The potential of strong light-matter interactions remains to be further explored within a chemical context. Towards this end, we here study the electromagnetic interaction between molecules and plasmonic nanocavities. By means of electronic structure calculations, we show that self-induced catalysis emerges without any external driving due to the interaction of the molecular permanent and fluctuating dipole moments with the plasmonic cavity modes. We also exploit this scheme to modify the transition temperature $T_{1/2}$ of spin-crossover complexes as an example of how one can ultimately control materials response through strong light-matter interactions.
Plasmonic Nanocavities Enable Self-Induced Electrostatic Catalysis
Clàudia Climent,* Javier Galego, Francisco J. Garcia-Vidal and Johannes Feist*

Departamento de Física Teórica de la Materia Condensada and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, E-28049 Madrid, Spain
E-mail: claudia.climent@uam.es, johannes.fesit@uam.es

Abstract: The potential of strong light-matter interactions remains to be further explored within a chemical context. Towards this end we here study the electromagnetic interaction between molecules and plasmonic nanocavities. By means of electronic structure calculations, we show that self-induced catalysis emerges without any external driving due to the interaction of the molecular permanent and fluctuating dipole moments with the plasmonic cavity modes. We also exploit this scheme to modify the transition temperature $T_{1/2}$ of spin-crossover complexes as an example of how one can ultimately control materials response through strong light-matter interactions.

The principal challenge that chemists face in the field of nanoscience is to be able to manipulate individual molecules. This is a key point in order to ultimately control the properties and response of materials as well as the course and outcome of chemical reactions. In the last decade, novel ways of altering chemical reactions have been developed. For example, mechanochemistry aims to shape the potential energy surface (PES) connecting reactants to products by applying a mechanical force.\[214\] Another example, closer to the strategy we propose in the present work, is to apply external electric fields to catalyze or inhibit chemical reactions. This was computationally predicted by Shaik and coworkers\[6,8\] and recently achieved experimentally for a Diels-Alder reaction,\[7\] boosting the field of electrostatic catalysis.\[9\] It is important to highlight that prior to these works, much effort was spent to elucidate the contribution of electrostatics to enzymatic catalysis,\[9\] lately inspiring the optimization of catalysts by mimicking the electrostatic environmental effect of the protein scaffold.\[10\] Plasmonic catalysis is another field popularized in recent years due to the ability of hot carriers to lower reaction barriers and enable new reaction pathways.\[11-14\]

Herein we propose an alternative strategy to catalyze chemical reactions, tackling the situation of strong coupling between plasmonic modes and molecular dipole moments. This can be achieved, for instance, with the bowtie configuration shown in Figure 1, where the highly confined electromagnetic field within the antenna gap can strongly interact with the molecules in that region.\[15\] In the following lines we will exemplify this effect with classical examples of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ reactions. In addition, our proposal can also be exploited to modify molecular properties, as we illustrate with spin-crossover transitions in a series of Fe(II) complexes.

When molecular excitations and photonic modes strongly interact, hybrid light-matter states known as polaritons are formed. The confined light-modes necessary to produce these new eigenmodes of the system may be hosted in Fabry-Perot or plasmonic nanocavities. Polaritonic chemistry\[16-19\] is an emerging field aiming to manipulate the behavior of molecules with the formation of polaritons. In particular, Ebbesen and coworkers have reported two prime examples of polaritonic chemistry in Fabry-Perot cavities, experimentally demonstrating the suppression of ground\[20,21\] and excited state\[22\] reactions taking advantage of polaritons.

Figure 1. Sketch of a configuration to enable self-induced electrostatic catalysis consisting of a molecule within the gap of a metallic bowtie nanocavity. The charge distribution of the molecule and the one induced in the metal is also illustrated.

We recently tackled from a theoretical point of view the coupling of one or several photonic modes in a nanocavity to thermally driven chemical reactions in the ground state.\[23\] Starting from a purely quantum mechanical description of the coupled light-matter system, we found a novel phenomenon, different to the examples described above, which can be exploited to alter ground state chemical reactivity and molecular properties that (i) does not require the formation of polaritons (i.e. independent of resonance), (ii) has a clear interpretation in terms of Van der Waals or Casimir-Polder interactions, and (iii) is a single-molecule and not a collective effect. As a result of the interaction between the molecular dipole of the species involved in the reaction and the induced dipole in the nanocavity, the ground-state PES is modified according to the square of the molecular dipole moment. Note that, as opposed to the external electric field in the Stark effect, the field in the present case is generated by the molecule itself by light-matter interactions.
We used the following Hamiltonian in the cavity Born-Oppenheimer approximation (CBOA) to investigate the coupling of a molecular dipole to k cavity modes.

\[
\hat{H}_c(\mathbf{x}, \mathbf{R}, q) = \hat{H}_c(\mathbf{x}; \mathbf{R}) + \frac{1}{2} \sum_k a_k^2 q_k^2 + \sum_k a_k q_k \lambda_k \mu_k(\mathbf{x}, \mathbf{R}) \tag{1}
\]

The first term is the standard electronic Born-Oppenheimer Hamiltonian, the second one is the potential energy of the quantized electromagnetic (EM) modes, which are modeled as harmonic oscillators, and the third term represents the light-matter interaction. The frequency of the photon modes is given by \(\omega_k\), \(q_k\) are the photon displacements, related to the electric field of each EM mode, and the \(\lambda_k\) coupling strengths quantify the light-matter interaction along the direction of the molecular dipole. The molecular dipole moment operator is given by \(\mu\) while \(\mathbf{R}\) and \(\mathbf{x}\) refer to the nuclear and electronic positions, respectively. Within the CBOA, the cavity modes are additional nuclear-like degrees of freedom parametrized by \(q_k\), and thus one can benefit from the standard approaches available in quantum chemistry to optimize minima and transition states (Supporting information).

For the minimum energy path along all the \(q_k\) in the CBOA and within a single-molecule level, an effective coupling constant \(\lambda\) can be defined as \(\sqrt{\sum_k \lambda_k^2}\) together with an effective frequency \(\omega\) given by \(\sum_k \lambda_k^2 \omega_k / \lambda^2\).

Up to second order of perturbation theory, the energy shift on the PES when the molecular dipole couples to \(k\) modes of a plasmonic nanocavity can be simply written as.

\[
\delta E(\mathbf{R}) = -\frac{\lambda^2}{2} \left( \mu^2(\mathbf{R}) + \frac{\omega^2}{2} a_0(\mathbf{R}) \right) \tag{2}
\]

This is an important result showing that the profiles of the ground state permanent dipole moment \(\mu(\mathbf{R})\) and the static polarizability \(\alpha(\mathbf{R})\) dictate how the energy landscape is modified. It is worth noticing that this shift corresponds to the well-known Casimir-Polder interaction energy between neutral atoms and macroscopic conducting bodies arising from the vacuum fluctuations of the EM field. This was derived by Casimir and Polder within a quantum electrodynamics framework (QED), motivated by the discrepancies between theory and experimental results on colloidal particle stability, and led to a generalization of Van der Waals interactions. This connection leads to a straightforward interpretation of Eq. 2. In particular, if the cavity can be approximated by a point dipole, which would be valid for instance for a small enough plasmonic nanoparticle, then the two energy shifts in the PES of Eq. 2 represent: (i) the Debye energy of the Van der Waals interaction between the permanent dipole of the molecule and the dipole it induces in the nanoparticle and (ii) the interaction between fluctuating dipoles in the molecule and nanoparticle expressed by the London force. Note that the Debye term will always lower the energy in contrast to the London one which can act in both directions.

We first focus on how coupling to a plasmonic nanocavity can lead to changes in ground-state chemical reactivity. We have chosen the S_{N1} and S_{N2} reactions since the permanent dipole moment along their reaction paths varies considerably, thus making them ideal candidates to demonstrate chemical changes in the present QED scenario. We consider the hydrolysis of tert-butyl chloride, which is known to proceed via an S_{N1} mechanism. This reaction consists of three steps: (i) the separation of the leaving group leading to a carbocationic intermediate, (ii) solvent nucleophilic attack on the carbocation and (iii) deprotonation leading to an alcohol and HCl. Steps (ii) and (iii) are known to be fast, and thus we focus herein on the rate-determining step (i). In Figure 2 we show the reaction profile for different coupling strengths. In realistic multi-mode nanocavities, the effective global coupling constant can reach values of more than 0.02 atomic units (a.u.) thus we have here considered \(\lambda\) coupling strengths of up to this value.

Due to the separation of charge during the heterolytic fission, the dipole moment increases along the path from the reactant to the transition state (TS), with largest modifications of the reaction profile occurring near the TS. The barrier is significantly reduced by \(\sim 4\) kcal/mol (with \(\lambda = 0.02\) a.u.) representing \(-20\%\) of the bare energy barrier due to stabilization of the TS by the cavity mode, exclusively due to the Debye interaction. Another important result is that the position of the TS (circles in plot) is shifted to shorter C-Cl bond lengths as the light-matter interaction increases. Since these results are based on Eq. 2, which was derived from perturbation theory, we checked our results by performing direct optimization on the CBOA surface defined by Eq. 1. (triangles in Figure 2). Both results are in very good agreement, proving the suitability of Eq. 2 to calculate energy shifts when a molecule is placed in a plasmonic nanocavity and confirming that TS structures can be modified in such a scenario. In particular, the C-Cl bond length of the TS is shortened by \(-0.18\) Å and one of the C-C-Cl angles increases by \(13^\circ\) for \(\lambda = 0.02\) a.u. as compared to the case with no coupling (Supporting information).

In the Menshutkin reaction, an ammonia molecule attacks the carbon center in methyl chloride, leading to a pentacoordinate TS, with an energy barrier of \(-13\) kcal/mol and eventual formation of an ion-pair product complex. In this case the dipole moment also increases along the course of the reaction, thus the greatest modifications on the reaction profile are observed from the TS onwards, as shown in Figure 2.
3. The energy barrier decreases ~20% for \( \lambda = 0.02 \) a.u., with the Debye interaction contributing 84% and the London one accounting for 16%. Although the London force does not dominate the change in barrier, it serves to illustrate that in cases where the molecular polarizability varies along the reaction path, London interactions can play an important role. By means of the proposed self-induced effect, note also that the product complex in this reaction is greatly stabilized relative to the reactants by the presence of the nanocavity, making the reaction more exothermic. This suggests that the competition between forward and backward processes in some reactions may also be altered in such a scenario.

Serving as an example of manipulation of molecular properties in the present QED scenario, in the following we show how control over the spin states of spin-crossover[32] (SCO) complexes and their characteristic transition temperature \( T_{1/2} \) can be also achieved. In these systems, the electronic energies of two spin states are close enough that a transition between them can be thermally induced. This is because the high-spin (HS) state is entropically favored, and is thus the one preferred at higher temperatures while the low-spin (LS) state prevails at lower ones, and at \( T_{1/2} \), both spin states are equally populated. We propose coupling to a nanocavity mode as a novel way to control the relative energy of the LS and HS states in transition metal complexes and thus modulate their SCO behavior. To illustrate this, we have considered four-coordinated Fe(II) phosphoramidato complexes of general formula Pb(MeMesIm)Fe=PR\(_3\) with R=H, Me, "Pr, Ph (Figure 4) that undergo a thermally induced \( S=0 \) to \( S=2 \) spin-crossover transition in solution, and for which a correlation between \( T_{1/2} \) and the size of the phosphine ligand was found.\[33\] The intimate relation between the electronic structure and the corresponding SCO behavior was analyzed in further detail in a recent computational study.\[34\]

Figure 4. Chemical structure of the considered Fe(II) complexes with R=H, Me, "Pr, Ph. Schematic diagram of the d-orbital splitting corresponding to \( C_v \) point group symmetry.

As shown in Table 1, the computed electronic energies of the LS and HS states of the Fe(II) complexes are close enough, within 2-6 kcal/mol, a necessary condition to enable SCO. By considering the \( \Delta G \) temperature dependence, the \( T_{1/2} \) values were estimated (Supporting Information), reproducing the already observed trend of decreasing \( T_{1/2} \) with increasing phosphine size.\[33,34\]

| R    | \( E_{LS}-E_{HS} \) (kcal/mol) | \( \mu \) (D) | \( T_{1/2} \) (K) |
|------|--------------------------------|-------------|-----------------|
| H    | -5                             | 2.05        | 4.60            | 392 | 417 | 423 |
| Me   | -6                             | 3.21        | 6.20            | 340 | 351 | 384 | 396 |
| "Pr  | -4                             | 3.05        | 6.26            | 214 | 192 | 226 | 237 |
| Ph   | -2                             | 2.31        | 5.56            | 81  | 74  | 98  | 103 |

[\( a \)] \( \mu \)s and \( \mu \)_s aligned with the polarization of the plasmonic mode. [\( b \)] \( \mu \)s aligned with the polarization of the plasmonic mode and perpendicular to \( \mu \)s.

When coupling to a nanocavity mode, the molecular dipole moment is the key magnitude dictating how the electronic energy will be affected. In the present case, the dipole moment for the LS state lies along the Fe−N \( \equiv P \) axis, while for the HS state, linearity is lost and the dipole moment is practically parallel to the N \( \equiv P \) axis which is off by ~20º from the B···Fe axis. The different occupation of the MOs in both spin states leads to a dipole moment ~ 3 D on average from the B···Fe axis. The different occupation of the MOs in both spin states leads to a dipole moment ~ 3 D on average from the B···Fe axis. The different occupation of the MOs in both spin states leads to a dipole moment ~ 3 D on average from the B···Fe axis.

Table 1. Energy difference between the low and high spin state of the studied Fe(II) complexes together with their dipole moment and the experimental and estimated SCO transition temperature.

In summary, we have demonstrated how plasmonic nanocavities can modify chemical reaction pathways without...
the need of external stimuli, neither photonic nor electric. By taking advantage of the strong coupling between the dipole moment of the molecule and the confined EM field associated with plasmonic modes, a self-induced Casimir-Polder force, which critically depends on the reaction coordinate, is able to tailor the ground-state chemical landscape of the molecule. We illustrate this finding by analyzing how the rates of two prototypical $S_1$ and $S_2$ reactions can be altered when the molecules are placed inside a plasmonic nanocavity. In addition, we show how this strategy can also be exploited to manipulate spin states of spin-crossover complexes. This new capability of plasmonic modes to modify molecular properties adds a powerful tool to the long-established and fruitful relation between Chemistry and Plasmonics.

Acknowledgements

We are grateful to Dr. Jordi Cirera for advice regarding the modeling of SCO complexes. This work has been funded by the European Research Council (ERC-2016- STG-714870) and the Spanish MINECO under contract MAT2014-53432-C5-5-R and the “María de Maeztu” programme for Units of Excellence in R&D (MDM-2014-0377), as well as through a Ramón y Cajal grant (JF).

References

[1] C. R. Hickenboth, J. S. Moore, S. R. White, N. R. Sottos, J. Baudry, S. R. Wilson, Nature 2007, 446, 423–427.
[2] M. T. Ong, J. Leiding, H. Tao, A. M. Virshup, T. J. Martínez, J. Am. Chem. Soc. 2009, 131, 6377–6379.
[3] J. Ribas-Arín, M. Shiga, D. Marx, Angew. Chemie - Int. Ed. 2009, 48, 4190–4193.
[4] W. Quapp, J. M. Boill, J. Ribas-Arín, J. Phys. Chem. A 2017, 121, 2820–2838.
[5] S. Shaik, S. P. De Visser, D. Kumar, J. Am. Chem. Soc. 2004, 126, 11746–11749.
[6] R. Meir, H. Chen, W. Lai, S. Shaik, ChemPhysChem 2010, 11, 301–310.
[7] A. C. Aragonès, N. L. Haworth, N. Darwish, S. Ciampi, N. J. Bloomfield, G. G. Wallace, I. Díez-Perez, M. L. Coote, Nature 2016, 537, 88–91.
[8] S. Shaik, D. Mandal, R. Ramanan, Nat. Chem. 2016, 8, 1091–1098.
[9] S. D. Fried, S. G. Boxer, Annu. Rev. Biochem. 2017, 86, 387–415.
[10] V. V. Welborn, L. Ruiz Pestana, T. Head-Gordon, Nat. Catal. 2018, 1, 649–655.
[11] P. Christopher, H. Xin, S. Linic, Nat. Chem. 2011, 3, 467.
[12] S. Mukherjee, F. Libisch, N. Large, O. Neumann, L. V. Brown, J. Cheng, J. B. Lassiter, E. A. Carter, P. Nordlander, N. J. Halas, Nano Lett. 2013, 13, 240–247.
[13] Y. Kim, E. Kazuma, Angew. Chemie Int. Ed. 2018, 2–11.
[14] E. Cortés, Science, 2018, 362, 28–29.
[15] D. G. Baranov, M. Wersäll, J. Cuadra, T. J. Antosiewicz, T. Shegai, ACS Photonics 2018, 5, 24–42.
[16] T. W. Ebbesen, Acc. Chem. Res. 2016, 49, 2403–2412.
[17] J. Feist, J. Galego, F. J. García-Vidal, ACS Photonics 2018, 5, 205–216.
[18] R. F. Ribeiro, L. A. Martínez-Martínez, M. Du, J. Campos-Gonzalez-Angulo, J. Yuen-Zhou, Chem. Sci. 2018, 9, 6325–6339.
[19] M. Hertzog, M. Wang, J. Mony, K. Börjesson, Chem. Soc. Rev. 2019, 937–961.
[20] A. Thomas, J. George, A. Shalabney, M. Dryzhakov, S. J. Varma, J. Moran, T. Cherry, X. Zhong, E. Devaux, C. Genet, et al., Angew. Chemie - Int. Ed. 2016, 55, 11462–11466.
[21] A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A. Vergauwe, J. George, T. Cherry, A. Shalabney, E. Devaux, C. Genet, J. Moran, et al., Science, 2019, 363, 615–619.
[22] J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, T. W. Ebbesen, Angew. Chemie - Int. Ed. 2012, 51, 1592–1596.
[23] J. Galego, C. Climent, F. J. García-Vidal, J. Feist, arXiv:1807.10846 2018, 1–22.
[24] J. Flick, H. Appel, M. Ruggenthaler, A. Rubio, J. Chem. Theory Comput. 2017, 13, 1616–1625.
[25] H. B. G. Casimir, D. Polder, Phys. Rev. 1948, 73, 360–372.
[26] P. W. Milonni, in Quantum Vac. (Ed.: P. W. Milonni), Academic Press, San Diego, 1994, pp. 77–114.
[27] C. Genet, F. Intravaia, A. Lambrecht, S. Reynaud, Ann. la Fond. Louis Brogie 2004, 29, 331–348.
[28] Casimir, H. B. G., J. Chim. Phys. 1949, 46, 407–410.
[29] S. Y. Buhmann, Dispersion Forces I: Macroscopic Quantum Electrodynamics and Ground-State Casimir, Casimir–Polder and van Der Waals Forces, Springer-Verlag, Berlin, 2012.
[30] J. Clayden, N. Greeves, S. Warren, in Org. Chem., 2012.
[31] A. N. Jay, K. A. Daniel, E. V. Patterson, J. Chem. Theory Comput. 2007, 3, 336–343.
[32] P. Gamez, J. S. Costa, M. Quesada, G. Aromi, Dall. Trans. 2009, 7845.
[33] H. J. Lin, D. Siretanu, D. A. Dickie, D. Subedi, J. J. Scepaniak, D. Mitcov, R. Ciérac, J. M. Smith, J. Am. Chem. Soc. 2014, 136, 13326–13332.
[34] J. Cirera, E. Ruiz, Inorg. Chem. 2016, 55, 1657–1663.
Supporting Information

Plasmonic Nanocavities Enable Self-Induced Electrostatic Catalysis
Cláudia Climent,* Javier Galego, Francisco J. Garcia-Vidal and Johannes Feist*

(I) Computational details

All electronic structure calculations were performed with density functional theory (DFT) and the Gaussian 09 (Revision E.01) package.[1] For both SN1 and SN2 reactions, calculations were carried out at the B3LYP/6-31+G(d,p) level and solvent effects of water were considered via a polarizable continuum model (PCM) with the IEF-PCM formalism.[2–4] Geometry optimization of minima and transition states were performed together with frequency analysis and reaction paths were computed via the intrinsic reaction path (IRC) approach. Note that we checked our results with different basis sets and found that the 6-31+G(d,p) basis set is the minimal necessary one (for the SN1 reaction) since we are dealing with charge separation as well as calculations with an electric field. Similar results to those with the 6-31+G(d,p) basis set were obtained with the analogous triple-ζ basis set or when including double diffuse or more polarization functions. For the London contribution in equation 2 of the main text we used an effective frequency $\omega$ of $3$ eV.

For the spin-crossover Fe(II) complexes, the hybrid-meta GGA functional TPSSh[5,6] was used and the fully optimized contracted triple-ζ all-electron Gaussian basis set developed by Ahlrichs and co-workers was employed for all the elements with additional polarization functions on the Fe atom. This level of theory was the one used in the previous study by Cirera and coworkers on the Fe(II) complexes we study herein, and proved to give satisfactory results.[7] The high and low spins states were optimized and their frequencies calculated to determine the temperature dependence of $\Delta G$. This was done by considering vibrational (within the harmonic approximation) and electronic contributions to the enthalpy and entropy of each spin state by means of the standard procedure with the statistical thermodynamics expressions for an ideal gas. The spin-crossover transition temperature was determined from its definition $\Delta G(T_{1/2})=0$. This approach has proved to give satisfactory results when modeling spin-crossover transition temperatures.[8–10] For the spin-crossover complex with R=Ph, a linear fit at higher temperatures (> 300K) was used to determine $T_{1/2}$ due to its low value. This is because at lower temperatures $\Delta G$ is no longer linear with the temperature due to the temperature dependence of the vibrational enthalpy and entropy contributions, and it is well-known that low-energy frequencies are problematic because the harmonic approximation fails. We point out that for the plasmonic nanocavity case we diagonalized the Hessian to find the frequencies of the coupled system,[11] for which the derivatives of the permanent dipole moment with respect to the normal modes are needed. The effective frequency $\omega$ used was in the IR range, and we found no resonant effect for the estimated SCO temperatures.

(II) Additional comments

SN1 reaction

For the initial step of the SN1 reaction, when the leaving group separates, we found two transition states (TS) very close in energy. The reaction profiles in both cases were very similar. The difference resides in that for one of the reaction paths, the two methyl groups rotate asynchronously in opposite directions until reaching the TS while for the other one, these two methyl groups do not rotate with respect to each other, and it is the remaining methyl group that rotates along the reaction coordinate. Note that after this transition state, a carbocationic intermediate would exist in solution, stabilized by specific solute-solvent interactions with water molecules. This cannot be taken into account in our calculations since we are only modeling the electrostatic effect of water by means of its dielectric constant in the PCM model and not considering explicit solvent molecules. However, in this work we are particularly interested in how the energy barrier is lowered in the initial step, which is the rate-determining one.

SN2 reaction

We confirmed the validity of the dipole approximation by considering the spatial dependence of the coupling between the molecular permanent dipole moment and the plasmonic mode (represented as a point dipole). Very similar profiles along the reaction coordinate for the couplings considered in (i)-(iii) were obtained.

(i) The interaction between the permanent dipole moment of the entire molecular system coupled to the electric field created by the plasmonic mode at the center of mass of the molecular system, $\mu(x,R) \cdot E(r_m)$
(ii) Analogous to (i) but considering the spatial dependence of the electric field
(iii) The interaction between all the charges of the molecular system (electrons and nuclei) with the potential created by the plasmonic mode at each position $\sum_j q_j \phi(r_j)$. 

Optimization with self-consistent electric field
The Hamiltonian in equation 1 of the main text can be optimized with respect to $q_k$ and $R$ in two consecutive steps. By first minimizing in $q_k$, one can then optimize with respect to $R$ with any electronic structure code which can include an electric field in the calculation, with this one being $E = \lambda \hat{\lambda} \cdot \langle \hat{\mu}(\hat{z}; R) \rangle$ at the minimum of all $q_k$. Note that the electric field depends on the molecular dipole moment.

(III) Tables and Figures

**Figure S1.** Profile of molecular dipole moment for the considered $S_N1$ (left) and $S_N2$ (right) reactions.

**Figure S2.** Reaction profile for the initial step of the $S_N1$ reaction involving leaving group separation of tert-butyl chloride. Increasing color darkness corresponds to increasing coupling strength ($\lambda = 0, 0.01, 0.015, 0.0175, 0.02$ a.u.). Blue circles correspond to the TS within perturbation theory.

**Table S1.** Geometrical parameters for the $S_N1$ TS optimized self-consistently with an electric field for different coupling strengths.

| $\lambda$ (a.u.) | d(C-Cl) (Å) | C-C-Cl angle (°) |
|-----------------|-------------|------------------|
| 0.0000          | 3.395       | 96 96 80         |
| 0.0100          | 3.417       | 95 96 82         |
| 0.0150          | 3.413       | 94 94 85         |
| 0.0175          | 3.356       | 93 93 90         |
| 0.0200          | 3.218       | 92 92 94         |
(IV) References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., Gaussian 09, Revision E.01, Gaussian Inc., Wallingford, CT, 2009.

[2] A. D. Becke, J. Chem. Phys. 1993, 98, 5648–5652.

[3] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785–789.

[4] B. Mennucci, E. Cancès, J. Tomasi, J. Phys. Chem. B 1997, 101, 10506–10517.

[5] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, Phys. Rev. Lett. 2003, 91, 146401.

[6] V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, J. Chem. Phys. 2003, 119, 12129–12137.

[7] J. Cirera, E. Ruiz, Inorg. Chem. 2016, 55, 1657–1663.

[8] K. P. Jensen, J. Cirera, J. Phys. Chem. A 2009, 113, 10033–10039.

[9] J. Cirera, F. Paesani, Inorg. Chem. 2012, 51, 8194–8201.

[10] J. Cirera, M. Via-Nadal, E. Ruiz, Inorg. Chem. 2018, 57, 14097–14105.

[11] J. Galego, C. Climent, F. J. Garcia-Vidal, J. Feist, arXiv:1807.10846 2018, 1–22.
