Measuring the sign of excited state displacement via impulsive spectroscopy to reveal molecular dynamics.

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ABSTRACT

Ultrafast photoreactions are governed by multidimensional excited-state potential energy surfaces (PESs), which describe how the molecular potential varies with the nuclear coordinates. Nature has tailored electronically excited PESs, in which the molecular geometry is specifically modified from the ground state equilibrium configuration to efficiently convert the absorbed light energy into specific nuclear rearrangements, driving the system photochemistry. This can be rationalized by the displacements between two different PESs, crucial quantities that are encoded in the Franck-Condon overlap integrals. Conventional spectroscopic approaches probe transition amplitudes, only accessing the absolute value of nuclear displacements; herein we introduce an experimental technique, based on broadband impulsive Raman response to directly measure the magnitude and the sign of excited state displacements, revealing the first steps of photoreaction processes.

Keywords: Raman Spectroscopy, Impulsive Vibrational Spectroscopy, Molecular Dynamics, Potential Energy Surfaces, Molecular Displacements, Coherent Raman Spectroscopy, Photochemistry

Significance. Ultrafast photoreactions are characterized by multidimensional excited state potential energy surfaces (PESs), which describe the variations in molecular potential with nuclear coordinates. Nature has tailored electronically excited PESs, in which the molecular geometry is specifically modified from the ground state (GS) equilibrium configuration to efficiently convert the absorbed light energy into nuclear rearrangements. These rearrangements, such as bond length alterations, torsional reorientations, and chemical bond formation or cleavage, determine the photochemistry of the system and play crucial roles in biological functions. They can be rationalized by the displacements between PESs, i.e. the positional shift between the excited-state (ES) and the GS minima along specific GS eigenvectors. Critically, their sign determines if these changes move closer or away two functional groups, ruling ES properties and dynamics. Importantly, the Franck-Condon overlap integrals encode these displacements, thereby dictating absorption spectra and complex-valued Raman excitation profiles (REPs). Conventional spectroscopic approaches probe transition amplitudes [1] (for example, spontaneous resonant Raman spectroscopy only accesses the absolute value of REPs), and thus are not effective for determining the sign of ES displacements. Here, we introduce an experimental technique, based on the broadband impulsive Raman spectroscopy, exploited to detect coherent vibrational motions at selected temporal delays and probe chirps. Employing a resonant probe and an off-resonant pump pulses, the measured responses depend linearly on the Frank-Condon (FC) overlaps, critically enabling time-domain sensitivity to the phase of the stimulated vibrational coherences. The proposed scheme is experimentally benchmarked on the Rhodamine B molecule [2] and it is exploited to unambiguously determine the sign of ES molecular displacements, ultimately revealing the initial stages of photoreaction processes.

Results and Discussion. Impulsive Stimulated Raman Scattering (ISRS) is a powerful nonlinear spectroscopic technique able to track nuclear wave-packet motions upon photoexcitation directly in the time-domain [3]. Here we employ an ultrashort pump pulse, that is tuned to be *off-resonant* with respect to the sample's absorption, to coherently stimulate vibrational oscillations only in the electronic GS. This results in modulations of the material's optical properties at the frequencies of stimulated normal modes. Then a broadband probe pulse tuned to be in *resonance* with a targeted electronic transition is used to monitor the differential sample transmissivity as a function of the pump-probe temporal delay ΔT (Figure 1a). The detected signal $S(\lambda, \Delta T)$ is hence reported in a bidimensional colormap, as a function of the monitored probe wavelength λ and ΔT (Figure1b). Fourier transformation of the time-domain data retrieves the usual frequency-

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domain Raman spectrum; however, this approach cancels the crucial information encoded in the phase of the coherent oscillations.

To retain and decode such information, we modeled the nonlinear response directly in the time-domain, employing a semiclassical approach and a diagrammatic formalism to isolate all the different processes concurring to the signal generation. Notably, two interactions with the off-resonant pump prepare a vibrational coherent state via the molecular polarizability derivative $\frac{\partial \alpha}{\partial Q}$. On the other hand, the resonant probe pulse is sensitive to the vibrationally structured excited-state, which is investigated through a summation of the FC overlaps $\mu_{g_i e_k} = \langle g, i | e, k \rangle$ (g denotes the electronic GS, e the targeted ES, while i,k the respective vibrational indices).

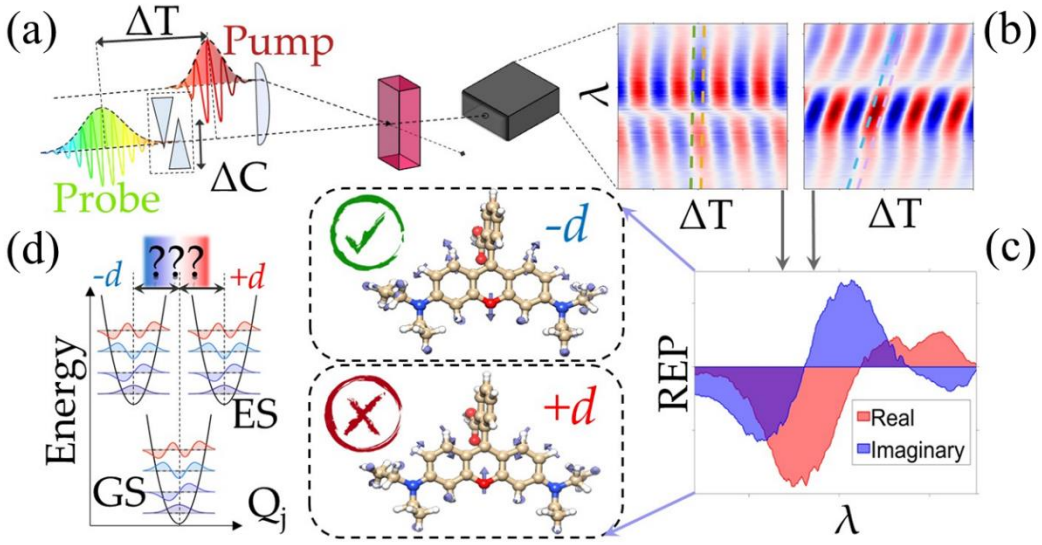

Figure 1: Concept of the ISRS scheme able to unravel excited-state absolute geometries. (a) In the two-color pump-probe experiment, the probe chirp C and the pulse delay ΔT are key experimental parameters to access complex REPs. (b) By performing two experiments with proper probe chirps, the ISRS spectral profiles taken at specific time-delays directly allow reconstructing the complex REP (c), which unveils the sign of the ES displacement along the investigated normal coordinate (d).

This two-color time-domain scheme critically introduces additional degrees of freedom with respect to Spontaneous Raman (SR), offering the opportunity to disentangle the resonance conditions of the pump/probe response part, yielding an experimental signal with a linear dependence over the FC overlaps and, ultimately, on the complex REPs [2]. Indeed, in resonance SR the excitation profiles for the Stokes/anti-Stokes processes - $R_S(\omega)$ and $R_{\mathrm{AS}}(\omega)$ - are given by the square modulus of the corresponding REPs, accordingly to:

$$R_S(\omega) = \sum_k \frac{\mu_{g_0 e_k} \mu_{e_k g_1}}{\omega - \omega_{e_k g_0} + i\Gamma} \; ; \qquad R_{AS}(\omega) = R_S(\omega - \omega_{vib}) \tag{1}$$

where $\omega_{e_k g_0} = \omega_{e_k} - \omega_{g_0}$, Γ is the electronic dephasing rate and ω_{vib} is the frequency of the considered mode.
Conversely, the ISRS response is originated by the interference between Stokes and anti-Stokes processes and, due to the heterodyne detection, it accesses a linear combination of $R_S(\omega)$ and $R_{AS}(\omega)$. Their real/imaginary parts can be isolated by performing measurements at properly chosen pump-probe delays ΔT and probe chirps C, as reported in the following table (m, n are integers, while $T_{vib} = 2\pi/\omega_{vib}$):

Probe Chirp (C)	$\Delta T = n\, T_{vib}$	$\Delta T = (n + 1/4)\; T_{vib}$
$C = mT_{vib}^2/(2\pi)$	$\Re[R_S - R_{AS}]$	$\Im[R_S + R_{AS}]$
$C = (m+1/4)\; T_{vib}^2/(2\pi)$	$-\Im[R_S - R_{AS}]$	$\Re[R_S + R_{AS}]$

Table 1: Reconstructing the complex REPs via a proper tuning of the probe chirp C and pump-probe delay ΔT.

The concept of the experimental scheme is sketched in Figure1. Two ISRS measurements are needed, with specific probe chirp values, to completely reconstruct the complex REP along a desired normal mode. In the two colormaps, oscillations at a given normal frequency (namely at 735 cm^{-1} in the considered dataset) are isolated, considering two slices at properly chosen time-delays ΔT (see Figure 1b). In this way, the measured signal directly corresponds to the real/imaginary part of the sum or difference of $R_S(\lambda), R_{AS}(\lambda)$, and complex REPs are readily obtained in the entire probed spectral region (Figure 1c). Crucially, as depicted in Figure1d for the Rhodamine B vibration at 735 cm^{-1}, the knowledge of the complex REP of the investigated mode directly discloses the sign of the displacement along the relative normal coordinate Q_j, revealing the corresponding excited-state nuclear reconfiguration. Applying this procedure over multiple Raman active modes reveals the molecular displacement occurring upon an electronic transition. This critically unveils the first steps of ultrafast photoreactions.

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