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Hyperbolic MoOCl₂ for Anisotropic Raman Enhancement and Sensing

Hyperbolic electromagnetic response is usually engineered in artificial anisotropic metamaterials, while natural hyperbolic crystals are rarer and often work mainly in the mid-infrared range.[1,2] Here we present MoOCl₂, a layered van der Waals material[3] with extreme in-plane optical anisotropy, as a natural platform that brings hyperbolic physics into the visible and near-infrared range used in Raman spectroscopy and SERS.

Angle-resolved polarized Raman spectroscopy shows that the vibrational response of MoOCl₂ is strongly controlled by crystal orientation. For light polarized along the metallic a-axis, several phonon modes show clear Fano-type asymmetric lineshapes, which indicate coupling between discrete phonons and an electronic continuum. When the polarization is rotated toward the dielectric b-axis, this asymmetry is strongly suppressed. This gives a direct Raman fingerprint of anisotropic electron-phonon coupling and also provides a simple way to identify the crystal axes of exfoliated MoOCl₂ flakes.

We also observe Raman polarization switching when the excitation wavelength is changed from 532 to 633 and 785 nm. The angular Raman patterns evolve and change their shape, revealing a wavelength-dependent anisotropy of the Raman response that is consistent with the strongly anisotropic optical constants of MoOCl₂. In addition, Stokes/anti-Stokes Raman measurements reveal highly anisotropic laser heating, with much stronger energy deposition for polarization along the metallic axis.

Finally, we use this anisotropic optical response for “Hyperbolic-Enhanced Raman” (HyperER) sensing on exfoliated MoOCl₂ flakes, without lithography, noble-metal nanoparticles, or engineered nanogaps. Rhodamine 6G molecules deposited on MoOCl₂ show strong and polarization-tunable Raman enhancement. The analytical enhancement factor (AEF) exceeds 10⁷ for polarization along the metallic axis, and the detection limit reaches about 10⁻¹⁰ M. Compared with reference Au nanoparticle substrates, MoOCl₂ gives a much lower detection limit while also offering an intrinsic polarization-controlled on/off contrast.

These results connect Fano-coupled Raman physics, visible-range hyperbolic electrodynamics, and SERS-style molecular sensing. MoOCl₂ therefore emerges as a simple, air-stable, and polarization-programmable substrate for Raman spectroscopy and lithography-free chemical sensing.

References

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