Supporting Information

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Probing Vibrational Strong Coupling of Molecules with Wavelength-Modulated Raman Spectroscopy

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(Supplementary Information)

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1 Raman spectra from a Silicon substrate for different pump wavelengths

Raman spectra of a bare silicon substrate at various pump wavelengths are shown in figure S1. The spectrum in orange is for a pump wavelength is 532 nm, the spectrum at 785 nm pump wavelength is shown in blue.

Figure S1: Raman spectra of bare silicon substrate (a) at 532 nm pump wavelength (b) at 785 nm pump wavelength.
2 AFM and SEM images of grating structures

Figure S2: **AFM images** (a) Grating structure of 4.7 \( \mu m \) pitch sample. (b) Grating structure of 13.8 \( \mu m \) pitch sample. The groove depth is around 50 nm.

Figure S3: **SEM images** The sample is a grating of period is 13.8 \( \mu m \) (a) at the edge of the grating structure (b) at the illumination region of the Raman pump laser.
3 Dispersion spectra of the grating structures calculated both with and without oscillator strength

Figure S4: Dispersion plots for grating structures Both figures are divided into two parts. The left side of both figures shows the computationally calculated dispersion plot for which we set the oscillator strength to zero. Later the oscillation strength was added and the calculated dispersion is shown in right side of both figures. The maximum polar angle for (a) is 12° and for (b) is 22°. The period of the grating for (a) is 13.8 µm and for (b) is 4.7 µm, with a 1.0 µm gap between metal stripes. The PMMA thickness is 1.250 µm. The dashed black and red lines are the ±1 scattered air and ±2,3 scattered silicon light-lines respectively. The horizontal dashed white lines indicate the energy of the C=O (1732 cm⁻¹) vibrational resonance.
4 Hopfield coefficients and Coupled Oscillator model

The coupled oscillators model, comprising the plasmonic mode/cavity mode $E_{\text{plas/cav}}$ and the vibrational modes C=O can be described with the matrix equation,

$$
\begin{pmatrix}
\omega_{\text{plas/cav}}(k_x) & \Omega_a/2 \\
\Omega_a/2 & \omega_{\text{C=O}}
\end{pmatrix}
\begin{pmatrix}
a_{L1,U1} \\
b_{L1,U1}
\end{pmatrix}
= E_{L1,U1}
\begin{pmatrix}
a_{L1,U1} \\
b_{L1,U1}
\end{pmatrix}.
$$

The eigenvalues $E_{L,U}$ can be obtained by solving the equation $\det |H - I \cdot E| = 0$, where $H$ is the $2 \times 2$ matrix in the equation above, $I$ is the $2 \times 2$ unitary matrix, and $E$ the eigenvalues of $H$. Then, for the two eigenvalues $(L,U)$, there is an associated eigenvector, $v_{L,U}$, that can be found by solving $H \cdot v_{L,U} = E_{L,U} \cdot v_{L,U}$, where the coefficients of $v_{L,U}$ are the Hopfield coefficients, $a_{L,U}, b_{L,U}$. In Figure S3, we show the eigenvectors of this matrix, they correspond to the generalised Hopfield coefficients, and are interpreted as the plasmon mode contribution, and the C=O mode contribution. The upper polariton is shown in green and the lower polariton is in blue.

Figure S5: **Hopfield coefficients** Hopfield coefficients for the 13.8 $\mu$m plasmonic structure. The upper polariton is shown in green and the lower polariton is in blue. For a given polariton a fraction of 0.5 indicates an equal contribution of plasmon and molecular resonance to that polariton etc.
5 Experimentally measured dispersion plot of strongly coupled microcavity mode and the vibrational mode

An experimentally determined dispersion plot for strong coupling between a cavity mode and the C=O vibrational mode is shown in figure S5. The horizontal dashed line shows the position of vibrational mode. The numerically calculated dispersion of the mode of the bare cavity is also shown as a white line. Calculations were performed using COMSOL with the same parameters as in the main text, except that here the oscillator strength was set to zero.

Criteria for strong coupling: From figure S6 we estimate the Rabi splitting as $150 \text{ cm}^{-1}$. This compares with the measured Gaussian FWHM of a bare resonance cavity mode of $45 \text{ cm}^{-1}$ (± 2 cm$^{-1}$) and the C=O molecular resonance width of $60 \text{ cm}^{-1}$ (± 5 cm$^{-1}$), confirming that we are within the strong coupling regime.

Figure S6: Planar cavity modes Experimentally calculated dispersion plot of Cavity mode strongly coupled with the vibrational mode. The horizontal white dashed line shows the presence of c=o vibrational mode. The parabolic white dashed line shows the numerically calculated empty cavity dispersion plot.
6 Microcavity FTIR and Raman spectra over an extended energy range

Here we show the FTIR and Raman spectra in the range 500 cm\(^{-1}\) to 2500 cm\(^{-1}\) for the microcavities, the data are the same as for figure 3 in the main manuscript, but here we give an extended range.

![Graphs showing FTIR and Raman spectra over extended energy range](image)

Figure S7: Microcavity FTIR and Raman spectra over extended energy range. Details are as for figure 3 in main manuscript.
7 Electric far-field for grating structures

The numerically calculated dispersion of a metal stripe array (grating) of period $13.8 \mu m$ and gap width $1\mu m$ is shown in panel (a). A line spectrum through this plot for $k_x/2\pi = 45cm^{-1}$ is shown in panel (b). The plots that follow show the calculated electric field in cross section over one period of the grating for the different energies indicated. We chose a non-zero value of the in-plane wavevector (rather than normal incidence) since some features in the dispersion plot are absent at normal incidence owing to symmetry considerations. The energies correspond to candidate features as follows. 1604 cm$^{-1}$: the approx. energy at which the Raman feature that might be associated with a lower polariton appears. 1715 (1794) cm$^{-1}$: the approx. energy at which the lower (upper) polariton appears in FTIR for this grating structure (that has no metal in the grating gaps). 1740 cm$^{-1}$: the approx. energy of the C=O bond.

Figure S8: (a) Computational dispersion plot of $13.8 \mu m$ grating structure showing strong coupling between the vibrational mode and the plasmon mode. The maximum polar angle for these data is $30^\circ$. (b) Transmission plot calculated by slicing the dispersion plot near $45$ cm$^{-1}$. Field profiles. Normalised electric field profiles are taken at different points of the dispersion plot. (c) The electric field is strong at the edge at $1604$ cm$^{-1}$, (d) field profile of LP at $1715$ cm$^{-1}$ (e) C=O bond at $1732$ cm$^{-1}$ and (f) field profile of UP at $1798$ cm$^{-1}$.
8 Line spectra of coupled 4.7 µm and 13.8 µm grating structures

Here we plot some line spectra taken from the data obtained from the 4.7 µm grating, i.e. we extract some of the data shown in figure 6. The left-hand column shows standard Raman spectra from the four grating groove regions seen in figure 6. The right-hand column shows wavelength-modulated Raman spectra from the same four groove regions. For each groove we see that there are weak features associated with the 1450 cm$^{-1}$ and 1730 cm$^{-1}$ resonances in the PMMA, but the spectra are dominated by broad features at $\sim$ 1320 cm$^{-1}$ and $\sim$ 1590 cm$^{-1}$, seen in both the standard and wavelength-modulated data.
Figure S9: Showing line spectra extracted from the data shown in figure 6. The left-hand column shows standard Raman spectra from the four grating groove regions seen in figure 6. The right-hand column shows wavelength-modulated Raman spectra from the same four groove regions.

Next we do the same thing for the data obtained form the 13.8 µm grating. Again, the left-hand column shows standard Raman spectra from the three grating groove regions seen in figure 6. The right-hand column shows wavelength-modulated Raman spectra from the same three groove regions. For all grooves we see the PMMA features at 1450 cm\(^{-1}\) and 1730 cm\(^{-1}\). For grooves 2 and 3 we see that here the data are are dominated by broad features at \(\sim 1320\) cm\(^{-1}\) and \(\sim 1590\) cm\(^{-1}\), as they were for the 4.7 µm grating (figure S9 above). However, these features are absent from groove 1. Note however that groove 1 is
the last groove in the series of grooves that makes up the grating, i.e. it is NOT bounded on both sides by another groove.

Figure S10: Left side shows line spectrum of standard Raman coupled grating structure. Right side shows line spectrum of modulated Raman coupled grating structure. 13.8 µm grating structure was used.
Here we show that the additional feature observed at 1590 cm$^{-1}$ from the 4.7 µm grating is also present when the pump wavelength is 532 nm, and the numerical aperture is 0.55 (cf. 0.9 for the WMRS setup).

Figure S11: Standard Raman line spectra from 4.7 µm grating sample. (a) different spectra taken in the groove region (b) different spectra taken at the metallic region (c) average spectra from (a) and (b).