The Role of IR Inactive Mode in $W(CO)_6$ Polariton Relaxation Process

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ABSTRACT: Vibrational polaritons have shown potential in influencing chemical reactions, but the exact mechanism by which they impact vibrational energy redistribution, crucial for rational polariton chemistry design, remains unclear. In this work, we shed light on this aspect by revealing the role of solvent phonon modes in facilitating the energy relaxation process from the polaritons formed of a T_{1u} mode of $W(CO)_6$ to an IR inactive E_g mode. Ultrafast dynamic measurements indicate that along with the direct relaxation to the dark T_{1u} modes, lower polaritons also transition to an intermediate state, which then subsequently relaxes to the T_{1u} mode. We reason that the intermediate state could correspond to the near-in-energy Raman active E_g mode, which is populated through a phonon scattering process. This proposed mechanism finds support in the observed dependence of the IR-inactive state's population on the factors influencing phonon density of states, e.g., solvents. The significance of the Raman mode's involvement emphasizes the importance of non-IR active modes in modifying chemical reactions and ultrafast molecular dynamics.

Keywords: polariton; ultrafast dynamics; phonon assisted; vibrational strong coupling

1 Introduction

Molecular vibrational polaritons (MVPs) represent a fascinating class of hybrid photon-matter states arising from the rapid energy exchange between molecular vibrations and optical cavity modes surpassing their individual dephasing lifetimes.[1]–[3] In the energy domain, this manifests when the coupling strength between the cavity and vibrational modes becomes greater than their individual linewidths, the so-called vibrational strong coupling (VSC) regime, resulting in the formation of two distinct bright eigenstates: the lower polariton (LP) and upper polariton (UP), separated in energy by Rabi splitting (Ω). Additionally, there also exists an ensemble of eigenstates of weakly coupled vibrational modes known as dark modes.[2], [3] Notably, vibrational polaritons exhibit a unique energy signature and encompass both photonic and molecular-like properties. In contrast, dark modes are solely of molecular nature and become the dominating states when a significant number of molecules ($\sim 10^6$-10^{10}) are required to generate enough Rabi splitting to form polaritons in VSC inside of the Fabry-Perot (FP) cavities.[4]

Polariton chemistry has witnessed a notable yet debated discovery concerning the modification of chemical reactions through VSC.[2], [5], [6] However, a comprehensive understanding of how polaritons impact chemistry is still lacking, necessitating a clear mechanistic insight to inform rational design strategies.[4], [7] Using ultrafast spectroscopy, researchers have employed pump-probe and two-dimensional infrared (2D IR) spectroscopy[8]–[10] to investigate the energy redistribution of polaritons into dark modes, a crucial dynamic process with potential implications for chemical reactions. These works have demonstrated that polaritons can facilitate inter- and intra-molecular vibrational energy transfer[11], and even impede isomerization events[12]. While these findings qualitatively align with the theoretical expectations, achieving quantitative agreements remains a challenge to address.

In our pursuit of advancing the understanding of polariton energy relaxation dynamics, we conducted a detailed investigation into the ultrafast dynamics of MVP formed by the asymmetric T_{1u} mode of $W(CO)_6$ (triply degenerate C-O stretching mode, at 1980 cm^{-1}) and an FP cavity. In previous studies[13], we established that LP underwent a transfer to the second excited state of dark modes (D_2), before eventually relaxing to the first excited dark modes (D_1), exhibiting an initial rise followed by decay. This LP-to-D_2 channel was favored due to LP-LP scattering, where the double of LP resonance frequency ($2\omega_{LP}$) closely matched the 0->2 transition of dark modes (ω_{02}), a mechanism supported by theoretical studies[14].

In this work, we expanded our analysis by incorporating higher excited state transitions into the transfer matrix model (TMM) and employed a kinetic model to fit the dynamics. Our finding revealed that while D_2 was indeed populated, an additional phonon-assisted scattering process occurred, involving the transfer of LP to an IR inactive mode. We proposed that the scatter process from the T_{1u} mode to the E_g Raman mode, observed in uncoupled $W(CO)_6$ system,[15]–[17] was enhanced. Notably, this LP-to-Raman mode scattering process was a third order process, facilitated by solvent phonons. This mechanism is then supported by its dependence on solvents with various carbon chain lengths, which influences the solvent phonon density of states (DOS_{ph}). This exciting discovery highlights the involvement of IR-inactive modes in polariton dynamics and shed light to the potential intermediates of the polariton enabled intermolecular vibrational energy transfer[11] and changes of pseudo-rotation dynamics[12].

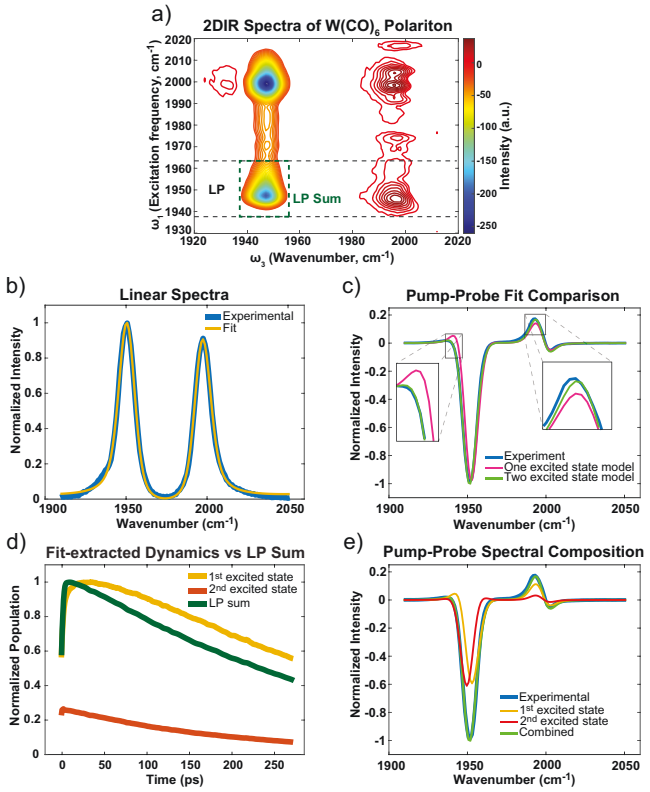

Figure 1. *a)* Representative broadband pumped 2DIR spectra of $W(CO)_6$ polariton system in DCM solvent with Rabi splitting of 55 cm^{-1} at 20ps time delay. The region demarcated by two dashed black horizontal lines represents the frequency range used for narrowband excitation of LP in the subsequent pump probe experiments. *b)* Linear spectra fitted with TMM model (see SI, Spectral Fitting). *c)* The narrowband LP pumped pump-probe spectra are fitted with one (ω_{12}) or two excited state transitions (ω_{12} and ω_{23}) for pump-on component, while other fitting parameters are fixed at the values obtained from the linear spectra fitting in (b). Including the 2nd excited state, D_2 improves the fitting fidelity. The example result is shown here for 15ps time delay. *d)* The relative population dynamics traces of the T_{1u} excited states compared to LP sum (dashed area in 1a) dynamics trace. LP sum may not faithfully represent the dynamics of D_1. This result emphasizes the need for multi-state TMM model. *e)* The corresponding compositions of the pump-probe fit in (c), with ω_{12} and ω_{23} kept the same as the uncoupled case while fitting the raw transient spectra. They appeared to be close to each other because of their convoluted response when coupled with the cavity.

2 Results

We conducted a study on the relaxation dynamics of polaritons composed of $W(CO)_6$ in dichloromethane (DCM) using 2D IR and tailored pump-probe spectroscopy.[18], [19] The 2D IR spectra revealed four distinct peaks attributed to Rabi splitting contraction and excited state absorption of dark modes (Fig. 1a)[8], [20]–[23]. Our focus was to understand the dynamics of how LP states relaxed to D_1. To achieve this, we selectively pumped the LP states (indicated by the two dashed lines in Fig. 1a) and probed them broadly. The significant absorption peak near ω_3 = 1950 cm^{-1} indicated the population of D_1. By tracking this peak at [$\omega_1 = \omega_{LP}$, ω_3 = 1950 cm^{-1}], we could observe the population transfer dynamics from LP to D_1. To extract this dynamic, we employed a semiclassical transfer matrix model (TMM) [8], [20], [24] to fit the linear and pump-probe spectra (Figure 1b and c). The TMM fitting incorporated higher-level transitions of dark modes (such as ω_{23}) in addition to ω_{01} and ω_{12} transitions, different from our previous work.[20] This improved model enabled a better agreement between the fitted and experimental dynamics (Fig. 1c and inset, S2). By fitting the pump-probe spectra for each time delay, the D_1 and D_2 population dynamics were extracted (Fig. 1d).

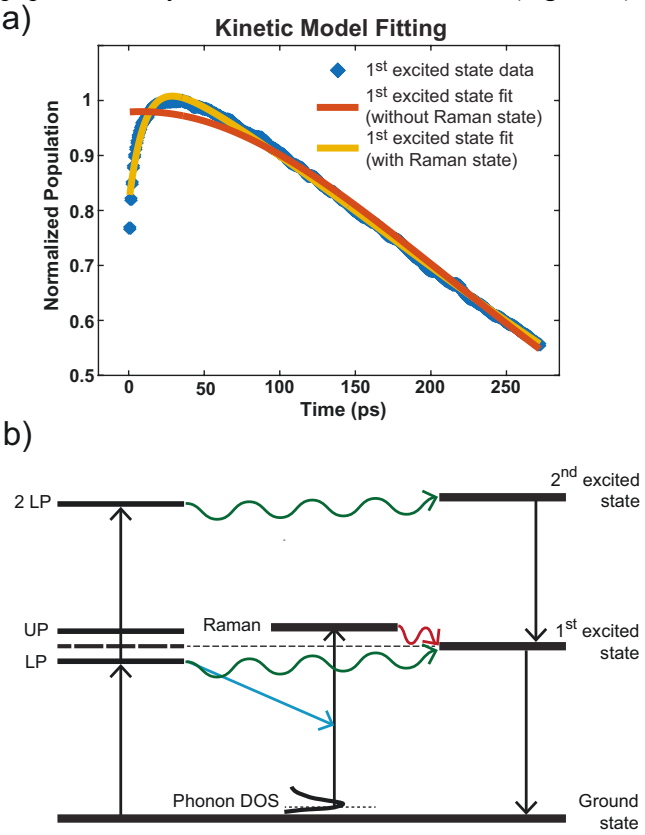

Figure 2. *a)* The dynamics fitting with and without the Raman pathway. *b)* The proposed energy relaxation pathway for the $W(CO)_6$ polariton system. The pump excites the LP state which relaxes into the 1st and 2nd excited state directly (green arrows), or scatters with the solvent phonons to excite the Raman mode (E_g) (blue arrow). The E_g mode then relaxes/equilibrates with D_1 (red arrow), following decaying to ground states.

Similar to our previous observations,[13] the rise in dynamics was observed primarily in the D_1 dynamics for narrowband LP excitation but not so for UP (Fig S4, 1d). While the previous study attributed the early rise to D_2 decaying into D_1, we found that the D_2 dynamics decay much slower than the rise of D_1 (Fig 1d), indicating the involvement of another state in the polariton relaxation process. This observation was further supported by the

inability to fit the LP- D_1 dynamics with a kinetic model. Treating the relaxation from the coherent polariton state to the dark state as a fast process, the kinetic model was simplified to only have the ground (D_0), and first (D_1) and second (D_2) excited states (eq. 1).

$$\frac{dD_2}{dt} = -k_{21}D_2; \frac{dD_1}{dt} = k_{21}D_2 - k_{10}D_1; \frac{dD_0}{dt} = k_{10}D_1 \ldots 1$$

However this model reached a poor agreement with the LP-D_1 dynamics (orange trace in Figure 2a, Table S2). This is in sharp contrast with the fact that the model fits UP- D_1 and D_2 dynamics well (Fig S4, Table S1). Considering this, the following discussions will primarily focus on the LP-excited D_1 dynamics to understand the reason of this unexpected dynamics.

When we introduced an additional state (P_{int}), feeding into D_1, into the kinetic model (eq. 2), the dynamics could be adequately described (yellow, Fig. 2a).

$$\frac{dD_1}{dt} = k_{21}D_2 - k_{10}D_1 + k_{\mathrm{int}}P_{\mathrm{int}}; \frac{dP_{int}}{dt} = -k_{\mathrm{int}}P_{\mathrm{int}} \ldots 2$$

Notably, the lifetime of this additional state (k_{int}) is ~11 ps, longer than that of the polaritons (< 5 ps)[8], indicating that the new state cannot be a coherent polariton state.

Based on the literature, we hypothesized this new intermediate state as the IR-inactive Raman E_g mode at 1999 cm^{-1} (Fig. S6). Previous experimental results from uncoupled $W(CO)_6$ systems have shown that transfer to E_g represents the fastest relaxation pathway for the T_{1u} vibrational mode, which forms the polaritons here. [15], [16] This process is a third order scattering mechanism that includes solvent phonon modes and occurs within a few ps.[16], [17] Since decaying into the ground state is a slow, multi-order process, the population in the T_{1u} and E_g modes were observed to equilibrate quickly with each other [16], [17] and thereby exciting either of them should lead to the transfer into the other mode. Extending this argument, we conjecture that due to the initial large E_g population and imbalance between the E_g and T_{1u} modes following LP relaxation, the E_g Raman mode could transfer population into the T_{1u} mode at the fast time scale and thereby serve as a relaxation channel for LP, involving an LP-phonon scattering process (Fig. 2b).

To directly examine this hypothesis, a time-resolved IR pump Raman probe experiment would be ideal. However, achieving such an experiment is challenging due to the difficulty in designing proper cavity optics that are reflective to IR to form cavities and transmissive to visible for the Raman measurements. Instead, we focused on examining the relation between the initial population of E_g ($P_{int}(0)$) state, obtained from the combined TMM and kinetic model fitting (see SI, example of fitting results see Fig 3a), and the solvent phonon modes involved in the proposed phonon-assisted LP-to-E_g scattering process. This dynamic is a third order process, where LP scatters with one quantum of phonon modes, transferring its energy to the E_g mode. Consequently, the outcome of the scattering, i.e., E_g population, should be linearly proportional to the product of phonon density of states (DOS_{ph}) and occupation number (n)[25].

To validate this mechanism, we compared the initial population of intermediate states across three alkane solvents, i.e., pentane, hexane, and heptane for the same Rabi splitting (thereby same $\omega_{Phonon}=\omega_{Eg}-\omega_{LP}$). These solvents share comparable chemical properties but increasing DOS_{ph} with longer carbon chain (Fig 3b), indicated by the experimental inelastic neutron scattering (INS) spectra. We note that excessively long alkane chains decrease the solubility of $W(CO)_6$ and lead to weak coupling regime. Consequently, the options for solvents become constrained under these conditions.

The DOS_{ph} spectra were directly measured from INS measurement at room temperature, with the DOS_{ph} increasing as a function of the number of carbon atoms in the alkane chains. The intermediate state (E_g) population of alkanes follows the increase in DOS_{ph}, i.e., it elevates as carbon chain length increases (Fig 3b). These experimental findings thus support the claim that the energy transfer from LP to E_g depends on phonon DOS, and thereby is a third order process. This also explains why there is no significant energy transfer from UP to D_1 (Fig S4): because the energy of E_g and UP modes are near each other, the phonon DOS_{ph} approaches zero for $\omega_{ph}=\omega_{Eg}-\omega_{UP}$, inhibiting the energy transfer of UP to E_g, an inherent dipole-polarizability interaction with the aid of phonon modes.

In principle, the Raman modes should, theoretically, be affected by other factors including the phonon/LP frequency and temperatures, which can either influence the $DOS_{ph}(\omega_{ph},T)$ or $n(\omega_{ph},T)$. Our preliminary experimental observations suggest that these anticipated dependencies, primarily of phonon frequency, measured through changes in Rabi splitting, differ from this intuitive expected pattern, with initial Raman population deviating from the DOS_{ph} * n spectra (Fig S8, see SI). This deviation implies that certain low frequency modes, contributing to a distinct subpopulation of overall DOS_{ph}, play a pivotal role in the phonon-scattering process, as opposed to the inclusive involvement of all phonon modes. Further investigation is warranted to comprehend this aspect.

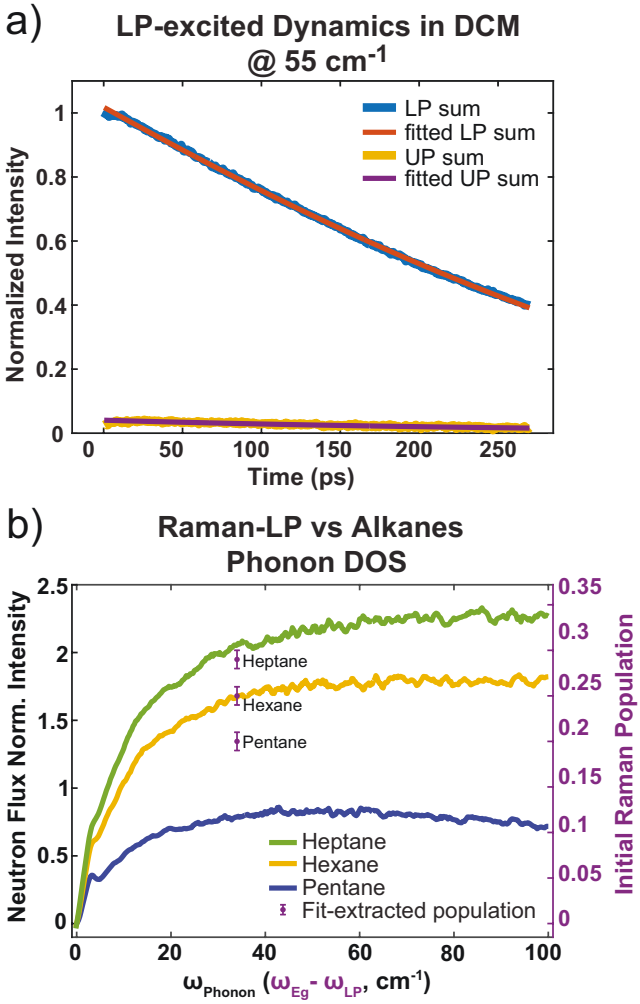

Figure 3. a) Representative fitting results of the combined TMM and kinetic model, where the amplitude of each vibrational states (D0, D1, D2 and Eg) are directly determined by the kinetic models (see SI, Combined Spectral and Kinetic Fitting). The fitted and experimental results are compared by integrating the LP-excited pump probe spectra over the LP and UP peak region along w3. Initial intermediate (Raman state) population was extracted through this fitting method. b) The Raman state population at the same Rabi splitting of 34 cm-1 increases between polariton systems formed in pentane, hexanes, and heptane solvents, respectively, following their phonon DOS spectra at room temperature.

3 Conclusion

This study has opened a promising avenue in vibrational polariton dynamics. While the explicit spectral signature of the E_g modes awaits validation through an IR pump and Raman probe experiment, significant insights have already emerged. Notably, Raman modes have not been considered in polariton dynamics. However, this unexplored Raman pathway illustrates how polaritons could influence chemistry: exciting polaritons can enhance the excited state population of IR-inactive vibrational modes relative to the coupled IR-active mode and thereby promoting the LP-to-Raman energy transfer pathway that is otherwise unfavorable in pure molecular systems. In a case where the reverse energy transfer from Raman mode to IR mode is constrained, the polariton-populated Raman mode could shift chemical dynamics on longer time scales. The involvement of Raman modes holds promise across a broad spectrum, particularly for molecules that have low frequency modes. Whereby, an intramolecular scattering between polariton and the low frequency vibrational modes could occur, thereby impacting the associated molecular dynamics. This mechanism thus could lead to the polariton-enabled energy transfer[11],and pseudo-rotation[12] which remain to be further delved into.

ASSOCIATED CONTENT

Supporting Information.
Experimental, theoretical, and analytical procedures, additional and detailed results, and discussion of the DOS model (PDF)

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Author Contributions

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Research Informed Consent Statement

All authors have accepted responsibility for the entire content of this manuscript and approved its submission.

Research Funding

O.H. was supported by NSF (CHE-2101988) and H.H.B. was supported by ASOFR (FA9550-22-1-0317). W. X. thanks the Alfred P. Sloan Foundation Research Fellowship (FG-2020-12845).

Conflict of interest

The authors state no conflict of interest.

Acknowledgement

We acknowledge Luke Daemen for collecting the INS spectra at Oak Ridge National Laboratory for us. Furthermore, we thank Dr. Judy Kim for allowing us to use her Raman setup to collect our Raman spectra. We acknowledge Garret Wiesehan for fruitful discussion and Zimo Yang for technical support on the laser table.

Data availability

Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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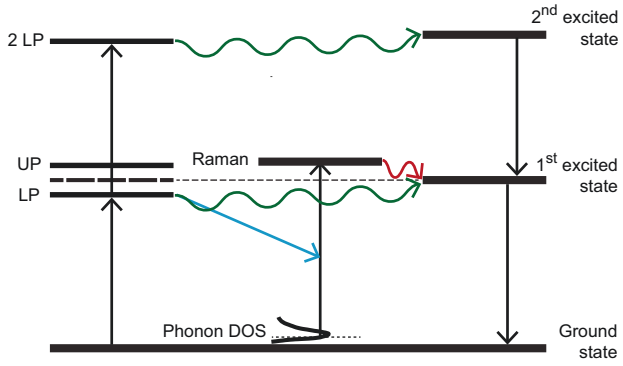
2 LP
2nd excited state
UP
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