

Supporting Information for “Near-field infrared spectroscopy of monolayer MnPS₃”

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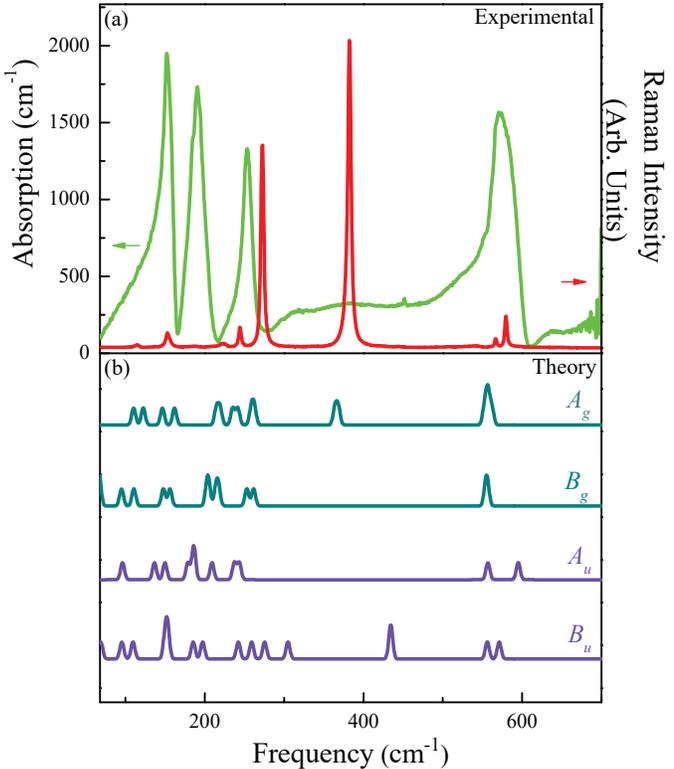
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Traditional far field infrared and Raman spectra with mode assignments

Figure S1 displays the traditional infrared and Raman scattering response of the MnPS₃ single crystal at room temperature. Our complementary lattice dynamics calculations are also included. The full frequency window is available for these traditional spectroscopies - different from the near field infrared which is currently limited to 330 cm⁻¹. The corresponding vibrational mode assignments are summarized in Table S1.

FIG. S1. (a) Traditional infrared absorption (green) and Raman scattering (red) spectra at 300 K. (b) Lattice dynamics calculations of MnPS₃ projected according to mode symmetry. Recall that the ungerade modes are infrared-active, and the gerade symmetry modes are Raman-active. The calculated frequencies are within 3 % of the experimental peak positions. The calculated modes have a Gaussian line shape with 2 cm⁻¹ broadening. The higher peak intensity indicates nearly degenerate modes.



Signal-to-noise ratio in near-field infrared response of atomically-thin materials

The signal-to-noise ratio in the near-field infrared spectra of few- and single-layer MnPS₃ is lower than one would obtain in a “traditional” infrared spectrum of a “traditional” sample. We are not, however, dealing with either one. The “samples” are exfoliated flakes. They are small in size and have almost no optical density. As a result, even a traditional measurement of such a thin sample will have signal-to-noise limitations. Taking more scans can offer some improvement, but it will not make a small spectral feature get larger. This is because the signal-to-noise ratio goes as the square root of the number of scans. Far infrared spectroscopy is much more challenging than traditional middle infrared and Raman scattering spectroscopies, and the signal is orders of magnitude smaller. As a result, comparable signal-to-noise ratios shouldn’t be expected because the source is less intense and the

TABLE S1. MnPS₃ mode assignments in cm⁻¹

ω FIR	ω Raman	Assignment
152	116	T' (Mn)
-	156	R' (PS ₃)
191, 254	245	T'_{xy} (PS ₃)
-	274	δ (PS ₃)
-	385	ν (PS ₃)
452	-	T'_z (PS ₃) + ν (P-P)
573	567, 581	ν (PS ₃)

ν = symmetric stretch, T' = translational motion, R' = rotational motion, δ = bend

detector is less sensitive. Employing the synchrotron at the Advanced Light Source in an attempt to obviate the first issue, and while it certainly helps, it does not fully compensate for the fact that we employ a tip for the near-field work. The bottom line is that while the signal-to-noise ratio of near-field spectra in the far infrared is not perfect, it is state-of-the-art at the present time. And we have employed this state-of-the-art technique to reveal for the first time the infrared response of a van der Waals material in few- and single-layer form.

Additional substrate studies

MnPS₃ showed poor adhesion on glass and sapphire substrates requiring the use of glue. Bare aluminum and silicon proved to be much better candidates - at least in terms of adhesion. The aluminum substrate allowed for high quality spectra for multilayer samples, however, sharpness of features decreased dramatically with sheet number. This substrate was especially unencouraging because we were unable to get down to the thinnest sheets. Different issues arise with silicon. Although adhesion was reasonable, substrate phonons can potentially overlap with those of the target material. This is especially problematic when the near-field infrared signal is small. For our specific case, the substrate phonons complicate the spectral response of the MnPS₃ sheets.