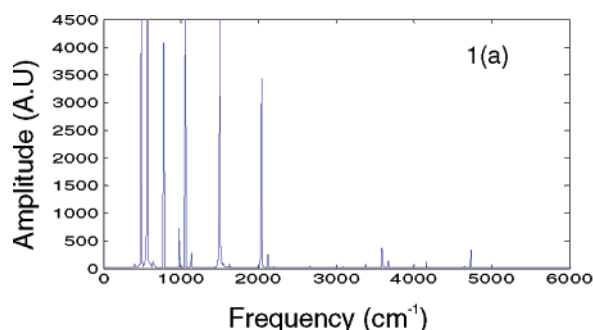
Figure 1. (a) Fourier transform of the velocity autocorrelation function $C(t)$ for a single *trans*- and *cis*-HONO molecule. (b) The plot of wavelet coefficients at different values of scale (*a*) and time obtained from the wavelet transform of $C(t)$ using the Morlet wavelet. The scale is unitless.
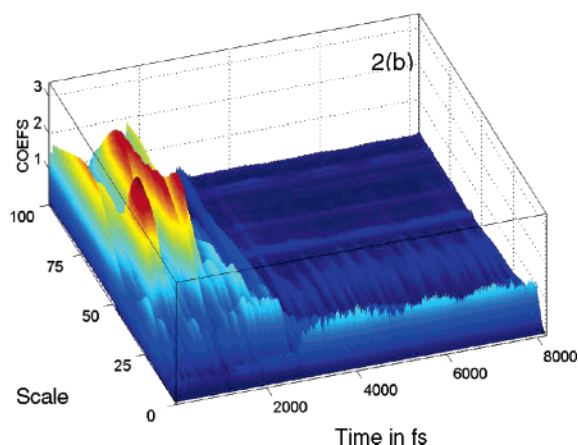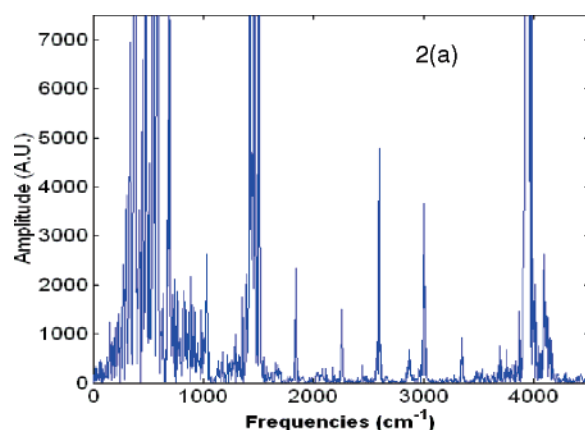
Figure 2. (a) Fourier transform of the velocity autocorrelation function $C(t)$ for the trans−cis isomerization of a single HONO molecule. (b) The plot of wavelet coefficients at different values of scale (*a*) and time obtained from the wavelet transform of $C(t)$ using the Morlet wavelet. The scale is unitless.

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the higher pseudo-frequencies, a result that can be understood in terms of the uncertainty principle. At low scale, the time localization is more precise for WTs and, thereby, the uncertainty in pseudo-frequency increases. The high pseudo-frequencies corresponding to low scales, therefore, differ more from the ab initio quantum chemical results than the low pseudo-frequencies.

The velocity autocorrelation function for the trans−cis isomerization of a single HONO molecule was also generated from ab initio molecular dynamics simulations,[20] and its FT (Figure 2a) and WT (Figure 2b) were calculated. From the FT in Figure 2a, we cannot tell when the transition occurs from one conformation of HONO to another. The WT displayed in Figure 2b, however, shows discontinuities in wavelet coefficients along the scale at times corresponding to the conformational changes of HONO observed by monitoring the time history of the dihedral angle.

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