Dynamic process measurements in the complex plane with vibrational phase contrast CARS

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In the coherent anti-Stokes Raman scattering (CARS) process, the emitted signal carries both amplitude and phase information of the molecules in the focal volume. These components form a vector in the complex plane, with the magnitude given by the amplitude and the angle between the vector and the real axis determined by the phase. Most CARS experiments ignore the phase component, but its detection allows for two advantages over amplitude-only CARS. First, the pure resonant response can be determined—and the non-resonant background rejected—by extracting the imaginary component of the complex response, enhancing the sensitivity of CARS measurements[1]. Second, selectivity is increased via determination of the phase and amplitude, allowing separation of individual molecular components of a sample even when their vibrational bands overlap[2].

The vibrational responses of individual molecular species trace different trajectories through the complex plane as functions of driving frequency. Chemically selective images can be made by locating the regions of the complex plane belonging to each substance at a given driving frequency. Dissolutions and chemical reactions can be followed by tracking the complex-plane positions, relative to the initial compounds, of each location in the sample. Furthermore, quantitative concentration measurements can be accurately performed, even on homogeneous solutions containing molecules with congested spectra.

Figure 1 illustrates the CARS spectra of two common plastics. For each vibrational frequency the amplitude of the CARS signal is designated as the length of a vector in complex space, with the phase defined as the angle separating the vector from the horizontal axis. The horizontal and vertical axes correspond to the real and imaginary components of the $\chi^{(3)}$ tensor, with vibrational frequencies plotted on the third axis. The real and imaginary components can be directly extracted from this plot.

Figure 2 shows the complex plane trajectories of ethanol and methanol around 3000 cm^{-1}, as well as concentration measurements of five volumetric mixtures at two different driving frequencies. Line (I) indicates a driving frequency where only the amplitudes of the vibrational responses differ between the two molecular species, while line (II) lies at a frequency where the amplitudes are similar but the phases are well separated. In both cases the measurements agree with predicted values of the complex location of the mixture.

[1] C.L. Evans, E.O. Potma, and X.S. Xie, "Coherent anti-Stokes Raman scattering spectral interferometry: determination of the real and imaginary components of nonlinear susceptibility χ(3) for vibrational microscopy", *Opt. Lett* **29**(24), 2923 (2004).

[2] M. Jurna, J. P. Korterik, C. Otto, J. L. Herek, and H. L. Offerhaus, “Vibrational Phase Contrast Microscopy of Coherent Anti-Stokes Raman Scattering”, *Phys. Rev. Lett*. **103**, 043905 (2009).

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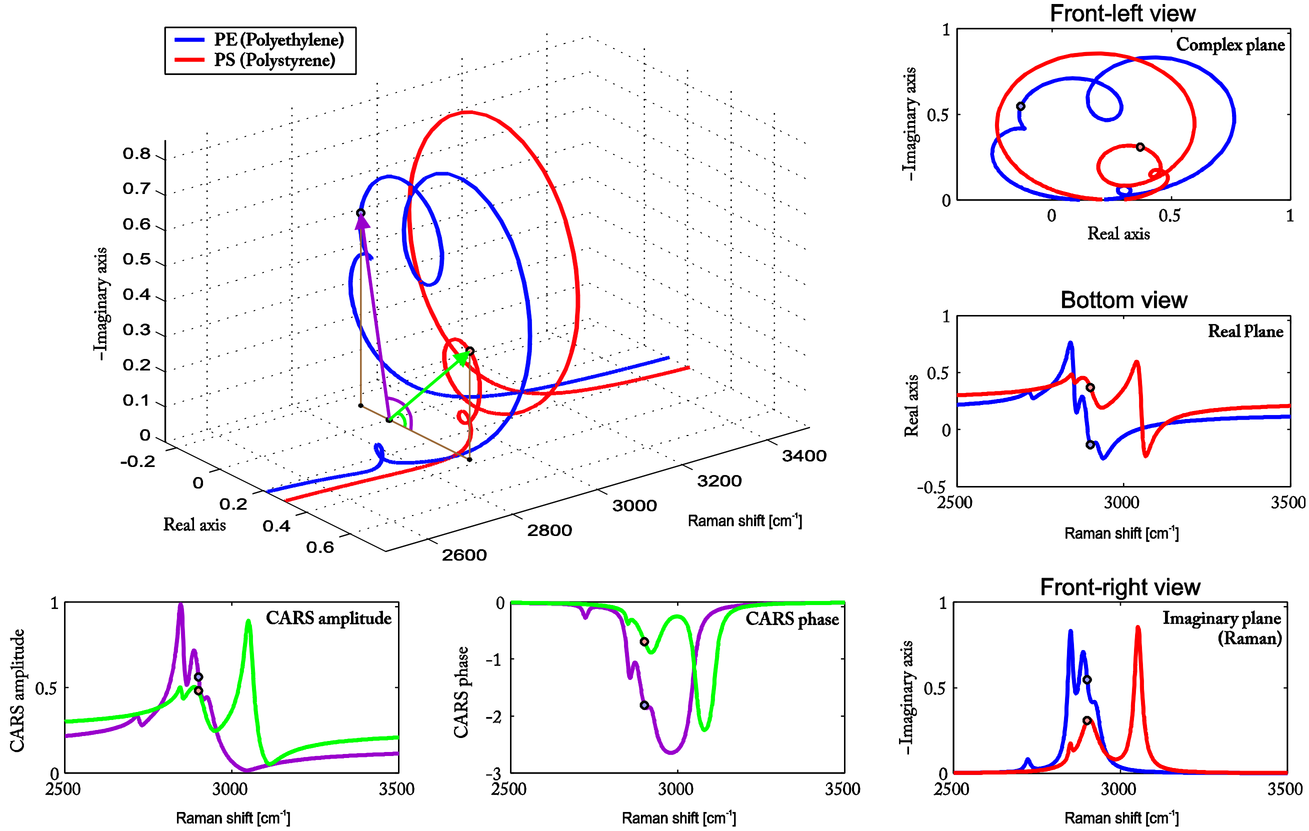

FIG. 1: The complex vibrational responses of polystyrene and polyethylene around 3000 cm-1. The imaginary plane (front-right view) can be recognized as the Raman component, while the real plane (bottom view) shows the dispersion.

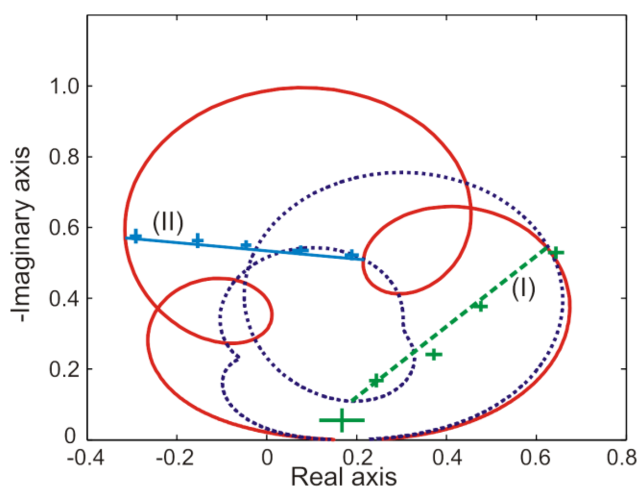

FIG. 2: The complex plane trajectories of ethanol (solid curve) and methanol (dotted curve) near 3000 cm-1. The lines (I, dashed) and (II, solid) indicate the predicted complex plane values for mixtures of ethanol and methanol at 2871 and 2934 cm-1, respectively. The crosses are measured data points with error bars for five volumetric mixtures, each containing the two pure compounds in 0/100, 25/75, 50/50, 75/25, or 100/0 percent ratios.