

# Coherent Signatures of Conical Intersections in Ultrafast Raman and Photoelectron Spectroscopy

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**Abstract:** We present two ultrafast spectroscopic X-Ray schemes for the detection of electronic coherences. TRUECARS employs attosecond pulses to map the energy gap, while TRPES can provide signatures through fast oscillations in the time domain.

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## 1. Conical Intersections and Electronic Coherence

At a CoIn, electronic potential gap shrinks to zero and the electronic and nuclear degrees of freedom become strongly coupled, in violation of the Born-Oppenheimer approximation (BOA), and nuclear wavepackets no longer evolve independently on the various electronic potential surfaces [1]. This coupling can facilitate ultrafast non-radiative decay to lower electronic states, thus determining the ultimate fate of an excited molecule. In this way, CoIns control reaction rates and product yields in a wide variety of photochemical and photobiological processes and are a subject of considerable interest [2]. Unfortunately, the ultrafast time-scale of the nuclear wavepacket's passage through the CoIn, combined with the broad band of the electronic gap of several eV, makes it difficult to directly observe the passage of a wavepacket through a CoIn using standard techniques (e.g., transient absorption) as this requires high spectral, as well as temporal, resolution.

The non-BOA couplings in the region of a CoIn are generally thought of as providing a path for population transfer between electronic states, thus permitting radiationless decay. However, this population transfer is also accompanied by the creation of electronic coherences. These coherences leave a signature temporal oscillation in a variety of pump-probe signals that can be used to time the arrival of a nuclear wavepacket at the CoIn. Moreover, the period of the coherent oscillation evolves with delay time and is indicative of the evolving electronic energy gap. Thus, electronic coherences generated by passage through a CoIn can be used to time the CoIn itself but also reveal spectroscopic information temporally. By focusing on the time-domain, this approach does not have as stringent spectral-resolution requirements as transient absorption. Recent developments in high-harmonic and free-electron X-ray sources have demonstrated the ability to generate bright, coherent pulses in the attosecond regime, making such ultrafast time-domain techniques possible [3, 4].

## 2. TRUECARS

To concretize the previous discussion, we consider the situation in Fig. 1 (a). A nuclear wavepacket is photo-excited to a higher electronic potential surface where it then evolves toward a CoIn. At the CoIn, the wavepacket splits and a coherent oscillation is set up. We then use a linear, hybrid narrowband-broadband (femtosecond-attosecond) Raman process to connect the two wavepackets (i.e., the upper (lower) wavepacket can be de-excited (excited) via a single off-resonant Raman interaction). In the absence of electronic coherences (or if the nuclear wavepackets no longer overlap) this linear Raman signal vanishes. We term this signal Transient Redistribution of Ultrafast Electronic Coherences by Attosecond Raman Spectroscopy or TRUECARS [5]. The signal can be depicted diagrammatically as in Fig. 2 (a) and is formally given by the time-resolved, frequency-dispersed photon number change of the as field

$$S_{TRUECARS}(\omega, T) = 2\Im \int dt e^{i\omega(t-T)} \mathcal{E}_0^*(\omega) \mathcal{E}_1(t-T) \langle \psi(t) | \hat{\alpha} | \psi(t) \rangle \quad (1)$$

where  $\Im$  is the imaginary part,  $\mathcal{E}_0$  ( $\mathcal{E}_1$ ) is the as (ps) field,  $T$  is the pump-probe time delay, and  $\hat{\alpha}$  is the molecular polarizability. Note that the TRUECARS signal differs from the quadratic Raman signal (SXRS), the latter of which includes two Raman interactions, does not vanish for populations, and does not require control of the relative pulse phases (the phases of the pulses cancel in SXRS due to the two conjugate interactions with each field).

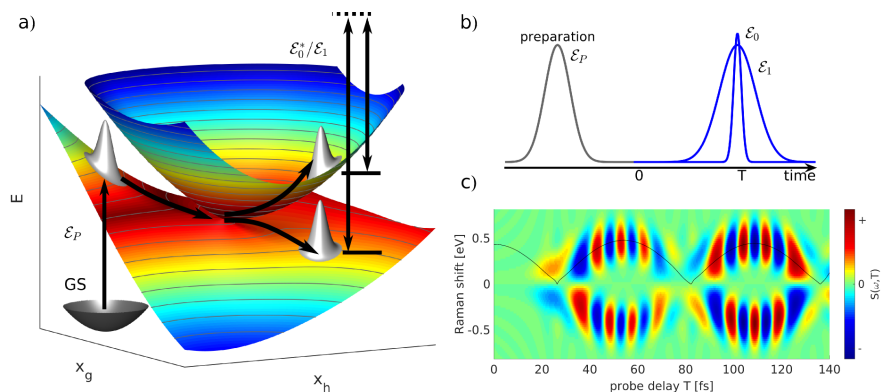


Fig. 1. Schematic representation of the TRUECARS detection scheme. (a) A nuclear wave packet is promoted from the ground state (GS) by a pump-pulse  $\mathcal{E}_P$  to an excited electronic state. As it passes the coupling region around the CoIn, an electronic coherence is created between that is later probed in a hybrid Raman process. (b) Schematics of the pump and hybrid-probe pulse sequence. (c) Illustration of the signal calculated for a one-dimensional nuclear model. The energy splitting of the electronic states involved in the coherence (solid line) can be read from Raman shift.

We simulate the TRUECARS signal (Fig 1 (c)) using a simple model with harmonic surfaces. Since the pumping process results in a single electronic excited population, there are no coherences initially and the signal vanishes. As the nuclear wavepacket enters the CoIn region, electronic coherences build up and the TRUECARS signal comes alive. The signal consists of a pair of peaks with opposite sign signal strength as well as opposite sign Raman shift that oscillate with delay time. The spectral location of the Raman peaks also evolves with delay time as the nuclear wavepackets travel up the potential surfaces before falling back down toward the CoIn. The instantaneous spectral location of the Raman peaks is obviously indicative of the separation between the electronic surfaces at that time but, for sufficiently fast dynamics, the spectral resolution will be Fourier-limited owing to the ultrafast pulses necessary to capture the process. Fortunately, this same information is available temporally via the period of the coherent electronic oscillations.

### 3. TRPES and Beyond

The TRUECARS signal offers a dramatic, background-free detection of the electronic coherences induced by non-adiabatic dynamics but it is far from the only signal altered by these coherences. Another example is time-resolved photoelectron spectroscopy, in which the pumped system is allowed to evolve for a delay time before being ionized by an ultrafast pulse. The signal is the kinetic-energy-resolved photoelectron yield as a function of delay time

$$S_{TRPES}(\epsilon_p, T) = \int dt \int dt' \mathcal{E}^*(t) \mathcal{E}(t') e^{-i(\epsilon_p - \omega)(t-T)} \langle \Psi(t) | \hat{\mu} e^{-i\hat{H}(t-t')} \hat{\mu}^\dagger | \Psi(t') \rangle \quad (2)$$

where  $\epsilon_p$  is the photoelectron kinetic energy,  $\hat{\mu}$  is the transition dipole operator,  $\hat{H}$  is the molecular Hamiltonian, and  $\mathcal{E}$  and  $\omega$  are the amplitude and frequency of the ionizing field. A simulation of TRPES from a model CoIn system using 200 as pulses is shown in Fig. 3 [6]. The signal consists of a wide band of energies corresponding to the bandwidth of the electric field and there is little time-dependence initially and no spectral resolution of the two surfaces. After the passage through the CoIn, an oscillation in the signal strength is clearly visible. As before, the period of one of these temporal oscillations corresponds to the electronic potential gap averaged over the nuclear wavepacket at the time of the oscillation.

Time-resolved photoelectron signals are readily measured as photoelectron currents in state-of-the-art experiments and can deliver information on the coherences given sufficiently short pulses. Moreover, it has recently been demonstrated that the addition of an IR streaking field can provide greater resolution, enhancing the usefulness of TRPES for ultrafast dynamics [8]. TRUECARS comes at a greater experimental effort, requiring phase-stable hybrid pulses, but delivers direct information about the electronic energy gap and is insensitive to electronic populations. Notably, in both signals, the electronic coherences initiated in the CoIn region oscillate in  $T$  with periods that reveal the time-

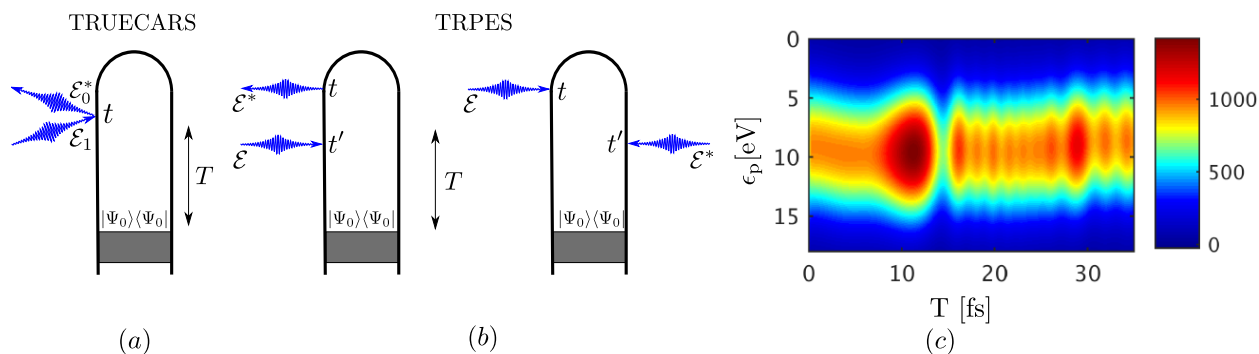


Fig. 2. Diagrammatic representations of the TRUECARS (a) and TRPES (b) detection schemes. In both cases, the shaded box stands for the unspecified pumping process, assumed to be non-overlapping with the probe pulse, and  $|\Psi_0\rangle$  is the state of the molecule immediately after the pumping process. In (a), the attosecond and femtosecond field amplitudes are given by  $\mathcal{E}_0$  and  $\mathcal{E}_1$  respectively while, in (b), the ionizing field amplitude is given by  $\mathcal{E}$ . For diagram rules, see [7]. (c) TRPES signal for a model CoIn system obtained with an ionizing pulse of 200 as FWHM and 20 eV central frequency. The magnitude of the signal is given in arbitrary units via the colorbar.

evolving electronic energy gap. Importantly, this information is of a transient nature, and thus not open to study via purely frequency-domain techniques.

The signals discussed here are just two of the broad variety of spectroscopic observables that can be employed in this manner. Other possibilities include time-gated fluorescence measurements as well as Auger spectroscopy. A recent study of an array of Raman spectroscopies for static nuclei offers another exciting toolkit of techniques appropriate for different circumstances and objectives [9]. The fact that CoIns generates electronic coherences thus offers a variety of versatile methods for tracking the associated nonadiabatic dynamics.

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