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Vibronic Engineering for Quantum Functional Groups

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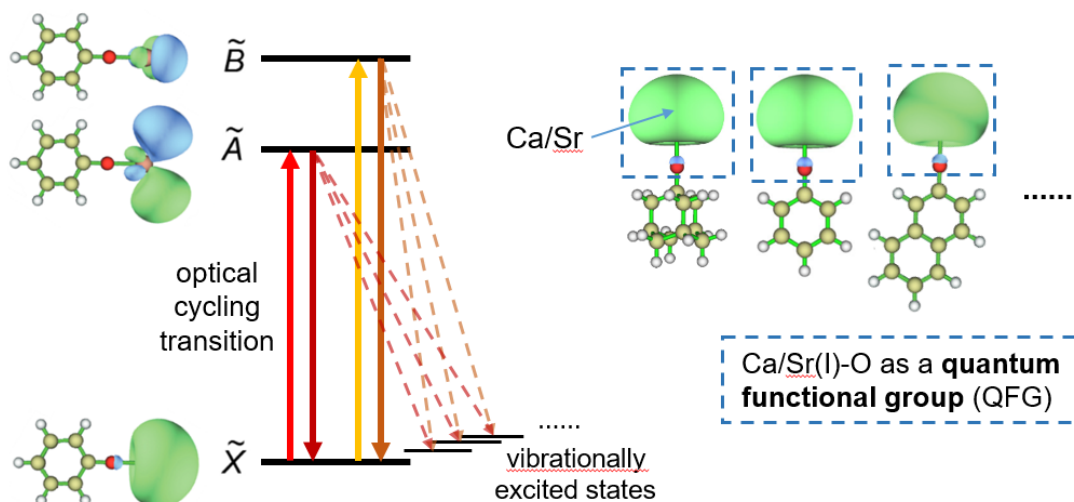
Chemists have a firm understanding of the concept of a functional group, a small molecular moiety that confers properties (reactivity, solubility, chemical recognition) onto a larger scaffold. Analogously, a quantum functional group (QFG) would act as an isolated ‘quantum handle’ that could attach onto an extended molecule and enable quantum state preparation and measurement (SPAM). However, the complexity associated with molecular chemistry is often at odds with the requirements of non-thermal state preparation. The rest of the molecule acts as a local bath that leads to dephasing and loss of quantum information upon excitation and relaxation. Yet, there exists an enormous chemical space of potential chemical bonding motifs to design isolated QFGs. The goal of this account is to explore the underlying chemical design principles for optimization of QFG performance.

For typical state preparation an applied field is used to put the qubit into a specific known state (via optical cycling and laser cooling), where it can be manipulated or entangled with other species. That same field (or another) can be used to read out or report on the qubit state at the end of operation. For example, in trapped ions/neutral atoms, state preparation is accomplished by pumping a specific transition using a narrowband laser. From there, further operations can be performed on the qubit via selective RF or laser excitation, and the state can be read out via fluorescence. However, extending this paradigm to molecular systems is highly challenging -- molecules have many more degrees of freedom which can couple to the absorbed or emitted field. Overcoming this requires greatly limiting the

number of these “off-diagonal” decay pathways through judicious selection of the QFG and vibronic engineering of the molecular substrate.

Our work has demonstrated that alkaline earth (I) alkoxides (MOR) may meet the necessary requirements for efficient SPAM. In particular, we capitalize on the -OM (M=Ca, Sr) motif, which acts as the quantum handle that has been attached to a variety of aliphatic and aromatic hydrocarbons. The precise breakdown of the optical cycling property depends on familiar chemical concepts, including conjugation, conformer formation, electron-withdrawing abilities, and symmetry. In this Account, we review the recent efforts in the field to construct QFGs and co-design molecular scaffolds that can host them without destruction of their desired quantum properties. QFGs are explored as attachments to photoswitching scaffolds, and mounted in pairs to larger hosts. A variety of physical phenomena relevant to the ability of these QFGs to function as qubits, from Fermi resonances to superradiance, have been explored. We thus began deriving the first set of rules for vibronic engineering toward QFG functionality. Prospects toward increasing number densities of these QFGs through molecular and material design are also presented.

TOC Figure



Key References

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- Zhu, G.-Z.; Mitra, D.; Augenbraun, B. L.; Dickerson, C. E.; Frim, M. J.; Lao, G.; Lasner, Z. D.; Alexandrova, A. N.; Campbell, W. C.; Caram, J. R.; Doyle, J. M.; Hudson, E. R. Functionalizing Aromatic Compounds with Optical Cycling Centers. *Nat. Chem.* **2022**, *14*, 995–999. (2) *This experimental work demonstrates the successful OCC functionalization on phenol and phenol derivatives. Favorable optical cycling properties are measured for Ca/SrOPh-X, validating the usage of OCC as a quantum functional group.*
- Zhu, G.-Z.; Lao, G.; Dickerson, C. E.; Caram, J. R.; Campbell, W. C.; Alexandrova, A. N.; Hudson, E. R. Extending the Large Molecule Limit: The Role of Fermi Resonance in Developing a Quantum Functional Group. *J. Phys. Chem. Lett.* **2024**, *15*, 590–597. (3) *This experimental work measures the presence of Fermi-resonance in the OCC functionalized molecules. These effects arise from various couplings within complex molecules and must be mitigated.*
- Lao, G.; Khvorost, T.; Jr, A. M.; Morgan, H. W. T.; Lavroff, R. H.; Choi, R.; Zhou, H.; Usvyat, D.; Zhu, G.-Z.; García-Garibay, M. A.; Alexandrova, A. N.; Hudson, E. R.; Campbell, W. C. Bottom-up Approach to Scalable Growth of Molecules Capable of Optical Cycling. *arXiv*, **2024**. <http://arxiv.org/abs/2411.03199>. (4) *This work demonstrates that the quantum functional group can be attached to molecules as large as diadamantane ($-C_{14}H_{19}$) without reducing its performance, paving the road of extending into larger diamondoids and bulk diamond surface.*

1. Introduction

Molecules, given their many internal electronic, vibrational, and rotational degrees of freedom, are a rich and tunable platform for quantum information science (QIS), from computing to sensing.^{5–9} This same dense manifold of states accessible at a wide range of frequencies from THz to UV-Vis, present a fundamental problem for targeted state preparation and long coherence times. It has been a long-term goal for physicists and chemists to manipulate the dense and complex state manifold in molecules with quantum state precision. Ultimately, as molecules get larger, their internal energy distribution tends toward thermal equilibrium – a tyranny to overcome via combination of molecular and excitation design. We hypothesize a possibility of orthogonal¹ “quantum functional groups” that permits optical state control without perturbation of the rest of the molecule.

An ideal optical transition for quantum state preparation would permit reliable and repeated photon scattering without loss to other degrees of freedom (*optical-cycling*), which enables preparation of specific, known, electronic, vibrational, rotational and translational quantum states in an ensemble of molecules. Optical cycling is the essence of *laser cooling*¹⁰ and *magnetic-optical trapping*¹¹ – prerequisites for quantum computing with neutral molecules. Most electronic transitions in polyatomic molecules are not suitable for optical cycling as they are irretrievably coupled to vibrational and rotational loss channels. Transitions that are suitable are considered “*closed*” – repeated excitations cycle back to the original quantum state and lack coupling to other vibrational states, feature diagonal Franck Condon Factors (FCFs).¹² Note even a tiny nondiagonal decay can be detrimental to optical cycling. For example, for a decay channel of 1%, only ~37% of the molecules remains in the original transition after 100 cycles. In general, knowledge (or elimination) of any decays with $>10^{-3}$ probabilities are necessary for state preparation and readout. For laser cooling where thousands of optical cycles are required, even finer accuracy of 10^{-4} should be reached.¹³

Researchers have been searching for suitable molecules with closed optical cycling over decades.^{14,15} In 2004, Di Rosa¹⁶ showed that for molecules having similar ground and excited state geometries, its vibrational state is not likely to change when spontaneously

¹ This use of orthogonal here refers to independent and non-interacting functionalization, e.g. bio-orthogonal chemistry, awarded the nobel prize in 2022.

emitting a photon. The optical cycling transition can thus be closed with a few extra lasers - used to repump the population back into the desired excited state from a loss channel. Following this scheme, direct laser cooling have been demonstrated for diatomic molecules such as $\text{CaF}^{17,18}$, SrF^{19} , BaF^{20} , YO^{21} , and triatomic molecules such as $\text{CaOH}^{22,23}$, SrOH^{24} , YbOH^{25} . Notably, in these molecules, the metal center is bonded ionically with an electronegative element such as halogen or oxygen. The remaining valence electron is strongly localized on the metal, due to repulsion by the electron pair on the electronegative atom. The minimization of the repulsion between the radical and the electron pair results in nearly linear MOR motifs.² The frontier orbitals of these molecules resemble laser-coolable Ca^+/Sr^+ atomic cations: electronic excitation promotes an electron from the *s*-like HOMO to the *pd*-hybrid LUMO. This excitation involves (mostly) non-bonding orbitals resulting in limited change in geometry.

Since the optical cycling property is a result of the strong ionic character of the $\text{M(I)}\text{-O}$ bond, opportunity arises to attach a more complex -R in place of -H , extending the laser cooling scheme to larger molecules.²⁸ In 2020, Mitra et al. reported laser cooling of the first nonlinear molecule, CaOCH_3 .¹⁵ This generalization is non-trivial since the reduced symmetry of symmetric top CaOCH_3 greatly increases the number of possible coupled states. Nonetheless, the addition of -CH_3 fragment did not significantly deteriorate the “diagonal” nature of the radical-centered transitions. Recent spectroscopies have demonstrated that even larger molecules such as $\text{Ca/SrOC}_6\text{H}_5$ ² and $\text{Ca/SrO-adamantanes}^4$ can retain their diagonality. Therefore, the Ca/SrO group is analogized as a quantum functional group (QFG) -- a group of atoms containing an optical cycling center (OCC) Ca/Sr(I) . This analogy suggests how chemistry can add hitherto unrealized logic to QIS and we are certain that chemists can bring so much more!

Prior to optical cycling and cooling schemes, alkaline earth(I) compounds were explored as atom-like molecules in 1980s.²⁹ These compounds are readily produced by reacting alkaline earth metal with organic precursors in a hot oven or supersonic beam, enabling extensive gas-phase spectroscopic studies for Ca/Sr(I) species including halides,

² The CaOR bond is linear rather than tetrahedral as in H_2O . However, we should note that the linear configuration is not a strict prerequisite for laser cooling. For example, CaSH has a 90° bond angle and is proposed to be a possible candidate with reasonably good FCFs^{26,27}.

hydroxides, amides, thiolates, alkoxides, and so on. With improved light sources^{32–34}, cryogenic techniques^{35,36}, electronics, and advanced theory^{37,38}, current studies continues to reach higher precisions, with the focus on optical cycling applications by quantifying the decay pathways. Various unique systems, including chiral species, zwitterions, photo-switching species, have also been proposed with OCC functionalization for immense potentials.^{39–41}

Can QFGs retain OCC characteristics on any host? Is there a limit on the size of the hosts amenable to cooling? Are there design principles for the host that enhance or diminish its optical cycling properties? We present our recent progress on QFGs and explore the molecules to which QFGs can be attached, demonstrating the possibilities and sketching the limits of laser cooling and quantum state preparation. We find that added chemical complexities is not strictly detrimental, but could provide design handles for next generation qubits^{42,43}, and additive functionality for ultracold chemistry, chemical sensing.^{44,45}

2. Electronic structure of quantum functional groups

All current examples of neutral laser-coolable molecules rely on closed transitions of the highly localized radical electron in pseudo-atomic orbitals of OCCs. This electron does not participate in chemical bonding, and optical excitation and decay occur to and from overlapping vibrational wavefunctions. We illustrate this via the computed potential energy surfaces (PESs) for the lowest two electronic states of isoelectronic CaF and CaO⁺ (Figure 1). In Figure 1 on the right side, we also show the HOMO and LUMO for the two species. In CaF, the MOs are highly localized on Ca, whereas the CaO⁺ HOMO is a π -bonding MO and the LUMO is antibonding σ^* , consistent with a change in bond order upon excitation.

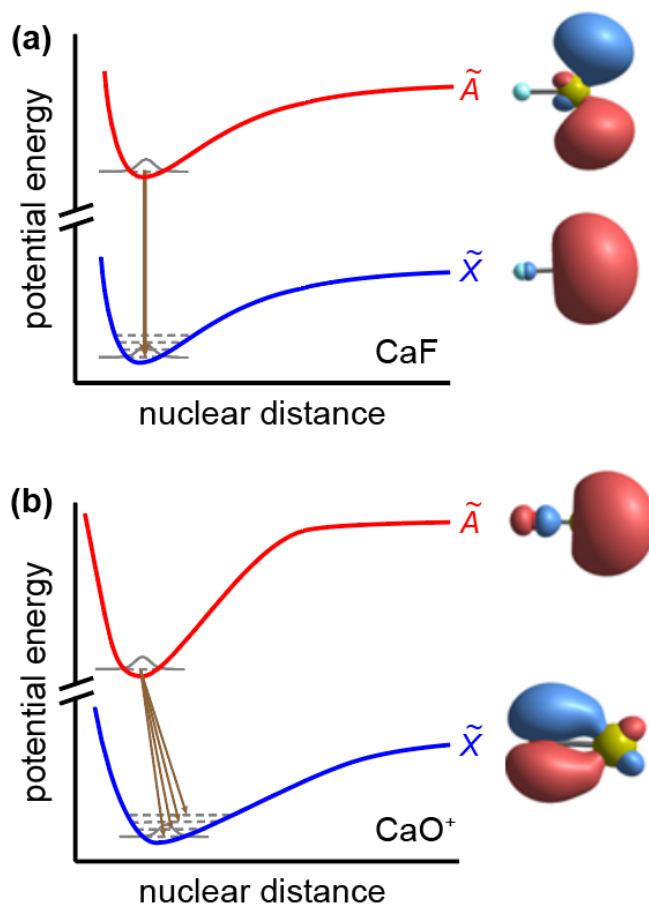


Figure 1. PESs and MOs of the first two electronic states $\tilde{X}$ and $\tilde{A}$ for CaF (a) and CaO^+ (b). The CaF MOs are both centered on Ca(I), and the PESs are largely parallel resulting in good overlap of vibrational wavefunctions. For CaO^+ , the HOMO and LUMO are centered on different atoms, leading to a change in equilibrium bond distance upon excitation, causing poor overlap of vibrational wavefunctions.

A minimal geometric shift between ground and excited states minima is rare in chemistry. Usually, lowest-energy excitations result in reduced bond order. A transition that is most likely to be as diagonal and laser-addressable is the one involving two *localized* non-bonding MOs (though rare exceptions to this statement exist⁴⁶). However, delocalized non-bonding orbitals will tend toward degeneracy, and are not suitable for optical cycling. For non-frontier transitions the optical cycling are disturbed by the electronic states between the cycling MOs.

The first assessment of the likelihood of a QFG to optically cycle can be done by pencil-and-paper reasoning through chemical bonding, and then by examining the

computed natural transition orbitals (NTOs). Figure 2 displays the NTOs of CaOPh. The molecule is built by attaching the QFG to a phenyl ring, and the QFG retains its optical cycling property because of the preserved Ca-O bond ionicity. Note that, although NTOs are Ca-centered, they differ from atomic orbitals in that they are not a result of the centrosymmetric potential of a single nucleus, and can contain admixtures of orbitals on O (and beyond) of the same symmetry. In Figure 2, we show the orbitals of isolated Ca^+ and PhO^- . In the CaOPh molecule, the forming MOs are largely unchanged from their isolated forms, centering on the PhO^- ligand or on Ca^+ . We note that the positions of Ca-centered orbitals also must lie in the HOMO-LUMO gap of PhO^- , otherwise the OCC excitation would oxidize or reduce the phenyl.

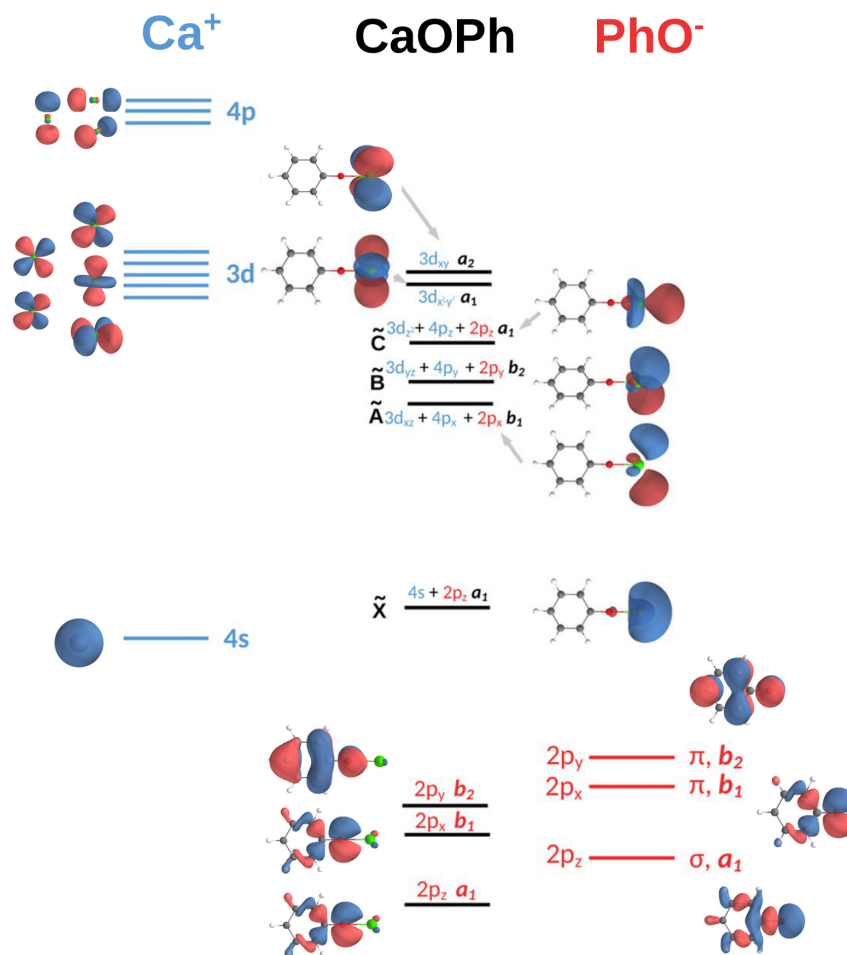


Figure 2 NTOs and correlation diagram of CaOPh. MO energies of Ca^+ and PhO^- are shown on the left and right side for comparison. Energies are not to scale. The NTOs of CaOPh can be viewed as orbitals of Ca^+ perturbed by the presence of the ligand field of

PhO⁻: they shift in energy, and slightly mix with the orbitals of the ligand. The optical cycling transitions are labeled $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$.

For QIS applications even tiny off-diagonal elements standardly neglected in chemistry may result in loss of quantum information upon repeated excitation. The precision of our calculations and measurements is therefore central to the success of the field. In addition to minimal displacement between ground and excited PESs, their curvatures have to agree to avoid off-diagonal decays. Furthermore, the OCC excited state has to be isolated from other excited states, in order to not mix via anharmonic effects, non-adiabatic, and spin-orbit coupling, all of which result in off-diagonal coupling. For experiments, greatly enhanced signal-to-noise, systematic chemical modification, and improved synthetic pathways are needed to probe each effect. For theory, a reliable harmonic calculation of the FCF, and then accounting for anharmonicity and all couplings are required. For great many molecules, the initial screening for possible OCC properties can be done with time-dependent density functional theory (TD-DFT), though overdelocalization error of DFT can sometimes prevent even a qualitative assessment. When higher precision is desired, and we can use equation-of-motion coupled-cluster (EOM-CC) methods such as EA-CCSD, DEA-EOM-CCSD,^{47,48} and/or multireference methods including CASPT2 (complete-active-space second-order perturbation theory), NEVPT2 (N-electron valence state second-order perturbation theory), and CASMRCI (complete-active-space multi-reference configuration interaction), though computing the ground and excited state vibrational frequencies can be prohibitively expensive. The harmonic Franck-Condon factors (FCF) $q_{v',v''}$ (1) provide good zeroth-level estimation for the vibrational branching ratios (2):

$$q_{v',v''} \equiv |\langle v' | v'' \rangle|^2 \quad (1)$$

$$|\langle e, v' | \mathbf{d} \cdot \mathbf{E} | g, v'' \rangle|^2 \approx q_{v',v''} |\langle e | \mathbf{d} \cdot \mathbf{E} | g \rangle|^2 \quad (2)$$

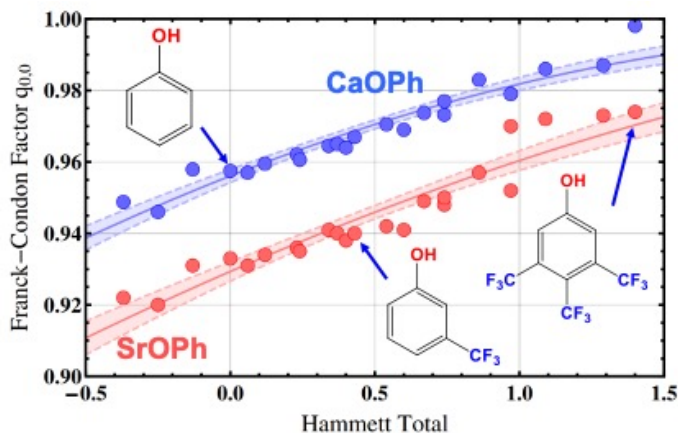
where g and e denote the ground and electronically excited states, and $\mathbf{d} \cdot \mathbf{E}$ is the dipole moment operator. However, harmonic calculations will miss the dependence of the electronic transition moment on the nuclear coordinates, vibrational mode coupling arising from anharmonicity, and spin-orbit coupling that mixes states of different symmetry. Spin-Orbit coupling effects may be introduced, for example, the Breit-Pauli formalism.^{49,50}

Vibrational perturbation theory (VPT) can reproduce mode mixing and intensity borrowing via Fermi resonances. Combined experimental and theoretical work have provided successful understanding for the spin-orbit coupling and nonadiabatic vibronic couplings of CaOH and YbOH in great details.⁵¹ It is an ongoing effort to extend these treatments to more complex molecules.

3. Selected sample systems

Phenoxides and derivatives: tuning optical cycling properties through substitution

The aromatic system of alkaline earth (I) phenoxides allows for a rich playground to test chemical intuition for QIS design, with transitions to the first two electronic excited states ($\tilde{A}$ and $\tilde{B}$) allowing for detailed investigation (see Figure 2 for NTO). The $\tilde{A}$ state is in resonance with the π -system of the benzene ring, and $\tilde{B}$ state is orthogonal to it. We theoretically predicted that substituting the ring with electron-withdrawing groups, such as F and CF₃ in the *meta*- and *para*-positions, leads to a systematic enhancement of the FCF for the A and B transitions of the Ca and Sr phenoxides (Figure 3). The electron withdrawing character of the substituents can be characterized by the Hammett parameters (or the pK_a of the parent phenol), with which FCFs are correlated. The substituents in the *ortho*-position leads to the bond formation between the substituent and the metal radical, causing the molecule to bend and significantly degrading the diagonal FCFs.³



³ This effect illustrates that -OM is a transferrable but not entirely universal QFG, and its properties to some extent depend on the structure of the molecular host. Other notable example of hosts that cause the loss of the QFG function include unsaturated hydrocarbons such as ethylene, and (car)boranes, where in both cases the radical forms a bond to the host and bends the QFG.

Figure 3. Theoretically predicted trends of the harmonic diagonal FCFs as a function of the sum of the Hammett parameters of the *meta*- and *para*-substituents on the phenyl ring in Ca/SrOPh (TD-DFT level of theory). Adapted with permission from ref (1). Copyright 2021 American Physical Society.

The predictions were tested experimentally using a series of phenoxide derivatives: 3-CH₃, 3-F, 3-CF₃, 3,4-2F and 3,4,5-3F, in the *meta*- and *para*-positions. In our experimental setup, the QFG functionalized molecules are produced by reacting laser ablated Ca/Sr metal with the corresponding organic precursor vapors in a cryogenic buffer gas cell held at ~20 K. The molecules are excited by a tunable pulse dye laser. The laser-induced fluorescence is then focused, dispersed through a spectrometer, and imaged onto an ICCD camera. In Figure 4 we show the sample dispersed laser-induced fluorescence (DLIF) spectra of CaOPh. From the spectra, we are able to identify the decay channels from the electronic excited states $\tilde{A}$ and $\tilde{B}$ into various vibrational modes of the ground state $\tilde{X}$. In both spectra, however, we noticed that the measured vibrational-preserving (0-0) decay is much stronger compared to the vibrational-changing decays. In fact, we derive the vibrational branching ratios (VBRs) of ~95% from the spectra for both $\tilde{A} \rightarrow \tilde{X}$ and $\tilde{B} \rightarrow \tilde{X}$ decays, confirming the theoretical prediction of optical cycling ability. Theory also predicted main population loss channels: the M-O stretching mode, and the Ph-O-M bending mode (shown as blue vertical lines). Their vibrational frequencies and relative intensities are well captured by experiment. Note that because the VBRs are derived from the relative ratio of the peak intensities, we choose to compare the relative intensities against theoretical results.

The results of the phenoxide and derivatives are summarized in Figure 5. In Figure 5a,b we plot the intensity of vibrational decay channels for both $\tilde{A}$ and $\tilde{B}$ states. In Figure 5c we plot the 0-0 VBRs estimated from the DLIF spectra as a function of the pKa of the phenol ligand in solution. The experimental trend is less regular than predicted from harmonic FCFs, but is evidently present. Deviation occurs mainly in CaOPh-3-CF₃ (and to a lesser extent CaOPh-3,4-2F). The lower symmetry and large electron inductive effect may lead to larger vibronic mixing between the $\tilde{A}$ and $\tilde{B}$ states, which can increase vibration-changing decay. This is not captured by our current level of theory. We also notice that the CaOPh-3,4,5-3F $\tilde{B} \rightarrow \tilde{X}$ transition is observed with the highest 0-0 VBR

(~99%) among the considered species, implying that laser cooling is possible with current technology. In fact, if we additionally repump the three main vibrational decays ν_6 , ν_{24} , ν_{16} , ~1000 photons may be scattered repeatedly, achieving optical cycling. Additional lasers may be necessary to repump decays that change the rotational state of the molecule. But in total, we estimate that approximately six to eight lasers would be necessary to perform a near-closed optical cycle. Interestingly, this is similar to the number of lasers required to achieve an equivalent photon budget in molecules with roughly an order of magnitude fewer vibrational modes.¹⁵

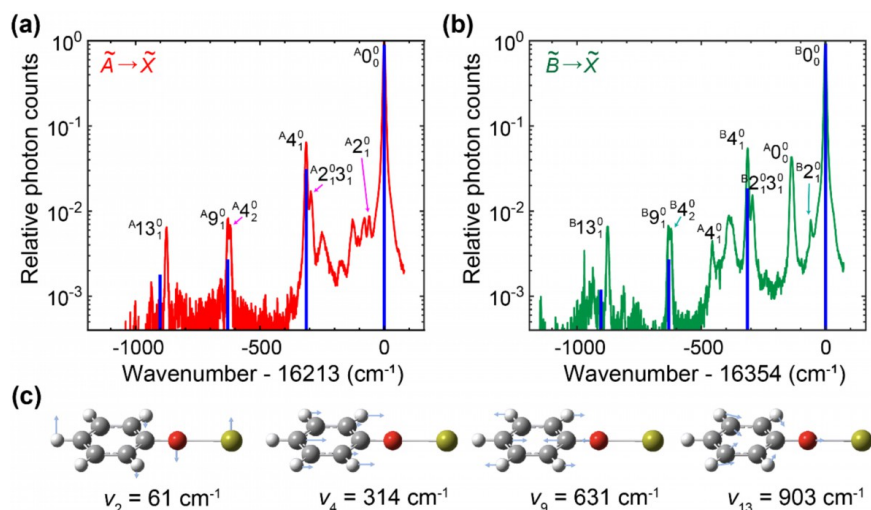


Figure 4. (a,b) Sample DLIF spectra of CaOPh from the first two electronic excited states $\tilde{A}$ and $\tilde{B}$. Blue vertical lines indicate peak positions and intensities from theoretical prediction. Peaks are labeled as $^S\nu_f^i$, where S defines the excited state, ν denotes the vibrational mode, i and f define the vibrational quantum number in the excited and ground electronic state of the mode ν . The y-axis is in log-scale to show the weak off-diagonal decays. VBR of the 0-0 (optical cycling) transitions can be determined from peak intensities. (c) Major vibrational branching channels. Besides the lowest-frequency bending mode ν_2 , rest of the modes are along the Ca-O stretch direction.

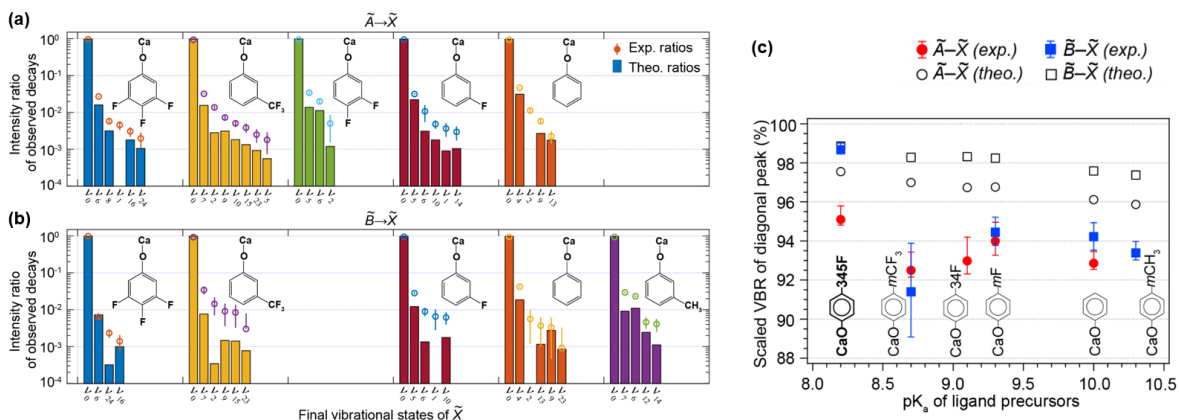


Figure 5. (a,b) The main population loss channels from the experiment (colored bars) compared to theory (empty circles) from $\tilde{A}$ and $\tilde{B}$ states. (c) Scaled VBR from the DLIF spectra as a function of phenol pK_a. Theoretical results are noted with empty symbols. Reprinted with permission from ref. (2). Copyright 2022 Springer Nature.

We also explored theoretically how electron-withdrawing substituents might affect the properties of the OCa/Sr QFG when the host molecule is aliphatic, such as methyl, butyl, or adamantyl. In the absence of π -resonance, only the inductive effect is expected to play a role. Unsurprisingly, fluorination of aliphatic hosts leads to noticeable but milder improvements in the diagonal FCFs.⁵²

To summarize the first lesson in vibronic engineering for QFGs, the electronic structure of the host can be predictably modified toward improvement of the optical cycling efficiency. The substitutions with electron-withdrawing groups generally improve the diagonality of FCFs and the success of optical cycling. While perhaps unsurprising for chemistry, it is fairly unusual for QIS to identify a logical path toward improvement (or ruining) of molecules for optical cycling. The example of the substituted phenoxides illustrates the potential that chemistry has for the QIS field. In addition, it promises that OCa and OSr might indeed be QFGs, since their optical cycling properties, while slightly varied among the variants, are largely preserved despite the modifications of the host.

Naphthoxides and larger arenes: the importance of ligand HOMO-LUMO gap

Since we have demonstrated the optical cycling functionalization of a phenyl group, it is tantalizing to push the limit even further towards larger arenes. Polyaromatic hydrocarbons (PAHs) enable predictable electronic structure variation, this time with

molecular size. Because of the π -conjugation, the frontier orbitals of PAHs exhibit predictable splitting by the particle in a box model. Therefore, our “pencil and paper” expectation was that at some critical size of the PAH, its intrinsic HOMO-LUMO gap will become too small to enclose the optical cycling transition, which will therefore be ruined.

We performed TD-DFT calculations on the series of PAH, from benzene to ovalene, functionalized with -OCa (Figure 6).⁵³ For smaller hosts, the optical cycling transition stays within the intrinsic HOMO-LUMO gap of the PAH. However, the foreseen monotonic closure of the gap with the PAH size leads to the change of the order of unoccupied states at ovalene, where the LUMO now belongs to the PAH and the unoccupied radical orbital becomes the LUMO+1. As a result, the diagonal FCF are predicted to remain above 90% until coronene, and at ovalene it drops dramatically to mere 16%. Hence, we predict that QFGs can be mounted on a variety of aromatic hosts, but to a size limit up to ~ 10 aromatic rings. Naturally, one cannot expect a functional QFG to be bound to the edge of graphene – a zero band-gap semiconductor. Indeed, upon testing with periodic DFT, we found the frontier orbitals of the QFG to be strongly mixed with the delocalized states on the graphene.⁵⁴

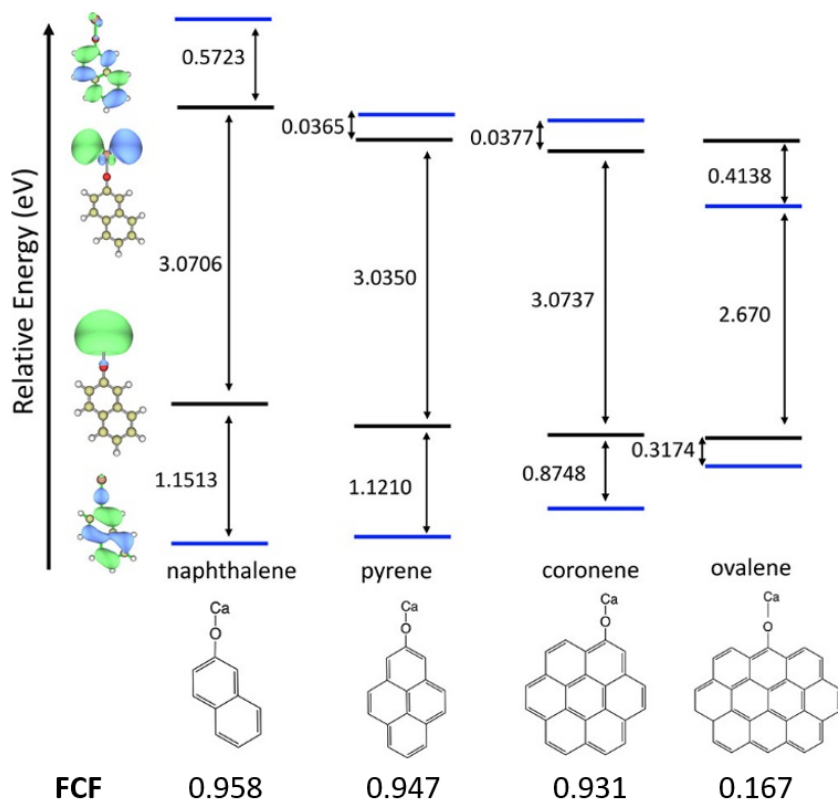


Figure 6. Theoretical prediction of the closure of the intrinsic HOMO-LUMO gap of the PAH hosts (in blue), and crossover with the orbitals of the optical cycling center, Ca (in black) at ovalene. Correspondingly, the computed FCFs get smaller with the growing PAH size, and fall abruptly at ovalene. Reprinted from ref. (53). Copyright 2021 American Chemical Society.

To confirm these predictions, we performed DLIF spectroscopy for Ca/Sr naphthoxides.⁵⁵ In the experiment, three different species CaO2Nap, SrO2Nap, CaO1Nap (Figure 7a) were measured, where 1Nap and 2Nap stand for isomers 1- and 2-naphthol. The measured VBRs are summarized Figure 7b,c. For all naphthoxides, we observed the 0-0 VBRs to be greater than 90%. And with 3-5 additional vibrational decay channels addressed, it is possible to reach a total efficiency of ~99%, indicating potential optical cycling schemes. Similar to the phenoxides, we observe that the decay is predominantly to the ground-vibrational level, and the predominant off-diagonal decay is to the Ca/Sr-O stretching mode: ν_5 for CaO2Nap and SrO2Nap, and ν_6 and ν_7 for CaO1Nap, in a good agreement with theory.

The dominant off diagonal decay mode changes depending on the arene size and symmetry. In Ca naphthoxide, the first two off-diagonal modes are the Ca-O symmetric stretch and a Ca-O out-of-plane bend. However, with coronene, the dominant off-diagonal mode is the Ca-O in-plane bending, followed by the Ca-O symmetric stretch. This is to the interaction of the unpaired *pd*-hybrid electron on Ca with the delocalized electronic states on the arene during bending, where a greater spatial overlap and match in energy occur with the larger arenes.

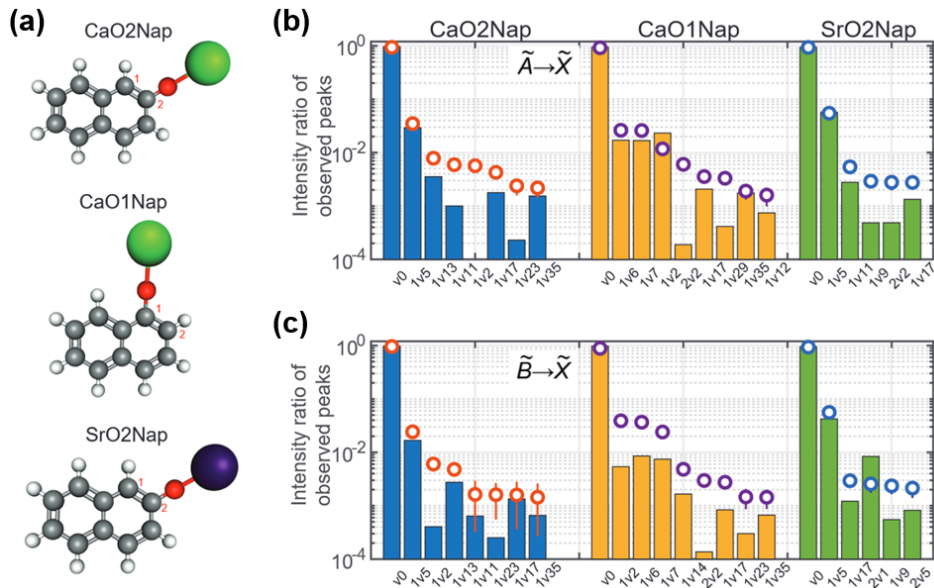


Figure 7. (a) The structures of naphthoxides. (b,c) The main population loss channels from the experiment (colored bars) compared to theory (empty circles) from the two excited states $\tilde{A}$ and $\tilde{B}$. Reprinted from ref. (⁵⁵). Copyright 2022 American Chemical Society.

Regarding the HOMO-LUMO energy match, a related example here is Mg phenoxide, which is not a good candidate for optical cycling. The reason it is useless is that the *p*-atomic orbitals of Mg lie lower in energy than the *pd*-hybrid in Ca/Sr, such that they bind to the aromatic system of phenyl. As a result, the first excited state of MgOPh is bent and has very poor FCFs. The Mg-O bond is also less ionic. In this case, ruining the optical cycling transition is achieved due to the choice of the metal.

Finer effects: the role of Fermi resonance

Adding additional complexity to the host molecule of QFGs raises several fascinating questions about the limits of quantum state preparation. While we work to limit the number of off-diagonal vibrational branchings, as the density of vibrational modes increases with the size of the molecule, at what point will the excitation information become practically irretrievable due to energy dissipation to the effective intramolecular bath? For example, in the condensed phase, when the quantum system becomes sufficiently large, it is not expected that one can manipulate single molecules into non-thermalized quantum states, unless they are in a highly protected subspace (e.g. spins^{56,57}) or we limit our experiment

to very short time scales (100s of femtoseconds^{58,59}). QFGs allow us to quantify all ways in which states are coupled upon excitation and relaxation.

One example is the exploration of additional VBRs due to resonance conditions.^{60,61} As the number of modes increases, the chance of accidental degeneracies between vibrational modes and a combination of two other modes increases. Specifically, for the intensity borrowing via the Fermi resonance mechanism, the direct product of combined states should have the same symmetry as the state from which they borrow the intensity, and the sum of the two frequencies should be close to the frequency of the mode from which they borrow. An example of Fermi resonances is found in higher-resolution DLIF spectroscopy on CaOPh (Figure 8a,b).³ The modes shown in Figure 8b combine and borrow intensities from two outlined transitions. Theoretically, VPT reproduces these resonances.

However, once the modes involved in the resonance have been identified, it became possible to engineer the resonances out. Specifically, since the bending mode is involved, the change of mass either of the metal or of the host should affect the corresponding frequency. Indeed, replacing Ca with Sr removed Fermi resonances from the spectrum (Figure 8c,d), greatly improving the chances of laser cooling SrOPh with fewer repump lasers.⁶²

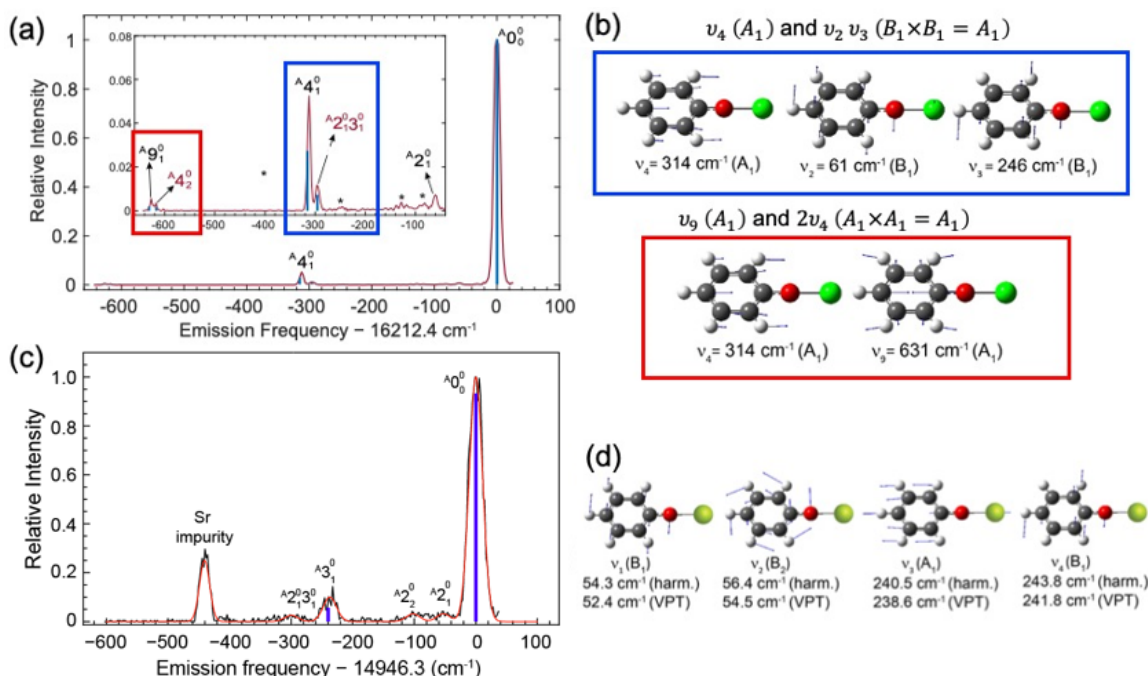


Figure 8. (a) Fermi resonances are seen in the high resolution DLIF spectrum of CaOPh ($\tilde{A} \rightarrow \tilde{X}$), outlined in the inset. Vertical blue lines are theoretical VPT results. (b) Combinations of frequencies involved in the intensity borrowing from DFT. (c) The corresponding spectrum of SrOPh does not exhibit the same Fermi resonances, because of the different magnitudes of the implicated frequencies (d). Reprinted from ref. (3). Copyright 2024 American Chemical Society.

The third lesson in vibronic engineering is that subtle effects such as Fermi resonances can get in the way of optical cycling, but they can be removed through rational molecular design. The design needs to focus on shifting the vibrational frequencies out of accidental resonances by manipulating the masses of fragments involved in the corresponding vibrational modes. However, we do need to point out that chemical modification may get less effective when molecules continue to grow larger. In a denser distribution of vibrational modes, it is less likely to find a spot to shift the vibrational frequencies with no accidental resonances. Furthermore, chemical modification shifts all the vibrational frequencies, which may result in new resonances occurring from other modes. In short, Fermi resonance and other nonadiabatic couplings can be ubiquitous in larger molecules, which limits the effectiveness of QFGs.

QFG arrays

Ordered arrays of QFGs are of interest to QIS for entanglement. High level of control over QFG separation and individual addressability are important requirements. Having multiple QFGs on the same molecule could also increase laser cooling efficiency. We began exploring this direction by theoretically studying aromatic hosts functionalized with two QFGs, which can be identical (e.g. both OCa) or different (e.g. OCa and OSr).^{63,64} We note that high-level theory confirmed that individual OCC states are strongly isolated. Therefore, modeling the bi-OCC molecules as triplets is safe at the DFT level of theory to obtain qualitative trends.

Two frontier orbitals of the metal radicals form pairs of linear combinations, according to the point group of the molecule. The result is superradiant states, which can be favorable for laser-cooling applications due to the increased oscillator strength. Indeed, theoretical calculations yield promising 0-0 FCFs of ~95% of the superradiant states for various molecules. However, the superradiance effect also suggests that there must sub-radiant (dark) states. Such intruder states are undesirable as they increase the chance of population loss via non-radiative transitions (internal conversion). The effect can be partly mitigated by changing the alignment of the transition dipoles of two QFGs, which plays a critical role in the properties of these molecules. For example, different placements of two -OM on benzyl changes the point group, and hence, the number of bright excited states and their order (Figure 9). The superradiant transition is desired to be bright and to the first excited state. We hope that an optimum could be found in the future.

While the superradiance makes use of the linear combinations of the two OCC states, it is possible to address each OCC individually. This can be done via making the two metals different (e.g., Ca and Sr), or by an asymmetric substitution of the host. The electronic states of the two QFG is thus shifted with respect to each other, and a different laser could excite them individually. This offers some instrumental flexibility to the experiment because both metal centers can be used simultaneously for such as laser cooling and sensing applications.

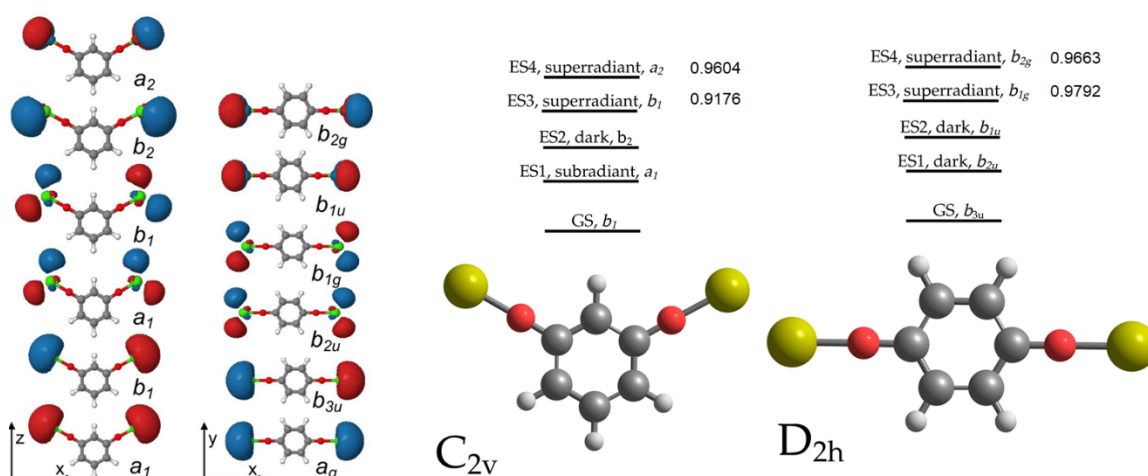


Figure 9. (a) Frontier orbitals of bi-OCCs based on benzyl scaffold. (b) The excited states order and respective symmetries for bi-OCCs. The FCFs of the superradiant states are given on the side. Reprinted from ref. (63). Copyright 2024 American Chemical Society.

Towards surface functionalization

An ultimate limit of arranging QFGs into arrays would be surface functionalization. If QFGs could still be optically addressed when mounted to a surface, the advantages of such constructs would be numerous. Firstly, the QFG separation can only be a multiple of the lattice constant, i.e. fairly well controlled. Secondly, a suitable phonon of the material may serve as a common mode useful for entanglement. Finally, very large number densities can be achieved, with the number of qubits being on the order of N_a . The question is which surfaces can serve as solid state hosts for QFGs.

We theoretically predicted that ultra-rigid materials with large band gap, e.g. diamond and cubic boron nitride, could work. The electronic structure of the OCCa and OSr QFGs mounted directly on their surfaces retain the desired optical cycling transition that does not interfere with the electronic states of the material. In contrast, materials such as oxides have band gaps that are either too small or shifted with respect to the OCC transition such that the frontier orbitals of the radical mix with the material's band edges. It is also predicted that the entire $-C_6H_4OCCa$ group can be mounted on diamond, in this case the whole entity being a QFG. We note that theoretical treatment of diamond mounted QFGs was not limited to periodic DFT, but done through the “aperiodic embedding” method with SA10-CASSCF(9,10)/NEVPT2 treatment of a fragment.⁶⁵

We began approaching surface functionalization in the experiment from the ground up: by constructing QFG-functionalized aliphatic hosts, adamantane, and larger diamondoids.⁴ The molecule series MOPh, MOPh-CH₃, MOPh-C(CH₃)₃, MOPh-Ad, MOPh-1diA and MOPh-4diA are synthesized with increasing sizes of the hydrocarbon ligands. Here, Ad refers to adamantyl, 1diA and 4diA refers to 1-diadamantyl and 4-diadamantyl. Despite the astronomical increase in the number of degrees of freedom, we find no systematic decrease of the optical cycling property (Figure 10a). The vibrational branching ratio remains ~90% for all ligand sizes. The most significant off-diagonal leakage channel is M-O stretch. Theoretical computations propose that the increase of the mass of the host toward larger diamondoids should shift the frequency sufficiently to begin suppressing this decay channel, which is observed experimentally (Figure 10b) (albeit within error). While diamond surface is still far out of experimental reach at this moment, these findings suggest that it is possible to functionalize the diamond surface (or at least very large diamondoids) using QFGs without reducing the performance.

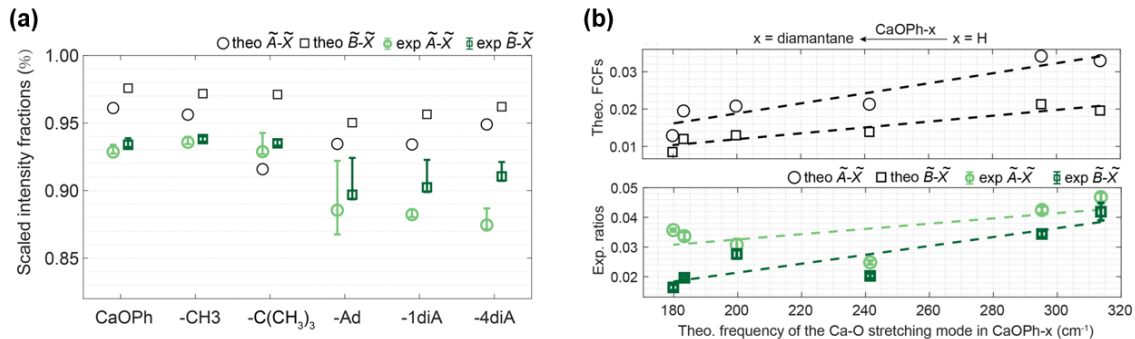


Figure 10. (a) Theoretical FCFs and experimental VBRs of the diagonal transition of $\tilde{A}$ and $\tilde{B}$ states for a series of aliphatic hosts functionalized with the QFG $-\text{C}_6\text{H}_4\text{OCa}$. The diagonality is generally maintained with the increase of the host mass. (b) Theoretical FCFs and experimental VBRs of the main leakage channel, plotted against the frequency of the mode. Lowering the frequency damps the loss of population into it. Reprinted from ref. (4).

To summarize this section, we propose that the best chance at engineering surface mounted QFG arrays is with the host materials that feature large band gaps and rigid phonon structure. The next consideration should be QFG spacing and transition dipole alignment in such arrays, and possible surface nanostructure engineering to avoid dark states and promote superradiance.

4. Perspective and outlook

In short, we proposed and demonstrated that the Ca/Sr(I)-O and Ca/Sr(I)-OPh can be used as quantum functional groups (QFG) attaching to a variety of molecular species. The strong ionic character of the Ca/Sr(I)-O bond gives rise to the localized electron density of HOMO and LUMO on the metal atom. The result is an electronic transition which is largely decoupled from molecular vibrations, leading to few vibrational decay channels, which is favorable for optical cycling. With QFG attached, >90% vibrational branching ratios can be reached for many molecules.

The exact performance of the QFG depends on the ligands to which it is attached. The isolated character of the metal atom requires a strong ionic bond manipulable through electron withdrawing substitutions, and the relatively wide ligand HOMO-LUMO gap tunable through the size/conjugation of the ligand and the choice of OCC. For example, arenes with >10 rings will not work. Ligands with higher symmetry are also favored as they are less likely to have Fermi resonances. Subtle effects such as Fermi resonance can be eliminated by examining the implicated vibrations and shifting their frequencies out of resonance with overtone and combination bands via molecular modifications (such as selective deuteration). Chemists must leverage their arsenal of tools, including shifting orbital energies and vibrational frequencies via novel synthetic strategies.

A current limitation of accessing QFG performance with DLIF spectroscopy is the possible unobserved peaks below detection threshold. For example, if there is a sufficient number (>10) of decay channels with possibilities $<10^{-4}$, they still add up significantly and contribute to the loss during optical cycling. This is particularly problematic when working with larger molecules where the numbers of decay channels can get easily overwhelming. One way to improve the sensitivity is by performing actual optical cycling (using extra laser to address the main vibrational decays), for instance in the work demonstrated by Zhang et al.⁵¹ After hundreds of optical cycles, enough molecules are accumulated in the excited state as well as dark states, leading to better sensitivities on the order of 10^{-5} . It may be possible to extend this schematic for even weaker transitions by adding more repump lasers for a more closed optical cycle despite instrumental complexity. Other parallel measurements, such as excitation scans which probe transitions from the ground state to

the vibrational modes of the excited states, can be helpful in identifying weak FCFs between vibrational modes as well.

QFGs may not only be a path toward Avogadro numbers of qubits, they also present a testing ground for fundamental questions in chemical physics. While their coupling to external modes is weak in comparison to a typical excitation across HOMO-LUMO gap, it is simultaneously exquisitely sensitive to every potential source “information” loss. One could thus use QFGs to benchmark all forms of non-adiabatic coupling (or entanglement between nuclei and electrons). Long standing questions regarding the source and nature of intravibrational relaxation (IVR)^{60,61} are accessible due to the highly localized nature of this excitation. If understood, and ultimately mitigated, QFGs could enable quantum functionality on complex molecular architectures, allowing multi-qubit interactions on short, yet controlled length scales.

One can imagine use of the QFG as an accessory knob to manipulate the molecule, or read out its state. Cooling and accessing the rich rotational and vibrational levels are applicable to robust encoding of quantum simulation and computing^{66–68} separate from the OCC electronic states. Molecules can act as extraordinary detectors of beyond standard model physics. Once a large molecule is cooled, one can create organic hydrocarbons via zero-energy photo-fragmentation⁶⁹ and explore ultracold chemical reactions and collision studies.

Finally, advancing this field requires team science. Initial spectroscopic studies are useful, but require robust computation to accompany any understanding of trends or emergent properties. Hypothesis testing via chemical substitution requires synthesis of new compounds amenable to laser ablation and preparation in the gas-phase. Finally, actually cooling a large molecule will require significant investment of physical resources, including (many) lasers, improved detection strategies, and better cryogenic cooling. Only via this virtuous cycle will progress be apparent.

Conflict of Interest

The authors declare no competing financial interest.

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