

Quantum Signatures of Unstable Dynamics in the Photodissociation of Ozone

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Abstract: - Weak oscillations in the Hartley absorption system of ozone have been interpreted as the quantum correspondence of unstable repeating orbits in the nonlinear classical dynamics. Time-domain analysis of the frequency-domain spectrum has proven invaluable in this regard. Current experiments are measuring the Raman excitation profiles in a unique continuous-scanning mode to determine more details about photoexcited ozone during dissociation. Extraction of the corresponding dynamical information, which requires recovery of phase information from the Raman signals, is complicated by both noise and finite length of the spectral data. In answer to both these issues, a time-frequency analysis via wavelet decomposition is being put into operation.

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1 Introduction

While Hartley first measured the ultraviolet absorption of ozone in 1881 [1], uncertainty yet shrouds the meaning of details of the spectrum. The extremely broad absorption continuum responsible for shielding us from much of the solar UV can be understood in standard molecular terms as a transition to an unbound electronic state in which one of the O–O bonds break. Much weaker oscillations with the appearance of broadened vibrational transitions are found superimposed across the entirety of the continuum, however, and these have not yielded to interpretation until recently. Investigations using classical mechanics have identified families of unstable repeating orbits whose periods correspond closely to dominant components in the Fourier analysis of the spectrum [2] [3], analogous to the situation found for Rydberg atoms in external magnetic fields [4]. Deeper

interpretation of the molecular dynamics of ozone determining the absorption spectrum is hampered by uncertainties in the potential energy surface of the excited state and by lack of a precise classical-quantal correspondence principle for calculation of the spectrum from isolated trajectories in a chaotic phase space. Potential surface and quantum dynamical calculations have been made, [5] [6] though the structure seen in the Hartley absorption band still resists accurate theoretical reconstruction.

A much more incisive experimental tool for determination of the excited state dynamics is Dissociative Resonance Raman Spectroscopy [7]. While the vast majority of photoexcited molecules dissociate, the tiny fraction that instead radiate a photon end up in a variety of vibrational levels in the ground electronic state. Analysis of the intensities of these transitions as functions of excitation wavelength provides vibration-specific

information about the quantum dynamics in the excited state which may in principle be inverted to yield the local shape of the excited state potential [8]. The difficulty is that the Raman signal is a real quantity proportional to the absolute square of a complex dipole polarizability. In order to implement this inversion, it is first necessary to recover the phase of the polarizability. This is made possible in ideal cases by using Hilbert Transform (HT) types of relations [9] [10].

In practice, the continuously-scanned Raman Excitation Profiles (REP's) obtained will be limited in both accessible wavelength range and in Signal-to-Noise ratio. Both of these factors hinder implementation of standard Fast Fourier Transform (FFT) methods for calculation of HT's. A wavelet-based analysis is therefore under development, inspired by their use for calculation of HT's by Beylkin [11]. The localized nature of the wavelet basis functions [12] holds promise for sorting out interfering spectral contributions from short- and long-time dynamics. Wavelet bases have also been shown to be nearly optimal for certain types of denoising [13].

2 Ozone Raman Spectroscopy

The Raman intensity measured for scattering from the lowest vibrational state (0) to state n (collective vibrational index) can be expressed as

$$I(\omega_i, \omega_s) \propto \left| \langle n, 0 | \hat{\alpha} | 0, 0 \rangle \right|^2, \quad (1)$$

where the molecular dipole polarizability can be expressed as a truncated Fourier transform over a complex correlation function [14]

$$\langle n, 0 | \hat{\alpha} | 0, 0 \rangle = \int_0^{\infty} dt \exp\left[it \left(\omega_i + E_0 / \hbar \right) \right] \times \left\langle n \left| \hat{\alpha}(t) \right| 0 \right\rangle \quad (2)$$

Here ω_i is the incident photon frequency and $\omega_s = \omega_i + (E_0 - E_n) / \hbar$ is the scattered photon frequency. For cases where there is more

than one nonzero molecule-frame component of the polarizability, these equations are straightforwardly generalized.

For Hartley band excitation of ozone, both absorption and Raman spectra are determined by the ultrafast quantum dynamics in the dissociative excited electronic state. The wave packet $\psi_0(t)$ evolves from $\psi_0 = \psi_0(0)$ (essentially the initial vibrational wave function) under the bidding of the time-dependent Schrödinger equation for the motion of the nuclei. The overlap of this wave packet with ψ_n yields a correlation function in which dynamical events are separated in time. In the absorption case, where only the autocorrelation function ($n=0$) is relevant, there is a clean separation of contributions due to direct dissociation ($t < 10$ fs) and indirect dissociation ($20 < t < 150$ fs). These manifest themselves, respectively, as a rapid initial falloff of the autocorrelation function and as minor recurrences due to small portions of the wave packet returning to the region defined by $\psi_0(0)$. The times of these recurrences have, as mentioned earlier, been identified with unstable nearly-periodic orbits in the classical dynamics of ozone; a qualitative interpretation has thus already been gained of the source of the spectral structure in terms of strongly correlated motion of the two O-O bonds. It is very clear that the time domain is the preferred representation for interpretation of the absorption spectrum.

Since the same wave packet $\psi_0(t)$ occurs in the dipole polarizability, cf. eq. (2), the same can be said for the Raman spectra. Furthermore, it is to be expected that the same spectral structure that occurs in absorption also occurs in the Raman intensities as functions of excitation wavelength for fixed final vibrational states, i.e., the REP's. There are two chief difficulties in exploiting this expectation, however. First, Raman scattering for dissociative systems is much, much harder

to measure accurately since, among other things, the vast majority of incoming photons result in dissociation rather than radiation. Second, in typical experimental setups, each different excitation wavelength of an REP corresponds to a distinct experimental run. The latter situation has recently changed, however, with the introduction of a novel apparatus which obtains continuously-scanned REP's through self-calibration using Rayleigh scattering. The ultraviolet tunable excitation laser is scanned simultaneously with a dual-wavelength spectrometer, all real-time controls being under computer control during operation. An example of a composite REP (normalized by the smoother Rayleigh signal at each wavelength) obtained through runs in overlapping laser dye regions is shown in Fig. 1.

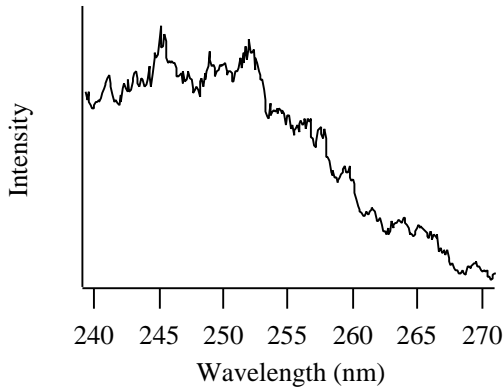


Figure 1. Composite REP for four quanta in the symmetric stretch mode as a function of excitation wavelength.

The above should only be regarded as preliminary data. There are issues that must be resolved before accurate recovery of the phase of the signal can be made. The spectral range on the short wavelength side is currently limited by optics. There is also a considerable amount of noise in the data, as evidenced by run-after-run comparisons. This complicates the compositing process as well as further analysis. A simple few-point

smoothing is an option to help here, but this would have the undesirable effect of partially rounding off the substructure.

Even with these caveats, however, the lower-resolution details in the individual runs making up Fig. 1 are distinctly reproducible. Furthermore, the reproducible features differ from one final vibrational state to another. Thus, it is now certain that (i) the Hartley band oscillations have their analogs in the REP's and (ii) there is vibrational specificity about the information which will ultimately aid in determining the quantum dynamics in the excited state.

3 Wavelet and Hilbert Transforms

The noise and incompleteness of the data both foil the use of FFT techniques for computing HT's. Even with noiseless data, accurate phase recovery [9] [10] requires application to band-limited signals. On the other hand, and potentially of use in the present work, rapidly-varying *components* of the phase in localized spectral regions may be obtainable if they are predominantly influenced by the local behavior of the modulus. Thus, a multiresolution analysis may still allow some partial phase information to be obtained about the spectral structure of interest. Wavelet analysis is a viable tool for this purpose. Beylkin [11] has given a prescription for computing the HT using orthogonal compact support wavelets which may readily be extended to biorthogonal systems,

$$\begin{aligned} \hat{f}(\omega) &= \frac{1}{P} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt \\ &= \int_{-\infty}^{\infty} \tilde{\psi}_k(\omega - \omega_k) r_{k-k} \langle f, \tilde{\psi}_k \rangle. \end{aligned} \quad (3)$$

Here $\tilde{\psi}_k$ is the biorthogonal dual to the scaling function ψ_k , and both are of compact support. The quantities r_{k-k} may be calculated once and asymptotically fall off inversely with index [11]. The remaining

ingredient $\langle f, \tilde{\cdot}_k \rangle$ is just the coefficient of $\tilde{\cdot}_k$ in a scaling function expansion of the function f .

An accurate quadrature technique for calculating these projections in the absence of noise has recently been developed which allows for nonuniform sample spacings [15, 16]; this accommodates the fact that the REP's are, as usual, measured in uniform steps of wavelength rather than frequency. This procedure can then be combined with wavelet denoising techniques [13, 17, 18] and the basic wavelet recursion between scales to obtain a multiresolution decomposition of the HT. With these ingredients in place, the effects of truncation of the range in Eq. (3) may then be systematically investigated, with the anticipation that the finer scale local components corresponding to the later dynamics will be relatively invariant to the longer range truncation.

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