Strong coupling of molecular vibrational resonances in a metal-clad microcavity below cut-off

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Many experiments on strong coupling of organic molecules, both in the visible and infrared spectral regions, make use of metal-clad microcavities. Coupling is usually investigated between the excitonic or vibronic molecular resonance (as appropriate) and the lowest order cavity mode [1, 2]. However, metal-clad microcavities also support a coupled surface plasmon mode that has no cut-off. This mode appears to have been ignored in previous work on strong coupling, probably because it exists beyond the light-line. Here, through the addition of a grating to the microcavity structure, we show that this coupled plasmon mode also interacts with molecular resonances to produce hybrid polariton modes.

We made use of the C=O vibrational resonance (1732 cm^{-1}) of a 2µm polymer (PMMA) film and incorporated this into a microcavity comprising two 30nm gold mirrors as shown in Figure 1. A dispersion plot showing the coupled surface plasmon mode that has no cut-off is shown in Figure 2, this mode is sometimes known as the TM_{-1} mode. To bring that mode inside the air light line and thus allow it to be coupled to incident light a grating structure was imposed on the lower gold mirror (not shown). The IR transmission of an experimental sample, obtained using a FTIR spectrometer, is shown in figure 3. The grating-scattered coupled plasmon mode is clearly seen to interact with the vibrational resonance, and an anti-crossing of ~125 cm^{-1} is observed.

Our results show that in addition to the usual cavity mode explored in metal-clad cavities, strong coupling also arises due to the coupled plasmon modes present in such structures. Our findings indicate that this mode should be taken into account when looking at how strong coupling may be used to alter/create molecular properties via strong coupling.

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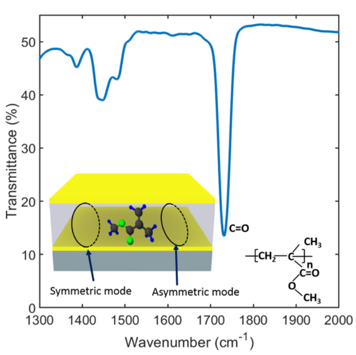

Figure 1: Transmittance of a 2 µm thick planar layer of PMMA on a CaF_2 substrate. The strong, narrow absorption peak at 1732 cm^{-1} is due to the C=O bond.

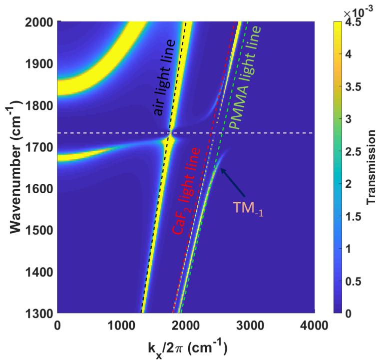

Figure 2: Calculated dispersion of the coupled surface plasmon mode (TM_{-1}) associated with a gold/PMMA/gold cavity structure on a CaF_2 substrate for a planar system (no grating). Air, CaF2 and PMMA light lines are shown as black, red and green dotted lines respectively. The vibrational mode C=O is shown with white dished line.

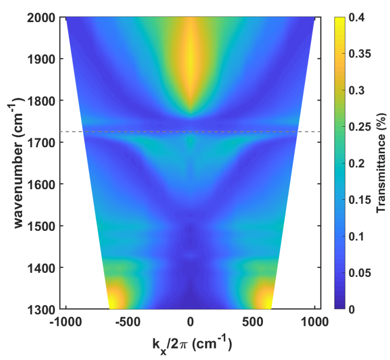

Figure 3: Experimental dispersion plot showing strong coupling between the coupled surface plasmon mode and the C=O vibrational mode.

[1] Shalabney, A. et al. Coherent coupling of molecular resonators with a microcavity mode. Nature Commun. 6, 5981 (2015).
[2] Long, J. P. & Simpkins, B. S. Coherent coupling between a molecular vibration and Fabry–Perot optical cavity to give hybridized states in the strong coupling limit. ACS Photon. 2, 130–136 (2015).