Supporting Information

Coherent coupling between a molecular vibration and Fabry-Perot optical cavity to give hybridized states in the strong coupling limit

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Field distribution inside cavity

For non-normal angles of incidence, s- and p-polarized excitation produce different field distributions and orientations within the cavity due to normal field-components present in p-polarized excitation. Electric field distributions may be solved using transfer matrix methods and are plotted in Figure S1 for an incident angle of 27°. As seen, s-polarized excitation results in purely in-plane fields peaked at the cavity center (black curve) while p-polarized conditions yield both in-plane and normal field-components with the normal component peaked at the mirrors. Although the modulation is modest in terms of field intensity, these results may have implications for selective coupling to dipoles of a given orientation as well as cavity location.

Branch splitting and widths for p-polarized incident radiation

Of fundamental interest are the branch splitting and widths of the two hybridized modes that arise from polaritonic interaction between a FP cavity and the carbonyl stretching-vibration of the polymethylmethacrylate (PMMA) filling the cavity. Figure 3 of the accompanying article shows the splitting and widths measured as a function of incident angle in FTIR transmission spectra for s-polarized excitation. For completeness, Figure S2 plots the same quantities for p-polarized excitation. The branch splitting, Figure S2a, reaches a minimum near the same 27° incident angle as for s-polarization, with a splitting of 141 cm^{-1}, compared to 140 cm^{-1} for the s-polarized measurement. Figure S2b plots the full-width-at-half-maximum (FWHM) measured for

the upper and lower hybridized branches (symbols). Also plotted (solid curves) are the FWHMs determined from transfer-matrix computations after broadening by the measured FTIR beam spread. (Note that we report all widths as FWHM.)

Branch splitting as a function of in-plane wavevector for p-polarized incident radiation

Accurate determination of the Rabi splitting requires one to examine resonance positions as a function of the in-plane wavevector, $k_{\|}$. Figure 4 of the accompanying manuscript presents this data for s-polarized excitation. Here, in Figure S3, we present the data corresponding to p-polarized excitation. These results reveal a Rabi splitting magnitude of 132 cm^{-1} which is identical to that achieved with s-polarization.

Fitting the absorption spectrum to estimate α_0 and Γ_H

Formulas in the accompanying article predict[1,2,3] that the vacuum Rabi splitting Ω depends both on the homogeneous linewidth Γ_H of the carbonyl stretching mode and on the homogeneous absorption-coefficient α_0 at the stretch frequency $\bar{\nu}_0$. Theory also predicts that the width Γ_{CM} of the cavity/vibration coupled modes is given by the average of Γ_H and the "empty cavity" width Γ_{cav}, i.e., the width of the FP etalon resonance unperturbed by the carbonyl absorption. However, α_0 and Γ_H are not directly available because the experimental absorption coefficient $\alpha_{expt}(\bar{\nu})$ exhibits a nearly Gaussian shape for the carbonyl stretch, which indicates significant inhomogeneous broadening. ($\alpha_{expt}(\bar{\nu})=-\ln[T_{expt}(\bar{\nu})]/L$, where $T_{expt}(\bar{\nu})$ is the transmission spectrum of bare a PMMA witness film, and L is the sample thickness.) To assess α_0 and Γ_H, we examine the lineshape of the absorption coefficient more fully. We use $\alpha_k(\bar{\nu})$ derived from the ellipsometrically measured optical constants for PMMA[4] because we deem an ellipsometric measurement to be quantitatively more reliable than our particular FTIR instrument, which requires stable background spectra and precise correction for nonlinearities in the MCT detector for an accurate transmission measurement[5] of $\alpha_{expt}(\bar{\nu})$. We note that both absorption coefficients give the same center-frequencies and linewidths to better than 1 cm^{-1}.

To obtain $\alpha_k(\bar{\nu})$, we employ a standard model[6,7] for the dielectric function ε, which for the time-dependence convention $e^{-i\omega t}$ is written:

$$\epsilon(\bar{\nu},\bar{\nu}_0) = \varepsilon_\infty + \frac{A}{(\bar{\nu}_0^2-\bar{\nu}^2)-i\bar{\nu}\Gamma_H} \qquad \text{(S1)}$$

where ϵ_∞ is the background dielectric constant and $\bar{\nu}_0$ is the carbonyl stretch frequency. The unknown amplitude A is proportional to the product of the carbonyl-bond density and the carbonyl-stretch oscillator-strength. From eq S1, one derives the (real) extinction coefficient $k = \sqrt{0.5(-\varepsilon_1 + \sqrt{\varepsilon_1^2+\varepsilon_2^2})}$, where ε_1 and ε_2 are, respectively, the real and imaginary parts of ε, and in turn one derives from k the homogeneous absorption coefficient $\alpha_H(\bar{\nu},\bar{\nu}_0) = 4\pi k(\bar{\nu},\bar{\nu}_0)\bar{\nu}$.[7] To model an ensemble of bonds inhomogeneously broadened by a Gaussian distribution of resonant frequencies, we construct the model absorption coefficient as:

$$\alpha_{fit}(\bar{\nu}) = \frac{1}{w\sqrt{\pi}}\int \alpha_H(\bar{\nu},\bar{\nu}_0')e^{-(\bar{\nu}_0'-\bar{\nu}_0)^2/w^2}d\bar{\nu}_0' \qquad \text{(S2)}$$

where the distribution width w depends on the distribution FWHM as $w = FWHM/2\sqrt{\ln(2)}$. eq S2 is often called a Voigt function.[8] To examine the degree of inhomogeneity, we performed nonlinear least-squares fits of $\alpha_{fit}(\bar{\nu})$ to $\alpha_k(\bar{\nu})$ with A and w as fitting parameters, and varied, as a fixed constant, the FWHM Γ_H until the fit deteriorated.

Figures S3a and S3b display the results for Γ_H = 2 cm^{-1} and Γ_H = 10 cm^{-1}, respectively, with accompanying residuals. The fit is insensitive to values of $\Gamma_H \leq 2$ cm^{-1}, improves slightly for Γ_H= 5 cm^{-1}, and deteriorates rapidly for $\Gamma_H > 10$ cm^{-1}. The corresponding values for α_0 are 3.4×10^4, 3.6×10^4, and 3.9×10^4 cm^{-1}.

Determination of the cavity 1st order width based on the 2nd order width

As noted above, expressions for the coupled-mode vacuum Rabi splitting Ω and width Γ_{CM} depend on the width Γ_{cav} of the empty-cavity resonance without carbonyl absorption. Because it is not possible to remove the carbonyl moiety from PMMA, directly measuring Γ_{cav} is not possible. However, an estimate can be obtained from the resonance at the second-order frequency where perturbations due to vibrational absorptions are insignificant. Figure S4a shows

the measured transmission spectrum at an incident angle of 0° over a frequency range that includes both 1st and 2nd order cavity resonances. Figure S4b shows the 2nd order resonance in greater detail, along with a fit to a Lorentzian lineshape with a FWHM, Γ_2, of 52 cm^{-1}. The excellent fit verifies the applicability of standard expressions for the transmission of a FP cavity (eq 1 in the accompanying article), which predicts for cavities with highly reflecting mirrors a Lorentzian transmission spectrum with a FWHM of[2,9]

$$\Gamma_m = \frac{\bar{\nu}_m}{m\pi}\frac{1-Re^{-\alpha L}}{\sqrt{R}e^{-\alpha L/2}} \qquad \text{(S3)}$$

Here $\bar{\nu}_m$ is the resonant frequency (in wavenumbers) at order m, α and L are the PMMA absorption coefficient and thickness, respectively, and $R=|r_1\ r_2,|$ where r_i is the field amplitude reflectance at FP mirror i.

Equation S3 permits estimating the 1st order cavity resonance-width once the 2nd order width is measured, if corrections for differing values of α and R at the two frequencies are available and if the ratio $\bar{\nu}_2/\bar{\nu}_1$ is known. Note that if R and α were constant and if $\bar{\nu}_1 = 2\bar{\nu}_2$, the two widths would be identical. In fact, α is negligible[4] at the measured 2nd order frequency $\bar{\nu}_2$ =3180 cm^{-1}, and we expect it would also be insignificant at $\bar{\nu}_1$ if the isolated carbonyl absorption were absent. This is confirmed by removing the oscillators constituting the carbonyl-stretch band from an oscillator model of the dielectric function for PMMA.[4] Similarly, once the carbonyl model-oscillators are removed, transfer-matrix computations gives an empty-cavity resonance frequency $\bar{\nu}_1$ =1730 cm^{-1}, which is confirmed by the agreement of the computed angular dispersion with the measured dispersion given in Figures 2a and 2b of the accompanying article. With α negligible and the resonant frequencies known, there remains only the correction to R due to the increasing optical conductivity of the Au mirrors at the lower $\bar{\nu}_1$ frequency. The relative increase in R was measured from the reflectance spectrum of Au witness films, and used to correct eq S3, yielding a 1st order empty cavity width of 34 cm^{-1}.

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