Coherent Raman Spectroscopy Based on Interference of Entangled Photon Pairs

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Overview

Classical light Raman spectroscopy is limited by the time–frequency trade-off: short pulses give high temporal but poor spectral resolution, and vice versa. Femtosecond Adaptive Spectroscopic Technique via Coherent Anti-Stokes Raman Scattering (**FAST CARS**) [1] addresses this by combining ultrashort broadband excitation with a narrowband probe, boosting resonant signals and reducing background, though it remains bound by classical uncertainty.

Quantum protocols overcome these limits by exploiting entanglement. Quantum Induced Coherence LiDAR (**QuIC LiDAR**) [2] uses SPDC photon pairs in an **SU(1,1)** interferometer, where induced coherence makes idler-only detection possible. This grants access to spectral or spatial information with strong resilience to noise.

Quantum Femtosecond Raman Spectroscopy (**QFRS**) [3] applies **entangled photons** to extend FAST CARS: the signal interacts with the sample while the idler provides a temporal reference. Coincidence detection retrieves vibrational coherences without the classical trade-off, but needs heterodyne detection to recover phase information.

The present study proposes a **interferometric scheme** that merges QFRS with QuIC LiDAR. Using SU(1,1) interference, it preserves vibrational coherence without heterodyne detection and inherits noise immunity from induced coherence. This points toward a robust quantum Raman protocol with applications in spectroscopy.

Theoretical Framework

Entangled photon pairs allow quantum-enhanced spectroscopy. They exhibit strong time–frequency correlations enabling Raman signals to surpass the classical Fourier limit of simultaneous temporal and spectral resolution.

The quantum state of a photon pair can be written as

$$|\Phi\rangle = \sum_k \int d\omega_s d\omega_i\, \Phi_k(\omega_s,\omega_i)\, a^\dagger_{\omega_s,k} a^\dagger_{\omega_i,k}\, |0\rangle\,, \tag{1}$$

where the joint spectral amplitude $\Phi(\omega_s,\omega_i)$ defines correlations between signal (s) and idler (i) photons.

The light–matter interaction in the off-resonant Raman regime is modeled as

$$V(t) = \sum_j \sum_b \alpha^{(j)}_{bg}\, |b\rangle\langle g|_j\,(t)\, E_s(t) E^\dagger_s(t) + h.c., \tag{2}$$

with α_{bg} the Raman polarizability.

The measurable spectroscopic response is given by the four-point field correlation function

$$S(\omega_s,\omega_i) = \langle\Phi| E^\dagger_s E^\dagger_i E_i E_s |\Phi\rangle\,, \tag{3}$$

which captures coincidence detections and encodes molecular coherence.

QFRS Model

Here the spectroscopic signal that carries the nonlinear dispersion information is expressed as

$$S_{QV}(\omega,\omega_i;T) = \frac{N(N-1)}{4\pi^2} |\mathcal{E}_{AS,\omega}|^6 |\mathcal{E}_{i,\omega_i}|^2 \left| \sum_b \alpha^*_{bg}\rho_{bg}(T)\, \Phi(\omega-\omega_{bg}-i\gamma_{bg},\omega_i) \right|^2, \tag{4}$$

where $\rho_{bg}(T)$ carries the vibrational coherence and γ_{bg} the dephasing rate.

The time evolution of the coherence between levels b and g is

$$\rho_{bg}(\tau) = \rho_{bg}\, e^{-[i(\omega_b-\omega_g)+\mathrm{sgn}(\tau)\gamma_{bg}]\tau}, \tag{5}$$

which encodes oscillation at the vibrational frequency and exponential decay.

The Raman line-shape function probed in QFRS is

$$f_{bg}(T) = 2\pi\,\theta(t-T)\,\rho_{bg}(T)\,\Phi(\omega-\omega_{bg}-i\gamma_{bg},\omega_i), \tag{6}$$

linking the vibrational coherence to the entangled two-photon spectrum.

In heterodyne detection, one accesses the phase-sensitive part of the signal:

$$S_{QVHD} = \frac{N}{\pi} |\mathcal{E}_{s,\omega}|^2 |\mathcal{E}_{i,\omega_i}|^2\, \mathrm{Im}\left[\sum_b \alpha^*_{bg}\Phi^*(\omega,\omega_i) f_{bg}(T)\right], \tag{7}$$

where interference with a local oscillator retrieves vibrational phase information.

Interferometric Proposal

When two SPDC sources $(k=2)$ are employed, the signal includes cross-terms:

$$\begin{aligned} S_I(\omega_s,\omega_i) &= \langle\Phi_1| E^\dagger_s E^\dagger_i E_i E_s |\Phi_1\rangle + \langle\Phi_2| E^\dagger_s E^\dagger_i E_i E_s |\Phi_2\rangle \\ &\quad + \langle\Phi_1| E^\dagger_s E^\dagger_i E_i E_s |\Phi_2\rangle + \langle\Phi_2| E^\dagger_s E^\dagger_i E_i E_s |\Phi_1\rangle \\ &= S_{QV1} + S_{QV2} + 2\,\mathrm{Re}\,(S_{QV12})\,, \end{aligned} \tag{8}$$

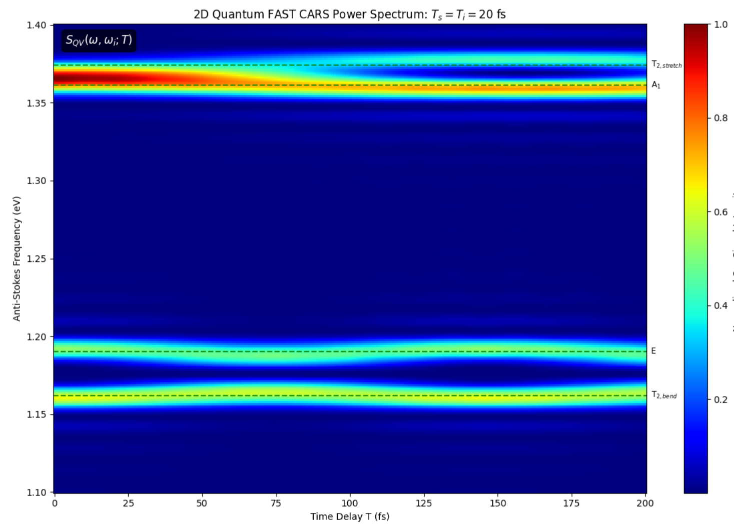
where S_{QV1} and S_{QV2} are QFRS-like contributions from each source, and S_{QV12} is the interference term that carries induced coherence.

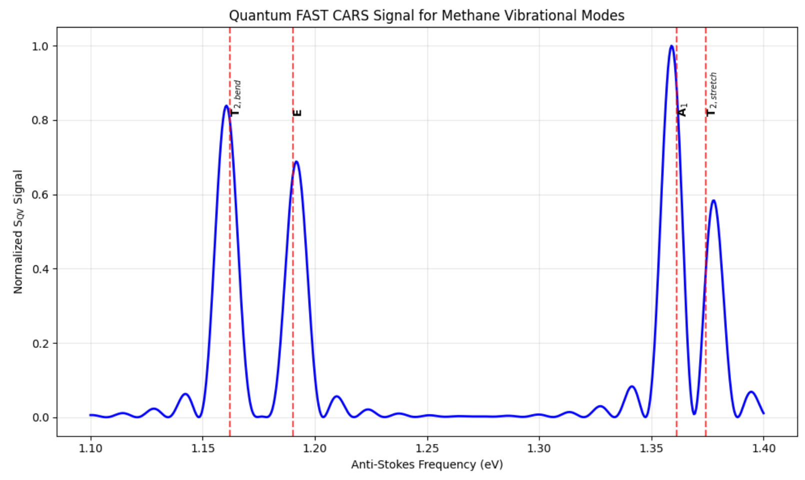
This structure shows how QFRS can be extended into an interferometric scheme, gaining both spectral resolution and resilience against noise.

Representation of Methane S_{QV} Signal

This research in progress focuses on simulating the QFRS signal for methane, a molecule with well-characterized vibrational modes. The goal is to validate the QFRS model and establish a baseline for comparing it with the interferometric protocol.

The S_{QV} signal is shown as a two-dimensional spectrogram in the frequency domain and pump-probe delay T. This representation highlights how vibrational coherences evolve in time while retaining spectral resolution. However to obtain a time resolution,the phase information has to be fully capture, heterodyne detection is necessary.





A spectral slice at a fixed delay of $T = 150$fs reveals the line-shape of the Raman resonance. This one-dimensional cut illustrates how vibrational features can be resolved directly from the QFRS signal, providing a clear comparison with conventional Raman spectra.

Conclusions and Perspectives

- By extending FAST CARS into the quantum domain, QFRS enables coherent vibrational sensing with entangled light.
- QFRS protocol successfully implemented and validated using methane S_{QV} signals.
- QFRS exploits off-resonant light–matter coupling to retrieve molecular fingerprints.
- SU(1,1) interferometric extension is purposed to enhance noise resilience and eliminate heterodyne detection.
- **Next:** Calculate S_{QVHD} and interferometric (S_I) signals.
- **Next:** Analyze espectral and time resolutions for a given molecule.
- **Next:** Compare S_{QV}, S_{QVHD}, and S_I for resolution, noise resilience, and feasibility.
- **Next:** Identify optimal quantum protocol for molecular spectroscopy applications.

References

[1] Dmitry Pestov, Marlan O. Scully, et al. Optimizing the laser-pulse configuration for coherent raman spectroscopy. *Science*, 316(5822):265–268, 2007.

[2] Gewei Qian, Da-Wei Wang, et al. Quantum induced coherence light detection and ranging. *Phys. Rev. Lett.*, 131:033603, Jul 2023.

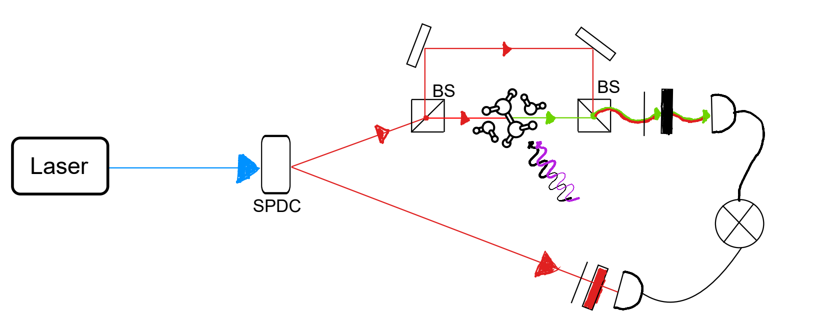
[3] Zhedong Zhang, Tao Peng, Xiaoyu Nie, Girish S. Agarwal, and Marlan O. Scully. Entangled photons enabled time-frequency-resolved coherent raman spectroscopy and applications to electronic coherences at femtosecond scale. *Light: Science & Applications*, 11(1):274, May 2022.

More information,
Complete references
and Contact

Spectroscopic Model Schemes

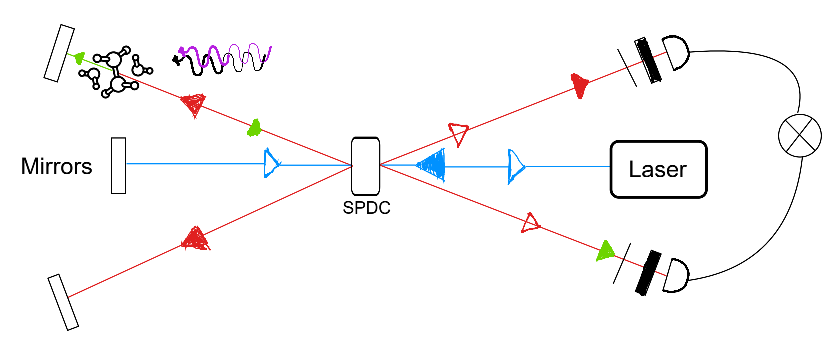
QFRS Model

- Single SPDC source $(k=1)$.
- Signal photon interacts with the molecule.
- Detection in coincidence.
- Idler photon serves as a reference.
- Heterodyne detection needed for phase estimation.
- Time delay T between entangled photons.



Interferometric Model

- Two SPDC sources $(k=2)$.
- Signal photon from one source interacts with the molecule.
- Singles detection allowed due to induced coherence.
- Phase estimation due to interference of two photon pairs.
- Time delay T between entangled photons.



Initial preparation of Coherence · Single photon Detector · Coincidence Measurement · Molecular Sample · Frequency Filter · Non-linear Crystal