# **Controlling and Probing Molecular Polaritons**

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## 1 Introduction

The goal of this chapter is to accelerate the ability of research groups to contribute quickly, accurately, and substantively, to the field of cavity-modified materials behaviors. The opportunity to tune fundamental chemical and physical properties with an engineered optical environment has inspired images of designer cavity-catalysis,<sup>1,2,3</sup> enhanced energy technologies,<sup>4</sup> and directed bio-assembly.<sup>5</sup> Although numerous demonstrations of cavity-modified chemistry have been made,<sup>6,7</sup> hesitancy remains due to a lack of mechanistic understanding,<sup>8,9,10</sup> experimentally precarious results,<sup>11,12</sup> and the generally enigmatic character of this phenomenon. In fact, corroborating results<sup>7</sup> have been met with doubt by even close colleagues. However, just as error bars are slowly shaved away, measurement by measurement, to eventually reveal the sought-after truth, so too must we continue to evaluate cavity-induced effects, troubleshooting and improving experimental techniques, refining analytical tools, and listening to and addressing legitimate criticism.

Key to achieving this is lowering the barrier of entry into the field. New groups could quickly enter and contribute with accepted best practices, improved and robust experimental platforms, and easily accessible analytical procedures. The following sections are arranged to provide a simple analytical platform for describing cavity-coupled systems, highlights of non-idealities that exist in real systems and guidelines for their magnitudes and avoidance, and finally, a discussion of analytical and experimental techniques that could be adopted.

# 2 Analytical description of cavities

### 2.1 Treatment of lossless mirrors bounding an absorbing medium

Having an analytical treatment to describe the spectrum of a cavity coupled system is invaluable in designing and interpreting experimental studies. Fortunately, closed-form expressions for transmission and reflection spectra have already been developed, <sup>13,14,15,16</sup> and even with simplifying assumptions such as lossless mirrors, angle-independent reflectivity, and ignoring the phase shifts that upon optical reflection, these treatments can be informative, predictive, and even allow for the description of time-varying response.<sup>17</sup>

Beginning with a lossless slab of material (see Fig. 1a), an incident field amplitude,  $E_0$ , generates a first pass transmitted amplitude of  $E_1 = E_0 t^2 e^{(i\omega t)}$ , where t is the transmission amplitude coefficient

through the top and bottom slab interfaces. Beams are reflected within the slab with some transmission occurring upon each round trip. In general, the transmission amplitude upon the  $N^{th}$  passage through the film is  $E_N = E_0 t^2 r^{2(N-1)} e^{i[\omega t - (N-1)\delta]}$ , where reflections are now accounted for with r and the total phase change per round trip within the slab is  $\delta = 4\pi nLv \cos\theta$ , where n is the refractive index, L the cavity length, v the frequency in cm<sup>-1</sup>, and  $\theta$  the angle of incidence. If we define  $a = E_0 t^2 e^{i\omega t}$  and  $b = r^2 e^{-i\delta}$ , then this infinite series of transmitted beams may be summed using a geometric series as  $E_{total} = \sum_N E_N = a + ab + ab^2 + \dots = \frac{a}{1-b} = \frac{E_0 t^2 e^{i\omega t}}{1-r^2 e^{-i\delta}}$ . Multiplying this expression by its complex conjugate gives the transmission intensity through a lossless slab, shown in **Eq. 1**, where  $T_m$  and  $R_m$  are the intensity transmissivity and reflectivity through the slab interface which act as lossless mirrors,  $T_m + R_m = 1$ . Absorptive material within the slab can be described through the slab, resulting in **Eq. 2**.

$$T_{\text{lossless}} = \frac{T_m^2}{1 + R_m^2 - 2R_m \cos(4\pi \nu nL \cos\theta)}$$
(1)

$$T_{\rm abs} = \frac{T_m^2 e^{-\alpha L}}{1 + R_m^2 e^{-2\alpha L} - 2R_m e^{-\alpha L} \cos(4\pi \nu n L \cos \theta)}$$
(2)

$$\varepsilon_{1} = \varepsilon_{\infty} + \sum_{j} \frac{S_{j}(\nu_{j}^{2} - \nu^{2})}{(\nu_{j}^{2} - \nu^{2})^{2} + (\nu_{j}\nu)^{2}}$$
(3)

$$\varepsilon_2 = \sum_j \frac{S_j \gamma_j \nu}{\left(\nu_j^2 - \nu^2\right)^2 + \left(\gamma_j \nu\right)^2} \tag{4}$$

$$n = \sqrt{\frac{\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}} \tag{5}$$

$$k = \sqrt{\frac{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}} \tag{6}$$

$$\alpha = 4\pi\nu k = 4\pi\nu \sqrt{\frac{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}}$$
(7)

$$A = \frac{\alpha L}{\ln(10)} = \frac{L}{\ln(10)} 4\pi v \sqrt{\frac{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}}$$
(8)

This convenient description of a Fabry-Pérot (FP) cavity allows for the calculation of transmission spectra, as a function of incident angle, as long as the absorption coefficient,  $\alpha$ , and interface (i.e. mirror) reflectivity, R, are known. A common approach to modeling the absorption coefficient is to describe each optically active transition as a Lorentzian oscillator. Then, the real and imaginary components of the complex permittivity,  $\varepsilon_1$  and  $\varepsilon_2$ , take the form of a summation over all the transitions one wishes to include, and are shown as Eqs. 3 and 4, where  $\varepsilon_{\infty}$  is the permittivity at long wavelength (i.e., background refractive index),  $\nu$  is frequency in units of wavenumbers (cm<sup>-1</sup>), the  $\nu_i$ 's are the resonant frequencies of the transitions, the  $S_i$ 's are scaling factors that determine the strength of each transition, and the  $\gamma_i$ 's are the linewidths of the Lorentzian forms describing the transitions. If all of these characteristics are known or assumed, one can build a dielectric function defined by Eqs. 5-7, insert it into Eq. 2, and begin modeling. Examples of such calculations are shown in **Fig. 1** and highlight the roles of the various terms. Transmission spectra are modeled for a range of absorber concentrations (i.e., amplitude of the oscillators modeled by Eq. 3-4) are shown in Fig. 1b and show an increasing peak separation (i.e., Rabi splitting,  $\Omega$ ) with increasing absorber concentration.<sup>15,18,19</sup> The role of mirror reflectivity is to determine, in part, the linewidth of the cavity mode is highlighted in Fig. 1c. Clearly, higher reflectivity results in narrower cavity and polariton modes, which has immediate relevance for attaining the strong coupling regime, typically defined as a Rabi splitting larger than both the cavity and absorber linewidths,<sup>16,20</sup> but there can be more insight had here. The cavity linewidth has implications for energy exchange and lifetime timescales since the relative loss rates between the molecular and cavity photon excitations depend on the cavity linewidth (i.e., lifetime).<sup>21,22</sup> The final aspect of the analytical modeling that will be highlighted here is the ability to model angle-dependent transmission response. This allows one to calculate the full dispersion of a Fabry-Pérot cavity, which tunes blue as the angle of interrogation increases, **Fig. 1d**.



Figure 1. Analytical modeling of etalon response. (a) depicts the propagating ray picture for an incident beam partially reflecting and transmitting upon its encounter with the front and rear partially reflective surfaces. Accounting for the infinite series of transmitted rays results in the analytical expressions presented in the text. Plots depict the cavity transmission spectra as a function of (a) absorber concentration, (b) interface reflectivity, and (c) incident angle.

With no knowledge of the amplitude factors, we can reformulate the absorption according to Eq. 8, which provides an expression for fitting an experimentally measured absorption spectrum (although one must know or assume the sample thickness and  $\varepsilon_{\infty}$ ) to yield all the pertinent transition characteristics. Specifically, the measured absorption in OD can be expressed as shown in Eq. 8, then the curve may be fit with Lorentzian amplitude factors, frequencies, and linewidths as fitting parameters. An example of such a treatment is shown in Fig. 2 where the absorption coefficient for the phenyl isocyanate is fit with two oscillators. Once the data is fit, Fig. 2a, the extracted oscillator parameters can be used to model the real and imaginary components of the permittivity, Fig. 2b.



Figure 2. Example of Lorentzian model generation. An absorption spectrum for material of interest (a) may be fit with an appropriate number of Lorentzian oscillators to yield amplitude, resonant frequency, and linewidth parameters which accurately describe the material. These parameters then define the real and imaginary components of the permittivity (b).

### 2.2 Semi-classical coupled oscillators

Although the classical approaches described in Section 2.1 do an excellent job of describing observed spectra, there is no explicit description or dependence on coupling strength (referred to as the Rabi coupling,  $\Omega$ ). On the one hand, this makes the treatments described in Section 2.1 equally applicable to weak and strong coupling regimes. On the other hand, if the goal is to explicitly define an interaction energy, one can turn to an approach that utilizes some degree of quantization. Whether one quantizes both the field and material oscillator (i.e., fully quantum mechanical) or only quantizes the material resonance and leaves the field classical (i.e., semi-classical), the end result is a Hamiltonian that includes three terms, one describing the photon, another for the material excitation, and a third

describing their interaction.<sup>16</sup> Applying a coordinate transformation referred to as the rotating wave approximation (RWA) results in an expression diagonalizable into a 2 × 2 matrix, Eq. 9, whose eigenvalues define the polariton energies according to Eq. 10.<sup>23</sup> With such an expression, a fixed material excitation energy,  $E_{\text{mat}}$ , and an expression describing the dispersive Fabry-Pérot cavity resonance,  $E_{cav}(\theta) = E_0 \left[1 - \left(\frac{\sin^2 \theta}{n^2}\right)\right]^{-1/2}$ , where  $E_0$  is cavity resonance at normal incidence (i.e., in plane wave vector,  $k_{||} = 0$ ),  $\theta$  the angle of incidence, and n the background refractive index of the material in the cavity, the angle-dependent dispersion of the normal modes can be generated. A dispersion, modeled to mimic typical experimental conditions, is shown in Fig. 3a. This dispersion shows an upper polariton (UP) that is relative flat and nearly isoenergetic to the material resonance at low interrogation angles. At higher angles, the upper polaritons disperses rapidly to higher energy and the lower polariton (LP) is now flat and resides near the material resonance energy. The Rabi splitting of such a dispersion would be calculated as the minimum energetic separation between the polaritons, which occurs for this example data near 25 degrees. These dispersing modes have varying photonic and material character,<sup>24,25</sup> represented by  $\alpha^2$  and  $\beta^2$ . Generally speaking, the closer a polariton is to the material excitation energy, the greater the

material character. Therefore, in the example data of **Fig. 3a**, the upper polariton is more material-like at low angle (i.e., in-plane wave vectors) and more photon-like at higher angles. The photonic character is explicitly expressed in **Eq. 11** and plotted in **Fig. 3b** for both polaritons. In addition to the general trends described above, one can see the curves crossing each other at the condition where both polaritons have equal photonic and material content.

$$\begin{bmatrix} E_{cav}(\theta) & V \\ V & E_{mat} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E_{UP,LP} \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$
(9)

$$E_{UP,LP} = \frac{E_{cav} + E_{mat}}{2} \pm \sqrt{\frac{(E_{cav} + E_{mat})^2}{4} + \left(\frac{\Omega}{2}\right)^2}$$
(10)

$$\alpha_{UP,LP}^{2} = \frac{\left(\Omega/2\right)^{2}}{\left(E_{cav} - E_{UP,LP}\right)^{2} + \left(\frac{\Omega}{2}\right)^{2}}$$
(11)

$$\beta_{UP,LP}{}^{2} = 1 - \alpha_{UP,LP}{}^{2} \tag{12}$$

# 3 Non-idealities - that we must, nevertheless, deal with

### 3.1 Details for dealing with cavities

Despite the broad utility and robustness of the classical and semi-classical treatments described in Sections 2.1 and 2.2, there are additional experimental details that should be considered. The first discussed here is conversion of angle-dependent spectra to a true dispersive relationship. To extract the coupling strength (i.e., Rabi splitting,  $\Omega$ ), one finds the minimum separation between the UP and LP modes in the dispersion response. Angle-tuning of a FP cavity is a convenient method for generating the required dispersion contour. However, it must be remembered that the two polariton modes revealed at any given interrogation angle actually have different internal wavevectors. This means that a single spectrum does not accurately reflect the coherence of the polariton states. Therefore, the dispersion response should be converted from angle- to wavevector-dependence. The in-plane wavevector is  $k_{||} = k_0 \sin \theta = 2\pi v \sin \theta$ , where v is the frequency and  $\theta$  is the angle of incidence. This dependence on both incident angle and frequency are what make this conversion necessary for accurate determination of the Rabi splitting since the conversion does not simply stretch or contract the dispersing axis. Instead, it causes a correlated distortion in both the dispersing and energy directions. In practice, we carry out this conversion by first defining an empty array which will eventually house the converted data. Each element is located at  $[k_{||}, v]$ . Returning to the original data, each data point has a defined v and  $\theta$  value, which determines



Figure 3. Dispersion and photonic character modeled according to **Eqs. 10-11**. In (a), the upper and lower polariton branches are seen to anti-cross. A minimum in the branch separation occurs where the bare cavity resonance is coincident with the material excitation (~25 degrees in this example). The Hopfield coefficient describing the fraction of each polariton that is of photonic character is calculated in (b). The material component is simple unity minus this value.

the  $[k_{||}, v]$  location where this intensity value should be placed in the destination array. Since the exact  $k_{||}$  likely does exist in the destination array, one can use bidirectional interpolation to place the most accurate value in the most appropriate element location. Correcting the dispersion in this way<sup>26</sup> can alter extracted Rabi splitting values by ~5%.

Next, it is important to identify an outstanding challenge that has plagued several attempts to demonstrate, then verify, cavity-modified chemical reactivity. Accurate methods for monitoring reaction progress in a strong coupling environment are key to establishing this field and visible absorption spectroscopy is a common method for monitoring product distributions, the formation of reaction intermediates, and overall reaction kinetics. As such, there have been multiple reports of using visible absorbance as a reporter for reaction progress, <sup>27,28,29</sup> as well as reports questioning the robustness of some these results.<sup>11,12</sup> These works utilize thin metal mirrors (~10 nm Au) which are reasonably reflective in the infrared (~90 %) and modestly transmissive in the Although there is transmission of several visible. percent in the visible, the inevitable formation of weak

cavity modes in the visible and significant absorption make quantitative interpretation of absorption spectra problematic. There will be no analytical answer presented here but an important, and very practical, contribution to the field would be an analytical treatment which accurately corrects for these unwanted and potentially misleading features. One can imagine a straight-forward treatment, such as that used to correct for weak fringing in organic thin films,<sup>30</sup> but with the inclusion of metal absorption. On the other hand, the optical properties for metal layers of this dimension may not be well-behaved.

One last detail researchers should be aware of, is the impact of the passivating coating applied to the mirror surfaces. It is common practice to coat the metal mirrors with an oxide to insure against materialspecific effects (e.g., metal catalysis) when comparing chemical behaviors inside and outside of a cavity. If one uses a refractive index shift as a report of reaction progress, which can be problematic in its own right,<sup>31</sup> one should note that the cavity is only partially filled with the reaction medium experiencing an index shift, with the remainder filled with an oxide layer exhibiting no index shift. Since the observed shift is due to only a portion of the cavity medium, the extracted modification of the reaction medium will be larger than if one ignores the invariable mirror coatings. For example, the frequency, in units of cm<sup>-1</sup>, of a resonant mode in a FP cavity is  $v = \frac{10^4 m}{2nL}$ , where m is the mode order, n the refractive index, and L the cavity length, measured in cm. The shift in fringe position can then be used as a measure of the evolution of the refractive index due to solution composition variation as a reaction proceeds. The refractive index in the cavity should be described as  $n_{true} = (1 - P)n_{rxn} + Pn_{ox}$ , where P is the fraction of the cavity length filled by the passivated layer rather than reacting solution,  $n_{\rm rxn}$  is the refractive index of the reacting solution, and  $n_{ox}$  the index of the passivating oxide layer. Admittedly, this only amounts to a small correction (~1%) for the systems found in the literature but this systematic error could become significant for systems where the refractive index difference between the reacting solution and passivation layer is large, the index change between reactants and products is very small, the thickness of the passivating layer is significant (e.g., ~10% of the total cavity), or some combination of these factors. In short, check.

There are other implications for a non-uniform medium filling the cavity. Not only does it amount to a correction that could be applied (described above), but it reminds us that the field distribution within the cavity it non-uniform. It is non-uniform due to the natural formation of nodes and anti-nodes, but also due to varying refractive index. If the passivation layer has a large refractive index, it will garner a greater fraction of the mode, and therefore, have a larger impact on any properties measured via the modes (e.g., fringe position, optical absorption, etc.). These spatial non-uniformities will be discussed below.

### 3.2 Spatially-dependent response

When recording cavity-modified physics or chemistry and trying to build an understanding of what processes could be modified, it is easy to imagine the functional material within the cavity as a monolith. In other words, place material in a cavity and see that material's response modified. In truth, there is an inhomogeneity of the cavity mode profile consisting of nodes and anti-nodes in Fabry-Pérot cavities, which immediately yields two important conclusions. First, material located at a modal node will experience a different environment (and potentially a different cavity-induced modification of properties) than material

placed at a mode peak. Second, optical probing of a material response will preferentially interrogate material at anti-nodes supported for the frequency of interrogation while neglecting material located at the nodes generated at the probe frequency. Considering the first point, that material at different mode positions *feels* different environments.<sup>32</sup> Although a single cavity mode extends across the entire cavity, and this delocalization has been cited as responsible for long-range excitation transfer, interaction rates are strongest at anti-nodes and weak at nodes.<sup>33</sup> In other words, although a single cavity mode might enable long-range energy transfer via mode delocalization, this transfer is most likely to occur between a material excitation located at or near an anti-node and material located some distance away but at another modal anti-node.<sup>33,34,35</sup> This exact concept is used to design cavities for maximal energy transfer.<sup>36</sup>

Considering cavity-inhibited chemical reactivity, one might propose that reactivity is slowed most for molecules located at regions of high field intensity and negligibly at nodal positions. If this were the case, the system as a whole would exhibit a smeared range of rates, however, the means of monitoring the chemical reaction now becomes key to determining what would be observed. First, consider electrical or ionic conductivity measured between the two mirrors of a FP cavity with the two mirrors could serving at contact electrodes. If the conductivity



Figure 4. These calculated results predict (a) what resistance would be measured as a function of modified behavior at the modal anti-node position. The dashed line plots the measured resistance normalized by the unmodified value and shows a linear relationship with a slope less than unity. The red curve is essentially a measure of how poorly the measurement captures the behavior at the anti-nodes. Panel (b) presents the same data but over a much smaller range to highlight the drastically erroneous measurement that could be made under conditions where the conductivity is reduced at the antinodes.

were modulated due to interaction with the cavity mode, and this modification were greatest at modal anti-nodes, the system resistance could be coarsely modeled as two resistors in series,  $R_{\text{measured}} =$  $R_{node} + R_{anti-node}$ , where  $R_{node}$  and  $R_{anti-node}$  are the resistances of material located at the node and anti-node. Intuitively, it's clear that the measures system resistance will underestimate the modification occurring at the most significantly altered regions. The effects of this spatial variation on measured resistance and its inaccuracy in measuring cavity-modified regions in shown in Fig. 4. The important points to note are, first, that any increased resistance occurring at the anti-nodes is systematically measured as a lower value. For example, in **Fig. 4a**, see the red curve at f = 10, indicating a 10-fold increase in resistance at the anti-nodes. This results in a measured value that has only increased by a factor of 5. On the other hand, for reduced resistance at the anti-node, the measurement error becomes much more significant. The overall error, measured as the measured resistance normalized by the resistance of interest (i.e., at the anti-node) is  $e = \frac{R_{\text{measured}}}{R_{\text{anti-node}}} - 1$  (red curves in **Fig. 4**). One can see that at large increased resistance, the error is relatively small since the relatively large  $R_{anti-node}$  value dominates the R<sub>measured</sub> expression. However, for reduced resistance, this systematic error becomes large (a factor 10 for a 90% reduction in resistance; see Fig. 4b for detail). Notably, measuring resistance in the perpendicular orientation (current passing in-plane in a FP cavity, modeled as a resistors in parallel) would experience the opposite effect (i.e., regions of reduced resistance will dominate the measured response rather than be obfuscated).

Considering the second point identified, that the modal structure results in preferential interrogation of certain regions over others,<sup>37</sup> we highlight ultrafast spectroscopic results.<sup>38</sup> A demonstration of the effect of molecule location within the cavity will be made by modeling the transient response of a first-order cavity under 1% excitation. However, the spatial distribution of these excited molecules will be confined to different positions within the cavity mode. The magnitude of the resulting differential transmission signal (defined as  $-\log^{T}/T_{0}$ ) will demonstrate preferential interrogation of material located at the anti-nodes. Figure 5 plots the transient response for molecular excitation centered at different regions of the cavity. Qualitatively, all curves show a significant peak near the lower polariton frequency and a derivative-like feature near the upper polariton frequency. The origin of these features is well-understood, discussed fully in the literature,<sup>39,40</sup> and are not to subject of this work. Instead, the focus here is on signal magnitude. Compare the red curve, associated with excitation localized to a cavity anti-node, to the blue curve, where the same magnitude of molecular excitation has been localized to a cavity

node. The positive peak located near the LP is still evident but it is greatly diminished in magnitude. Further confining the same amount of excitation to a narrower region at the cavity node (see purple curve) results in nearly complete erasure of the optical signatures associated with the excitation. However, when these data are normalized and replotted, **Fig. 5b**, it is evident that the optical signatures of the molecular excitation are essentially the same.<sup>38</sup> They only vary, albeit greatly, in their magnitude. The point here is that if one is using optical interrogation to report on a physical or chemical process within a cavity, the spatial structure of the mode at the frequency of interrogation with cause preferential reporting of the response from some regions (anti-nodes) while being relatively insensitive to changes occurring in other regions (nodes).



Figure 5. Differential transmission spectra are plotted for the same level of molecular excitation but localized to different regions of a first order Fabry-Perot cavity. In (a), it is shown that confining the excitation to a region of high field magnitude (anti-node) results in a much greater signal (red curve) than when localizing that same excitation to a cavity node (blue, purple curves). The spectra are normalized and plotted in (b) to demonstrate that the fundamental spectral signatures are essentially the same and only vary in magnitude.

### 3.3 Line broadening

Measured transmissions spectra can be broadened by several experimental realities. Two will be discussed here. First, it is inevitable that there is some degree of non-parallelism between the two mirrors. In a typical vibrational strong coupling procedure, mirrors are assembled and their parallelism evaluated by examining the number of visible fringes observed across the cavity face. Each visible fringe corresponds



Figure 6. Plots showing the effect of mirror non-parallelism on dispersion measurements. First, (a) an empty cavity dispersion is shown (black curve) along with the same dispersion assuming planarity variations over the interrogated area of ±100 nm (blue and red). A cavity exhibiting this degree of non-parallelism would have a dispersion broadening bounded by these curves. In (b) this same cavity is filled with an oscillator but the anti-crossing spectral signature is almost completely obfuscated due to non-parallelism. Lastly, (c) the effect of poor interrogation beam collimation, which results in a range of interrogation angles.

to a variation from fringe m to m + 1, which is the free spectral range. Since the cavity length,  $l = m \frac{\lambda_{res}}{2n}$ , where m is the mode order,  $\lambda_{res}$  is the resonance wavelength, and n is the refractive index, the difference in cavity lengths between adjacent modes is therefore  $\frac{\lambda_{res}}{2n} \sim \frac{600 \text{ nm}}{2*1.5} = 200 \text{ nm}$  for a fringe in the visible. The impact of this magnitude of cavity length variation will be much smaller in the infrared than the visible, but still present. Figure 6 presents calculated results showing the degree of line broadening in the infrared resulting from different degrees of non-parallelism. First, the effect of varying spacing between the mirrors, a result of non-ideal parallelism, is shown in Fig. 6a-b for empty and filled cavities. The black curves represent the response from the nominal cavity separation and the blue and red curves, the response for the cavity when mirror separation is varied by 100 nm. In a real experiment subject to these accuracies, the transmission spectra would experience a broadening bounded by the curves. In the case of strong coupling (Fig. 6b), nearly the entire anti-crossing feature is obscured. Another source of experimental broadening comes from divergence of the probing beam. Conventional FTIR spectrometers focus the infrared beam at the point of interrogation. This focus results in divergence angles of several degrees (the exact value depends on aperture settings and instrument specifics). Light impinging the sample off of the nominal angle will report a different resonance resonant frequency for the cavity due to the angular dispersion. This effect is quantified and pictured in Fig. 6c.

In addition to these straight-forward causes of measurement broadening, which can be addressed through improved experimental design, there may also be inherent inhomogeneities in the sample. A particularly relevant example is the OH vibrational band of water. This vibration has been the subject of several studies of strong coupling and its effect on chemical processes.<sup>2,27,28</sup> However, how to think about and properly describe this severely inhomogeneous vibrational band is an important and open question. Is it akin to "cooperative" coupling<sup>41</sup> since there are distinct vibrational modes contained within the broad envelope? Can one simply treat it as a very broad absorber or should one think about it as a series of discrete absorbers at different energies? Either gives the same modeled optical response but likely has very different chemical implications.

# 4 Current Challenges and Proposed Best Practices

The promise of cavity-modified chemical processes is not matched by its adoption. Although many excited results exist, such as suppressed and enhanced reactivity, skewed product distribution, and shifted charge exchange equilibria, pursuit and validation of these processes by a range of groups is not occurring. In fact, there are even reports of irreproducibility. A major obstacle is a reliable, robust, and convenient apparatus for evaluating the effects of cavity coupling on chemical processes. Certainly, a solution housed between two reflective surfaces is conceptually simple, however, the commercial tools available leave quite a lot to be desired in terms of flexibility, repeatability, and fortification against simple user error. It is with these obstacles in mind, and the desire to promote widespread testing and examination of cavity-coupling effects that this article, and the piezo-adjustable reaction cavity design contained within, is put forth.

After describing the most important experimental challenges and the shortcomings of commonly used systems, a new design will be presented. The various functions of this apparatus will be described and its function validated through repeatability, stability, and reversibility testing. The files needed to fabricate such a tool and a complete parts list are given in the supplemental materials.

### 4.1 Current Challenges

There is, no doubt, great desire to repeat, verify, and extend the published demonstrations of cavitymodified chemical processes. At the crux of these experiments is assembling a well-controlled cavity and measuring the chemical activity occurring therein. However, a research group aiming to contribute to this burgeoning field is immediately faced with several challenges. In addition to the overall need for a simple and easy-to-use system that junior researchers (graduate or undergraduate students) can fruitfully use to generate contributive data, the most pressing challenges are: 1. Achieving a desired cavity tuning: These studies require experimental trials carried out with cavity modes tuned to, or controllably detuned from, vibrational modes of interest. One must be able to achieve a targeted cavity resonance repeatedly to generate trustworthy statistics. Furthermore, one must ensure there is not unintended coincidence between higher order cavity modes and molecular vibrational modes, which could make experimental interpretation ambiguous. At odds with these requirements is the fact that commercial fluidic cells use polymer spacers that are only available in a few select thicknesses, which severely limits versatility.

2. Stability over time: Any chemical reaction will occur over some time interval (typically minutes to hours). The cavity tuning (at least to within a linewidth) must be stable over this time period. Commercial cells can be susceptible to mechanical relaxation of gaskets, O-rings, fastening screws, etc. Additionally, solvent leakage or evaporation into unintended head space with alter pressure within the cavity and therefore the cavity length and resonance frequency.

3. Cavity parallelism: The issue of mirror parallelism offers more subtle challenges. Departure from purely parallel mirrors results in a cavity tuning that varies with position (i.e., a cavity mode might be in resonance with a vibration of interest in one location but detuned from that desired mode a few millimeters away). The obvious pitfall is that any observable that samples the entire cavity (e.g., mass spectroscopy of product distribution, electrochemical charge passed, optical transmission that samples a large area), will effectively average the responses from regions of various tunings. Even if the measurement is localized to a region with acceptable tuning variance (e.g., a small spot size optical measurement or electrochemical current from a small electrode), experimentalists are still subject to diffusion effects which will mute the cavity-induced response in the same way, though more weakly, as the macroscale measurements described above.

4. Ability to reliably make electrical contact to access system response: Electrochemical tools represent an important opportunity for chemical interrogation of cavity-coupled species. Although metallic mirrors, which are commonly used in VSC experiments, can easily serve as a working electrode, commercial apparatuses for fluidic infrared transmission experiments are not easily amenable to making electrical contact to one or both mirror surfaces.

5. Real-time modulation of cavity tuning: When imagining potential uses and technologies based on cavity-modified materials, there is an immediate realization of the utility of real-time modulation allowing slowed or hastened chemical reactivity on command, periodic cycling of a work function for energy

control, or even incorporating diagnostic feedback to target a certain final product composition. Current commercial fluidic cells do not allow for real-time tunability.

### 4.2 Measuring Reaction Rates in Optical Cavities

If one hopes to observe any change in material properties or chemistry or under strong coupling, there are three kinds of experiments which are vital to perform: (1) The "out-of-cavity" experiment is a measurement of the system of interest performed outside of a cavity. This is a conventional control measurement which serves to establish a baseline for the system properties being studied. (2) In the "cavity on-resonance" experiment, the system is measured inside of a cavity that is tuned such that the energy of one of its optical modes coincides with that of a bare molecular mode *at normal incidence*— these are the conditions under which modified chemistry has been reported to occur under strong coupling.<sup>27,28</sup> (3) In the "cavity off-resonance" experiment, the system is measured inside of a cavity whose optical mode is detuned from the bare molecular mode *at normal incidence*. In this negative control, no modification of material properties or chemistry should be observed and its purpose is to rule-out measurement artifacts or mundane effects caused solely by the presence of the cavity mirrors. It is desirable to fix as many system parameters as possible across these three experiments in order to eliminate trivial sources of variability. For example, the sample path length should at least be comparable between out-of-cavity, cavity on-resonance and cavity off-resonance measurements even if detuning requires it to be changed slightly.

In this section, we will examine the case of chemical reactions under vibrational strong coupling monitored with FTIR spectroscopy. The out-of-cavity control is the same as a *conventional* infrared absorption measurement. Recall the Beer-Lambert law:

 $A \approx \epsilon CL$ 

(13)

The *molar* absorption coefficient  $\epsilon$  (units of L mol<sup>-1</sup>cm<sup>-1</sup>) is obtained from the slope of absorbance A versus concentration C of the absorbing species in a cell of fixed path length L. It is important to point out that the linear relationship in **Eq. 13** is only a good approximation for *weak* absorbers and *low* concentrations. Inconveniently, entering the strong coupling regime generally requires *strong* absorbers and *high* concentrations, so one must take care when utilizing **Eq. 13** and constructing a calibration curve. Rather than correlating the maximum absorbance of a particular absorber  $A(v_j)$  with its concentration  $C_j$ , it is advisable to use a more robust quantity such as *integrated* absorbance which is always directly proportional to concentration:

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$$\int_0^\infty A_j(\nu) \mathrm{d}\nu \propto S_j = s_j C_j \tag{14}$$

Here,  $S_j$  is the integrated absorptivity (the factor in the numerator of **Eqs. 3 and 4**, with units of cm<sup>-2</sup>) and  $s_j$  is the respective molar quantity (units of L mol<sup>-1</sup>cm<sup>-2</sup>). To construct a calibration curve, a series of absorbance spectra are measured for known concentrations  $C_j$  of the absorbing species j, and  $s_j$  is treated as a free parameter in a fit using Lorentz oscillator model (**Fig. 7a**). The best-fit values are then plotted vs concentration and  $s_j$  is extracted as the slope of the best-fit line (**Fig. 7b**). Whenever possible, any species present in the reaction (including spectators) should be isolated or procured in their pure form and calibrated in the intended reaction solvent. Out-of-cavity kinetic data can then be fit using **Eqs. 3 and 4** (substituting in  $S_j = s_j C_j$ ) allowing for concentration  $C_j$  to be extracted at each time point.

Tracking reaction progress within optical cavities requires some additional considerations. Due to the highly reflective broadband mirrors commonly employed for VSC, non-zero optical transmittance is limited to the narrow cavity resonances making the conventional infrared absorption measurement described above impossible. Luckily, the analytical description of cavity transmission in **Eq. 2** is very sensitive to the presence of molecular modes when they overlap in energy with optical modes. Consequently, if the cavity is resonant with a vibrational mode of the reactant, the rate of consumption during the reaction manifests as a time-dependent Rabi contraction. Therefore, reaction kinetics for "cavity on-resonance" systems may be directly extracted from transmission spectra taken at normal incidence via fitting to **Eq. 2**. However, this presents a problem: when the cavity is *detuned* from the molecular mode of interest, the transmission spectrum acquired at normal incidence no longer reports on the molecular concentration— how then can one perform the aforementioned "cavity off-resonance" control measurement? The frequencies of higher-order cavity fringes *do* respond to changes in the



Figure 7. (a) Concentration dependent absorptivity of phenyl isocyanate NCO stretching mode in tetrahydrofuran fit with a pair of Lorentz oscillators. (b) Calibration curve for linearly correlating the integrated absorptivity of the stronger oscillator with the concentration of phenyl isocyanate. Adapted from **Ref. 7**.

solution's refractive index taking place over the course of a reaction and this has previously been used to track reaction progress.<sup>44,45,46</sup> Unfortunately, this method can be an unreliable handle because the positions of these fringes are also susceptible to solvent leakage, evaporation, temperature changes, mechanical stabilization of the cell, and even strong coupling of optical modes in remote spectral regions.<sup>31</sup> A clever alternative approach for measuring reaction rates in off-resonant cavities was developed by Ahn *et al.* <sup>7</sup> Their strategy leverages angular dispersion and involves collecting on-resonance transmission spectra at small nonzero angles for cavities which are detuned at normal incidence. These spectra can then be fit using **Eq. 2** to extract molecular concentration. In the next section, we will construct a model experiment to computationally validate this method of analysis.

#### 4.3 Validating Angle-Independent Rate Extraction

The analytical approximation to the transfer matrix (TM) method in **Eq. 2** describes the transmittance of an optical cavity containing absorbers but neglects the angle dependent reflectance of the mirrors. To demonstrate the efficacy of this approximation for analyzing chemical kinetics measured in a cavity at different incident angles, we will simulate the time-dependent optical response of a model system using the full TM method and show that the approximation gives a result which is indistinguishable within the margin of experimental error.

The system is defined to emulate the cavity-coupled urethane addition reaction reported by Ahn *et al.*<sup>7</sup> This reaction involves the alcoholysis of an isocyanate (R-NCO) by an alcohol (R-OH) in tetrahydrofuran (THF) to form a carbonyl-containing carbanilate (R-C=O):

$$R-NCO + R-OH \xrightarrow{THF} R-C=O$$
(15)

This bimolecular reaction is first-order in each reactant, that is:

$$\frac{\mathrm{d}}{\mathrm{d}t}C_{\mathrm{CO}}(\mathrm{t}) = \frac{-\mathrm{d}}{\mathrm{d}t}C_{\mathrm{NCO}}(t) = kC_{\mathrm{NCO}}C_{\mathrm{OH}}$$
(16)

Where k is the second-order rate constant with units of  $M^{-1}s^{-1}$ . If we assume an equimolar (3.0 M) starting solution of these reactants, this differential rate equation can be rewritten in terms of a single reactant:

$$\frac{\mathrm{d}}{\mathrm{d}t}C_{\mathrm{NCO}}(t) = -kC_{\mathrm{NCO}}^2 \quad \text{when} \quad C_{\mathrm{NCO}}(0) = C_{\mathrm{OH}}(0) \tag{17}$$

Integrating both sides yields:

$$C_{\rm NCO}(t) = \frac{1}{C_{\rm NCO}^{-1}(0) + kt} \implies C_{\rm NCO}^{-1} = C_{\rm NCO}^{-1}(0) + kt$$
 (18)



Figure 8. Results of a numerical experiment intended to validate the angle-independence of reaction rate extraction. The simulated out-of-cavity spectra represent the consumption of the reactant NCO mode (left) and the subsequent generation of the product C=O mode. Parameters utilized in the calculation are provided as well as a schematic depiction of the model system.

The average of six out-of-cavity rate constants and their standard deviation as measured<sup>7</sup> by Ahn *et al.* is  $k_{OUT} = 2.34(\pm 0.2) \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$ . This empirical value will be used as an input to describe the time-dependent complex permittivity of the solution by substituting **Eq. 18** into **Eq. 3 and 4**. We could define a single Lorentz oscillator corresponding to the decaying reactant mode coupled to the cavity (e.g., the isocyanate NCO stretch at 2260 cm<sup>-1</sup>), but in general it is important to account for any nearby resonances as well, especially if they too vary in time. While not necessary in this case, we will also define the remote product carbonyl at 1730 cm<sup>-1</sup> which is produced over the course of the reaction. Given the stoichiometry of these two species in **Eq. 15**, we can rewrite the product concentration  $C_{CO}(t)$  in terms of the reactant concentration  $C_{NCO}(t)$ :

$$C_{\rm CO}(t) = C_{\rm NCO}(0) - C_{\rm NCO}(t)$$
(19)

Finally, the solvent tetrahydrofuran (THF) contributes a background dielectric constant of  $\varepsilon_{\infty} = n_{\infty}^2 =$  1.9802. The simulated time-dependent out-of-cavity absorption spectra for a 7.4 µm path length cell are presented in **Fig. 8**. This dataset represents a series of out-of-cavity control measurements, an analysis of which is expected to return the input reaction rate constant of  $k_{OUT}$ .

To accurately model the transmittance under cavity coupled conditions, we employ the TM formalism implemented in the tmm python package.<sup>47</sup> An unpolarized transmittance calculation was run for a cavity defined by two 15 nm thick gold mirrors with the complex refractive obtained by Rakić *et al.*<sup>48</sup> separated by a 7.4 µm thick solution layer. This configuration places the frequency of the 5<sup>th</sup> order cavity mode coincident with  $v_{NCO}$ . The TM simulated time-dependent cavity transmission spectra for on-

resonance ( $T_{\rm TM}^{\rm ON}$ ) and off-resonance ( $T_{\rm TM}^{\rm OFF}$ ) conditions are presented in **Fig. 9a and 9b** respectively and **Fig. 9b** illustrates the transition between these two system geometries. The on-resonance calculation is performed at normal incidence, requiring a specific path length  $L^{\rm ON}$  to meet the resonance condition. For the off-resonance calculation, the path length must first be slightly changed to  $L^{\rm OFF}$  in order to detune the cavity mode from the isocyanate mode at normal incidence (blue bold to black dashed in **Fig. 9b**). Next, the incident angle is changed from 0° until the optical mode disperses back into resonance with the



Figure 9. Results of a numerical experiment intended to validate the angleindependence of reaction rate extraction. (a) Cavity transmittance spectra calculated at 0° for the reactant NCO mode onresonance with an optical mode at normal incidence. A schematic depiction of the model system is provided. The bottom subplot shows the difference between the full TM result and a fit using the analytical approximation in **Eqn. 2**.

(b) Cavity transmittance spectra calculated for a series of path lengths intended to spatially detune the reactant NCO mode from the optical mode (blue) and for a series of incident angles intended to bring them back into resonance (orange). The bottom-most spectrum represents the geometry used in the off-resonance control measurement.

(c) Cavity transmittance spectra calculated at 13.5° for the reactant NCO mode offresonance from an optical mode at normal incidence. A schematic depiction of the model system is provided. The bottom subplot shows the difference between the full TM result and a fit using the analytical approximation in **Eqn. 2**.

The residuals at the bottom of (a) and (b) are very small suggesting excellent agreement between the full TM and approximate results.

isocyanate mode at some small, nonzero angle (black dashed to orange bold in Fig. 9b).

The most notable feature in the time-dependent spectra is the contraction of the Rabi splitting  $\Omega_{ON}$  and  $\Omega_{OFF}$  from ~48 to 18 cm<sup>-1</sup> over the 28-hour interval calculated— as expected, the splitting scales linearly with  $\sqrt{C_{NCO}}$  (see **Fig. 10b**). It appears that the amplitudes of the upper and lower polariton become more asymmetric as reactant is converted into product. This is caused by a passive detuning of the optical mode from the isocyanate due to a change in the solution refractive index during the reaction. This highlights that, to the degree with which the solution dielectric function is adequately described (i.e., Lorentz oscillators describing all relevant optical transitions), any impact on the spectral response due to reactant consumption or product generation will be represented in this model. Changes in the concentration of species whose optically active transitions coincide in frequency with the cavity mode will be the dominant factor defining the spectrum. When *L* is relaxed in the fit, it can compensate for small variations in the *effective* path length such as changes in the solution dielectric function not explicitly



Figure 10. Results of a numerical experiment intended to validate the angle-independence of reaction rate extraction. (a) Second order rate plot showing inverse reactant concentration as a function of time. The slopes represent the rate constants  $k_{ON}$  and  $k_{OFF}$  obtained from simulations of on-resonance (O's) and off-resonance (X's) cavities respectively. The grey shaded region represents the uncertainty in the measured out-of-cavity value  $k_{OUT}$  used as simulation input. The bottom subplot shows the negligible difference between the simulated on-and off-resonance cavities and a comparison to the empirical out-of-cavity control. (b) The time-dependent Rabi splitting on-resonant (O's) and off-resonant (X's) extracted from **Fig. 9a and 9c** respectively. Both datasets exhibit a strong linear correlation with  $\sqrt{C_{NCO}}$ .

modeled as well as mechanical instability of the cell.

The TM simulated datasets  $T_{\rm TM}^{\rm ON}$  and  $T_{\rm TM}^{\rm OFF}$  are fit using the approximation from Eq. 2 giving  $T_{\rm fit}^{\rm ON}$ and  $T_{\rm fit}^{\rm OFF}$  respectively— the difference between these two descriptions are plotted at the bottom of Fig. 9a and 9c. As evidenced by the small residual, the approximation does an excellent job of reproducing the essential features of cavity transmission for both the on- and off- resonance simulations. The concentrations  $C_{\rm NCO}(t)$  extracted from the analytical fits were used to construct the second order rate plot in Fig. 10a. Here, the slopes represent the reaction rate constants (with units of  $10^{-5} \text{ M}^{-1} \text{s}^{-1}$ )  $k_{\text{ON}}$  = 2.37 (O's) and  $k_{\text{OFF}}$  = 2.33 (X's) while the grey shaded region represents the uncertainty of ±0.2 in the empirical out-of-cavity rate constant  $k_{OUT}$  = 2.34 that was used to as input to generate the timedependent solution dielectric function. Both values obtained from the simulated cavity transmittance fall comfortably within the grey shaded region bounded by the experimental uncertainty as is clearly seen from the residuals plotted at the bottom of Fig. 10a. Thus, we have demonstrated the effectiveness of this approach in accurately determining reaction rates from cavity transmittance spectra, independent of incident angle. The on- and off-resonance simulations are nearly indistinguishable from each other (differing only by  $\sim 2\%$ ) despite being performed under different system geometries. This is not only expected given the correspondence between angular and spatial dispersion in Fabry Pérot cavities, but also reassuring since our model is purely optical and does not attempt to capture how light matter interactions might impact the dynamics in principle. This means that if the on-resonant result were to diverge from those of the out-of-cavity and off-resonant controls in a real experiment, it could be argued that be some intriguing chemical physics driven by light-matter interactions are at play. The dashed green line in Fig. 10a illustrates the kind of anomalous rate suppression that is frequently reported in chemical reactions under VSC.

#### 4.4 Proposed Cavity System Design

The field of VSC modified chemistry is still relatively young and there exist many limitations with "firstgeneration" experimental apparatuses which should be addressed to advance our understanding of cavity-coupled phenomena. The most common etalon systems employed are demountable, fixed path length microfluidic cells with mirrors consisting of gold film deposited on a transparent substrate and topped with an oxide or polymer-based passivation layer. The mirror separation is often coarsely defined by a polymer spacer which can be compressed slightly, allowing for some tunability. Computer-controlled nanopositioning systems are commonly available and easily afford the accuracy needed for infrared

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cavities (~100 nm). Versions of such systems have been assembled<sup>3,11,49,50</sup> but providing for a sealed liquid environment while maintaining a broad tunability range is challenging. Piezo actuated cavities have been used maintain site-selective VSC during chemical reactions while actively compensating for changes in the solution refractive index with a computer controlled feedback loop, ensuring that the desired coupling condition is sustained for the duration of the measurement.<sup>3</sup> A versatile solution is diagramed in Fig. 11 (.stl files suitable for 3D printing, or as a starting point for modified designs, are given in the supporting information in the arXiv version of this manuscript<sup>51</sup>). This apparatus consists of four main components (labeled a, b, c, and d). One mirror is mounted between components (a) and (b) and another between (c) and (d). One of these mirrors is machined in a stepped geometry (see Fig. 11e). The second window is a conventional size of 1 in diameter  $\times$  2 mm thick. These windows could be

Figure 11. Schematic diagram of proposed fluidic test cell. Such a system consists of 4 parts, which create two half-cells. Parts (a) and (b) join together to hold a stepped window or mirror in place. This is half-cell a-b. Retaining screws (dark grey) or a screw fitting (similar to common Harrick cells) provide the retaining force to clamp the window. Parts (c) and (d) retain a simple flat window in a similar fashion. The two half-cells are then joined with a-b sliding into c-d. Piezo or stepper motor adjuster (shown in red) provide accurate control of O-rings provide seals on the mirror separation. backside of the windows as well as between the two half-cells. A qualitative detail of the stepped window in shown in (e). Such a cell could be 3D printed and a link to preliminary design files is provided in the references. (f) shows the 3D printed components, each labeled in red and (g) shows the fully assembled configuration.

used uncoated and serve as transparent boundaries to an infrared transmission measurement or coated with a layered mirror structure to yield a FP cavity. Either mirror, stepped or flat, could be placed in either housing (a-b or c-d) except when electrical contact is desired. The current design utilizes retaining screws to hold (a) and (b) together, thus holding the window in place. Another option would be to compress (a) into (b) with a large threaded cover (similar to the conventional Harrick cell design). After installing the windows, the two halves of the system (a-b and c-d) are assembled with a-b sliding into c-d and retaining the two halves to one another with springs (e.g., 6 springs of type 1942N4 from McMaster Carr). This brings the windows into proximity of one another. Precise window separation is controlled by piezoelectric actuators (e.g., Newport model 8322NF linear actuator) mounted into part (b) and shown as red in Fig. 11. Fluidic sealing is maintained by o-rings (shown in black). A single o-ring is placed on the rear of each windows and two are used to seal the interface between the two half-cells. Fluidic channels allows solution to be flowed into or out of the call (indicated by black arrows). The design shown in Fig. **11** is really quite similar to what can be assembled with conventional piezo, stepper, or other precision adjustable optics components, however, there are two important contributions. First is placement of orings in relevant locations making the system compatible with liquid environments. Second is the incorporation of a stepped window, which allows for robust retaining of each window while still allowing micron-scale window separations.

The system described in **Fig. 11** was 3D printed, assembled, and a brief qualification of its function carried out (**Fig. 12**). First, rough alignment of the parallelism of the two half cells is carried out by manually adjusting the piezo screw drives (red in **Fig. 11**) to achieve autocollimation of laser reflections from the two windows. After this coarse alignment, the piezo drives were actuated via computer control and the cavity spacing extracted from infrared transmission fringe analysis. The repeatability of the cavity spacing upon cycling of the piezo drives is shown in **Fig. 12a-c** for progressively smaller piezo cycling distances. There is some drift representing the limits of cavity length repeatability. These behaviors are quantified in terms of the average displacement and standard deviation of this displacement as a function of number of piezo drive cycles (a single "cycle" is the smallest displacement each drive can accomplish). Several points can be made. First, the displacement (**Fig. 12d**) scales linear with number of cycles for the sparse data set here. Second, the slope, which represents the distance moved per cycle, is slightly smaller (~10 %) for contraction of the cavity than for extension. This may be due to insufficient force produced by the retaining springs used to hold the two half cells together. Third, the standard deviation of the

displacement realized per cycle (**Fig. 12e**) decreases with increased number of cycles, presumably due to averaging out the slippage events that occasionally occur. Lastly, a dispersion contour is presented in **Fig. 12f** generated by tuning the cavity length from 10-30 µm while recording infrared transmission spectra.

A second, improved in some respects, design is illustrated in Fig. 13. This system is similar in spirit to the model shown in Fig. 11, however, there are several differences. First, restoring force exerted against the piezo-stepper motors is accomplished by compressed springs (McMaster-Carr part#6547K272; 0.5" long, OD 0.198") held by retaining bolts (McMaster-Carr part#10F200KCSFT/X, 10-32, 2" long hex head screw), which are far easier to implement. Secondly, one mirror is mounted by gluing it in place rather than having both mirrors retained through compression. slightly different sealing This necessitates a mechanism which can be seen as components (a), (b), and (c) are bolted together with two square-profile orings between them. The fluidic connections are designed to be compatible with ¼-28 standard flat bottom HPLC fitting. Lastly, the general tolerances have been refined so the two halves fit much more

Figure 12. Preliminary qualification data for the function of cell design. The reproducibility of positioning, as one actuates the tuning positioners back and forth, is shown in panels (a), (b), and (c) for movements of ~8, 2, and 0.5  $\mu$ m, respectively (i.e., 400, 100, and 20 cycles of the piezo adjusters). These responses are used to generate the average displacement and standard deviations of the displacement plotted in (d) and (e) as a function of number of cycles applied. In (f), an example dispersion plot is shown for an air-filled cavity tuned from 10-30  $\mu$ m mirror separation.





#### Primary components for version 2 of microadjustable cell

(f) Photo of assembled cell



Figure 13. Second version of piezo-tunable cell. Schematic at top shows parts (a), (b), and (c), which are fastened together by three bolts (McMaster-Carr part#91251A113, 4-40 thread, 3/4" long hex head screw). O-rings fit between each of these to provide liquid seal. Mirror can be glued in place. This component slides into (d). Restoring screws (grey, McMaster-Carr part#10F200KCSFT/X, 10-32, 2" long hex head screw) pass through (a), (b), and (c) and screw into (d) and have a spring (McMaster-Carr part#6547K272; 0.5" long, OD 0.198") located between the screw head and part (a) to provide restoring force to oppose piezo-stepper (red) motion. Second mirror is fastened between (d) and (e) (McMaster-Carr part#91251A106, 4-40, 1/4" long hex head screw). Image in (f) shows digital rendering of full assembled system.

snugly together. The STL files for these components are also found in the supporting information of the arXiv version of this manuscript.<sup>51</sup>

Gold is a convenient choice of mirror coating for a mid-IR cavity given its simple fabrication and high reflectivity. However, the broadband reflectivity of gold and other metals supports many optical modes which can inadvertently couple to molecular vibrations outside the region of interest, making it difficult to infer a straightforward mechanism responsible for modified chemistry.<sup>7</sup> As mentioned in Section 4.2, the negligible cavity transmission over regions between resonant fringes makes conventional infrared absorption measurements impossible, and while the previous section describes a reliable strategy for side stepping this issue for measurements of chemical kinetics, this is far from ideal and a great deal of valuable spectral information remains inaccessible. This high reflectivity also extends to shorter wavelengths causing etaloning and reduced transmission in the visible and UV regimes where it may be desirable to optically interrogate a cavitycoupled system.<sup>12,27,28,29</sup> The resulting spectral artifacts can obfuscate any interesting VSC induced effects and must be carefully corrected for in order to make a confident determination.<sup>12,30,41</sup> Furthermore, the proximity of molecular absorbers to metallic interfaces can induce catalytic<sup>52</sup> or surface enhancement<sup>53,54</sup> effects. A passivating polymer or oxide layer deposited on the gold to safeguard against these effects, though this complicates sample fabrication and, under some circumstances, could

induce confusing optical effects. A better alternative to metallic mirrors for studying VSC might be distributed Bragg reflectors (DBRs) which consist of alternating layers of dielectric materials with different refractive indices. DBRs can have higher Q-factors than metallic mirrors due to their low loss and high reflectivity making them appealing for VSC applications. However, the effective coupling strength one can achieve with DBRs is limited by a reduction in the number of molecules within a given mode volume due to penetration of the EM field into the dielectric layers.<sup>55</sup> The optical properties of a DBR stack can be tailored by selecting different materials and varying the thickness of each layer. Analytical tools exist which allow for the optimization of these multilayer structures to produce the desired properties.<sup>56,57</sup> For example, DBRs can be designed to have a narrow reflective bands at arbitrary frequencies to enable VSC with a specific molecular vibration while simultaneously providing high, unstructured transmittance in other spectral regions. This enables optical pumping,<sup>58</sup> straightforward monitoring of reaction progress in the mid-IR or visible, and prevents unintended coupling between other cavity modes and material excitations.

### 5 Conclusion

This chapter is concluded. In it, guidance has been given regarding analytical modeling of simple etalon-type cavities, which allows researchers the ability to design and explore experimental regimes quickly on a laptop. Experimental non-idealities that scientists should be aware of, and are often neglected, were described along with estimates of their impact on experiment. Lastly, a preliminary design for a cavity apparatus was presented which gives greater reliability, experimental repeatability, and convenience of use. We wish for this design to stimulate ongoing experimental apparatus development.

The authors hope this information assists in the validation and understanding of cavity-modified materials behavior by providing tools to ease entry into this field of study. Not only will this lead to repeated and reliable demonstrations, but it will help participants from a wide variety of scientific disciplines make immediate contributions. Contributions from high-resolution spectroscopists, experts in reaction kinetics, physical chemists, and physicists will help establishing rigor, trust, and eventual technological impact to this field.

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