Toward Ultracold Organic Chemistry: Prospects of Laser Cooling Large Organic Molecules

Maxim V. Ivanov, Felix H. Bangerter, Pawel Wójcik, and Anna I. Krylov*

ABSTRACT: Ultracold organic chemistry enables studies of reaction dynamics and mechanisms in the quantum regime. Access to ultracold molecules hinges on the ability to efficiently scatter multiple photons via quasi-closed cycling transitions. Optical cycling in polyatomic molecules is challenging due to their complex electronic structure. Using equation-of-motion coupled-cluster calculations, we demonstrate that an alkaline earth metal attached to various aromatic ligands (such as benzene, phenol, cyclopentadienyl, and pyrrole) offers nearly closed cycling transitions with only a few additional repump lasers. We also show that aromatic ligands such as benzene can accommodate multiple cycling centers in various geometrical arrangements, opening new avenues in quantum information science, precision measurements, and ultracold chemistry.

Ultracold molecules provide exciting opportunities to probe chemical reactivity with reagents prepared in a specific quantum state, including vibrational, rotational, spin, and hyperfine levels. The pioneering studies of ultracold chemistry included collisions between atoms, an atom and a diatomic molecule, and a pair of diatomic molecules. By providing means to study reaction dynamics and mechanism in the quantum regime, emerging techniques in molecular physics now open access to more complex chemical systems. Representative examples include a study of the reaction between the conformers of 3-aminophenol and laser-cooled CaH, quantum state-controlled synthesis of CaOBO+, production of the cold beams of YbOH via excited-state chemistry, and quantum state-resolved collisions between OH and NO, between N2 and Rb, and between Kr and Rb molecules. Access to cold and ultracold molecules is also a prerequisite for precision measurements and quantum information storage and simulation.

Until only very recently, laser cooling was limited to atoms and a handful of diatomic molecules. Recent breakthroughs by Doyle’s group, who laser-cooled a series of a polyatomic molecules—from CaOH, SrOH, and YbOH to much more complex CaOCH3—inspire optimism that polyatomic molecules with virtually any degree of complexity can be laser-cooled.

The main challenge in laser cooling of large polyatomic molecules stems from multiple degrees of freedom and complex electronic structure. Laser cooling is achieved by a continuous scattering of a large number (>10^4) of photons off the target, with each cycle of absorption and emission slowing its translational motion. In a simple diatomic molecule with atomlike electronic structure, such as CaF, the spontaneous emission returns the excited molecule either to the original ground state or to a first few excited vibrational levels, thus providing an efficient means of laser cooling, with the aid of a few additional repump lasers. In contrast, emission in a large polyatomic molecule often populates numerous vibrational levels, thus requiring an unmanageably large number of repump lasers. It has been estimated that to bring at least 10% of molecules to rest by scattering 4500 photons, at least 99.95% of the emission has to be recovered by the lasers. That is why viable polyatomic candidates should afford electronic transitions with minimal structural relaxation, i.e., with diagonal Franck–Condon factors (FCFs), implying similar equilibrium geometries and normal-mode frequencies of the two electronic states involved in the cycling. The rotational degrees of freedom need to be cooled too, which requires working with carefully chosen rotationally closed transitions, as has been recently illustrated for CaOCH3.

One successful strategy of designing a laser-coolable molecule is to attach an alkaline earth metal (such as calcium or strontium) to a ligand that withdraws one of the two valence electrons of the metal creating a strong ionic bond. The second electron remains localized at the metal, both in the ground state and in the excited states, giving rise to highly diagonal FCFs and thereby closed cycling transitions, if an appropriate number of repump lasers is introduced. The success in exploiting highly localized excitation for optical cycling in trisatomic molecules (CaOH, SrOH, and YbOH) spurred explorations of optical cycling schemes in more complex polyatomic molecules. In CaOH (and similar molecules), the localization of the unpaired electron...
is facilitated by the strongly ionic Ca−O bond, which effectively blocks electronic communication between Ca+ and the rest of the molecule. Thus, various saturated and unsaturated hydrocarbon groups can follow the O atom without significantly deteriorating the FCFs. Recent laser cooling of CaOCH3 proves this concept, suggesting that optical cycling and laser cooling of large polyatomic molecules can be as efficient as in simpler linear species.

Prospects of optical cycling with polyatomic molecules are particularly promising for building novel quantum systems. It also paves the way toward (ultra) cold organic chemistry. Because unsaturated hydrocarbons, and in particular aromatic compounds, are at the heart of chemistry, the ability to laser cool molecules containing aromatic groups would enable the study of many important reaction mechanisms in the quantum regime. However, considering the delocalized nature of the spin/charge distribution in the aromatic systems, it is unclear whether the FCFs remain diagonal when alkaline earth metal is attached to an aromatic ligand.

Representative examples of the aromatic ligands include benzene (Bz) and phenol (Ph) as candidates for laser cooling (Figure 1). One can also exploit (hetero)cyclic π-conjugated ligands that become aromatic according to Hückel’s 4n + 2 rule, once the electron is transferred from the alkaline earth metal to the ligand. Representative examples of the aromatic ligands include cyclopentadienyl (C5H5− or Cp) and pyrrole (C4H4N− or Py) anions (Figure 1). By using high-level electronic structure calculations, here we demonstrate that calcium derivatives with various aromatic ligands (Figure 1) appear to be promising candidates for laser cooling, despite their structural complexity. All electronic structure calculations were performed using the Q-Chem package, the wave function analysis was carried out using the libwfa library. The computational details are described in the Supporting Information.

We begin with the analysis of the electronic structure of CaOH, an alkaline earth metal derivative that has been recently laser-cooled. One of the two valence s electrons of the metal is transferred to the ligand, yielding ionically bound Ca+ and OH− ions, with Mulliken’s charges on Ca and O of 0.76 and −1.00, respectively. The interaction between two ions results in the orbital hybridization on the metal atom, which minimizes the repulsion between the unpaired electron and a negatively charged ligand. In the ground X2Σ− state, the unpaired electron is localized at the metal and occupies the sσ−pσ hybridized orbital. The transitions from the X2Σ− state to the A2Π and B2Σ+ states can be described as atom-like transitions to pσ−dσ and pσ−dσ hybridized orbitals, respectively (Figure 2A). Accordingly, upon excitation, the molecule remains linear, with the most significant structural change being the contraction of the Ca−O bond. Relative to the ground state, the Ca−O bond shortens by 0.026 Å in the A2Π state and by 0.024 Å in the B2Σ+ state.

Our previous studies of alkaline earth derivatives showed that an equation-of-motion coupled-cluster method with single and double excitations (EOM-CCSD) yields accurate excitation energies (within 0.1 eV), bond length changes (within 0.006 Å), and normal-mode frequencies. Relative errors in the FCFs for the 0 − 0 transition calculated within double-harmonic parallel-mode approximation are in the range of 2−3%.

In CaOH, our calculations yield FCFs for the A2Π(ν = 0) → X2Σ−(ν = 0) and B2Σ+(ν = 0) → X2Σ−(ν = 0) transitions of 0.9287 and 0.9371, respectively, in good agreement with the experimentally derived values. Decays into the stretching Ca−O and bending Ca−O−H modes are also present and are not negligible (Figure 2B). Although there is no structural relaxation along the bending coordinate, the bending mode is Fränck−Condon active because of a noticeable change in the vibrational frequency between the ground and excited states, causing the decay into the bending mode; this relaxation channel may be further enhanced by anharmonicities.

Our calculations show that this electronic structure is preserved when Ca is attached directly to the ligand, in an in-plane configuration, for all three considered ligands (CaBz, CaPh, and CaPy). In particular, the pattern in the electronic excitation spectrum is quite similar to that in CaOH (Table 1), subject to the following differences. In contrast to linear CaOH, in which the first excited state is a doubly degenerate A2Π state, in CaBz, CaPh, and CaPy, the II state is split into a B1,2 pair (separated by 0.02−0.05 eV) due to lower symmetry (C2v).

Figure 3A shows Dyson orbitals of four lowest electronic states in CaBz as a representative example of this series. The unpaired electron is mostly localized at the metal and occupies...
Table 1. Excitation Energies (in Electronvolts) and Oscillator Strengths (in Parentheses) Calculated using EOM-EA-CCSD

<table>
<thead>
<tr>
<th>Molecule</th>
<th>A′Π</th>
<th>B′Σ⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaOH</td>
<td>2.03 (0.26)</td>
<td>2.34 (0.20)</td>
</tr>
<tr>
<td>CaCp</td>
<td>1.92 (0.19)</td>
<td>2.29 (0.16)</td>
</tr>
<tr>
<td>CaBz</td>
<td>1.90 (0.21)</td>
<td>1.95 (0.21)</td>
</tr>
<tr>
<td>CaPh</td>
<td>2.07 (0.24)</td>
<td>2.09 (0.25)</td>
</tr>
<tr>
<td>CaPy</td>
<td>2.04 (0.23)</td>
<td>2.09 (0.23)</td>
</tr>
<tr>
<td>iso-CaPy</td>
<td>1.92 (0.19)</td>
<td>1.96 (0.18)</td>
</tr>
</tbody>
</table>

*Molecules are arranged from more to less symmetric.

Figure 3. (A) Dyson orbitals and (B) NTOs of CaBz and CaCp plotted with an isovalue of 0.03.

Figure 4. (A) Illustration of the normal modes of CaBz with the largest displacements. (B) Optical cycling scheme for the A′B₁ → X₂A₁ and C₂A₁ → X₂A₁ transitions in CaBz with indicated FCFs for each vibronic transition.

Molecules are arranged from more to less symmetric.

hybridized orbitals that are visually similar to those in CaOH and other alkaline earth metal derivatives. This is especially surprising, given that the Ca−C bond in CaBz is less ionic than the Ca−O bond in CaOH. Mulliken’s charges on Ca and C are 0.47 and −0.42, respectively. Perhaps the requirement of a strongly ionic bond is less stringent than previously thought, and molecules with covalent bonding may be laser-coolable as well. This observation is consistent with a recent demonstration of laser cooling of BaH, a molecule with a bond that is much less ionic than those of other coolable diatomics (i.e., CaF and SrF).

Less ionic character of the Ca−C bond leads to a more extended delocalization of the unpaired electron. As Dyson orbitals in Figure 3A show, the unpaired electron distribution spills over the atoms of the ligand to a slightly larger extent than in CaOH. The excitation remains localized at Ca, with a minor involvement of the directly connected C atom, as revealed by the NTOs in Figure 3B. Accordingly, the changes in the Ca−C bond length are slightly larger than in CaOH: the Ca−C bond is elongated by 0.03 Å in the A′B₁ state and by 0.027 Å in the C₂A₁ state relative to the ground state. The structural relaxation is limited to the Ca−C bond: the C−C bond adjacent to Ca−C bond changes by <0.004 Å, while the remaining C−C bonds are completely unaffected by the excitation.

Estimated FCFs in CaBz are not as diagonal as in CaOH and are consistent with the structural relaxation pattern. The FCFs for the A′B₁(ν = 0) → X₂A₁(ν = 0) and C₂A₁(ν = 0) → X₂A₁(ν = 0) transitions are 0.7595 and 0.8849, respectively. The next largest FCFs are associated with the decays to the first vibrational level of the Ca−C stretching mode (Figure 4A) and are equal to 0.1318 and 0.1055 for the A′B₁ and C₂A₁ states, respectively. If both decay channels are addressed by the lasers, total populations of 0.8913 and 0.9904 can be recovered in the A′B₁ state relative to the ground state. The structural relaxation is limited to the Ca−C bond: the remaining C−C bond changes by <0.004 Å, while the remaining C−C bonds are completely unaffected by the excitation.

An additional source of population decay in the A′B₁ state is the Ca−Bz bending mode because of the frequency change. With the addition of a third laser, one could recover a total of 0.9552 of the population, which makes this transition viable for optical cycling despite modestly diagonal FCFs. Structural reorganization in B₂B₁ is similar to that in A′B₁ (Figure S1), giving rise to similar FCFs (Table S1). The other two molecules that we considered, CaPh and CaPy, show similar patterns in structural relaxation; their FCFs are listed in Table S1.

We next turn to the molecules with an out-of-plane arrangement of the cycling center (i.e., CaCp and iso-CaPy), which have been studied both experimentally and theoretically. Experimental studies have showed that CaCp has a...


Our calculations confirm that the electronic excitation spectra of CaCp and iso-CaPy are indeed similar and are consistent with the spectra of other alkaline earth metal derivatives (Table 1). In each electronic state, the unpaired electron occupies hybridized atom-like orbitals and electronic transitions are localized at the metal (see the example of CaCp in Figure 3). However, the involvement of the ligand is more significant than in CaBz, as the unpaired electron distribution spills over the aromatic moiety (Figure 3A). An increased bonding between the metal and ring translates into a significant structural relaxation in the excited states: in CaCp, the Ca–C bond distance is reduced by 0.070 Å in the $A^2E_i$ state. The spectrum of structurally similar iso-CaPy is similar to that of CaCp yet exhibits two closely lying but distinct $A$ and $B$ states due to lower $C_s$ symmetry. Despite the complex excitation spectrum, the dispersed fluorescence spectra of CaCp and iso-CaPy are quite simple and feature decays only to the metal-ring stretching mode (Figure 5). The small number of decay channels suggests that the structural relaxation in these molecules is small and, therefore, the FCF matrix is nearly diagonal.

![Figure 5. Ca-ring stretching modes of CaCp and iso-CaPy.](image)

Although the FCFs are not as diagonal as they are for the in-plane structure, more than 99% of the population can be recovered with an addition of more repump lasers. In the $A^2E_i \rightarrow X^2A_1$ cycling transition, 0.5435 of the emission decays back to the ground level while 0.4480 of the population is distributed across three quanta of the Ca–Cp stretching mode (Figure 6). Thus, a total of 0.9915 of the population can be recovered at each cycle with a total of four lasers. In the $B^2A_1$ state, the magnitudes of the bond length changes are smaller than in the $A^2E_i$ state and by 0.031 Å in the $B^2A_1$ state, while the intraring C–C bond changes are 0.003 Å.

![Figure 6. Proposed optical cycling schemes for the $A^2E_i \rightarrow X^2A_1$ and $B^2A_1 \rightarrow X^2A_1$ transitions in CaCp.](image)

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interactions in p-CaBzCa and switches to through-space in m- and o-CaBzCa, in part due to the greater proximity of the two centers.

The structure of the electronic spectrum in p-CaBzCa resembles that of CaCCCa (Figure 8). In particular, the lowest electronic states in p-CaBzCa arise from the excitonic splitting between the corresponding states in single-center CaBz. For example, the B1 and B2 states of CaBz are split by a value of 24–25 meV into the B1g/B2g and B2g/B1u pairs (Table S4). The value of the excitonic splitting shows a systematic variation with varied Ca–Ca distance across the three isomers, reflecting the varied change in the through-bond interactions between unpaired electrons (Figure 8).

In conclusion, here we computationally investigated the prospects of laser cooling large molecules in which an alkaline earth metal is attached to an aromatic ligand. Building upon previous successful frameworks, we designed laser-coolable aromatic molecules by attaching a cycling center to an electron-withdrawing ligand and propose CaBz, CaPh, and CaPy as viable candidates. We also explored (hetero)cyclic π-conjugated ligands that become aromatic once the electron is transferred from the cycling center to the ligand and propose CaCp and iso-CaPy. We focused on the extent of unpaired electron delocalization from the cycling center and how this delocalization translates into the FCFs. We demonstrated that, although the involvement of the ligand in these aromatic molecules is slightly more significant than in triatomic CaOH, the FCFs do not deteriorate significantly. We predict that with an additional few repump lasers, the cycling transition becomes nearly closed, with a total of 96–99% of the population being recovered. Although the diagonality of the computed FCFs suggests that scattering multiple photons off the proposed organic molecules is likely, additional experimental and theoretical investigations are required to quantitatively confirm that scattering of millions of photons is possible using a reasonable number of lasers to achieve efficient laser cooling. The incorporation of aromatic ligands provides a means for further functionalization; for example, the optical and structural properties of these molecules can be varied by introducing electron-withdrawing groups. Incorporation of multiple cycling centers further extends the scope of possible applications in QIS, precision measurements, and ultracold chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01960.

Computational details and additional results of the EOM-CC calculations (Dyson and natural transition orbitals, equilibrium bond lengths, excitation energies, and oscillator strengths) (PDF)

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Notes

The authors declare the following competing financial interest(s): A.I.K. is the president and a part owner of Q-Chem, Inc.

■ ACKNOWLEDGMENTS

This study was funded through the “Molecules Functionalized with Optical Cycling Centers” collaboration, supported by the U.S. Department of Energy (Award DE-SC0019245). The authors thank Professors Nick Hutzler (Caltech) and Eric Hudson (UCLA) for helpful discussions.

■ REFERENCES


