



DALHOUSIE UNIVERSITY

Retrieved from DalSpace, the institutional repository of
Dalhousie University

<https://dalspace.library.dal.ca/handle/10222/79652>

Version: Post-print

Publisher's version: Dale, Stephen; and Johnson, Erin. (2017). Thermodynamic cycles of the alkali metal-ligand complexes central to electride formation. *Physical Chemistry Chemical Physics*, 19, 12816-12825. <https://doi.org/10.1039/C7CP00882A>

Thermodynamic cycles of the alkali metal-ligand complexes central to electride formation

Stephen G. Dale^{1,2, a)} and Erin R. Johnson^{2, b)}

¹⁾*Chemistry and Chemical Biology, School of Natural Sciences,
University of California, Merced, 5200 North Lake Road, Merced, California 95343,
USA*

²⁾*Department of Chemistry, Dalhousie University, 6274 Coburg Rd,
P.O.Box 15000 B3H 4R2, Halifax, Nova Scotia, Canada*

(Dated: 20 April 2017)

Alkali metal-ligand complexes are the building blocks of the exotic organic alkalide and electride materials. In this work, density-functional theory is used to construct thermodynamic cycles for the alkali metal-ligand complexes, highlighting the energy changes that enable alkalide and electride formation. Strong alkali metal- and cation-to-ligand binding energies are predicted and Rydberg-like ground states of the alkali metal-ligand complexes are identified, consistent with previous work. Calculations on molecular electride species do not reveal consistency with the identified trends, suggesting that the molecular electriles are a class of material unto themselves. The ionisation potentials of the alkali metal-ligand complexes are calculated to be consistently between 1 and 2 eV, suggesting that a specific ionisation potential (IP) is central to electride formation. Further, the thermodynamic cycle for the simplest electride, $\text{Cs}^+(\text{15C5})_2\text{e}^-$, shows stabilisation of the solid crystal due to electride formation that is consistent in magnitude with the IP of the equivalent alkali metal-ligand complex. In light of this, computational screening of the alkali metal-ligand complexes' IP presents a new design criterion for alkalide and electride materials.

^{a)}Electronic mail: stephen.dale@dal.ca

^{b)}Electronic mail: erin.johnson@dal.ca

I. INTRODUCTION

Alkalides and electrides are two of the most unique and chemically counter-intuitive classes of materials available today. Both substances are ionic with exotic anions, specifically negatively-charged alkali metals and localised electrons, respectively. The peculiar make-up of the alkalide and electride crystals conveys unusual properties, which allow for numerous potential applications; existing examples include improved cathodes for fluorescent lights,¹ organic-light emitting diodes,² improved catalysts for CO₂³ and N₂⁴⁻⁶ splitting, in electrochemical reactions,⁷ and as powerful, selective reducing agents.⁸⁻²⁶ The structure, properties and potential uses of these materials has been the primary focus of existing research in this area.¹⁻⁴⁷ The exploration of the energetic mechanisms that allow the alkalide and electrides to exist stably are scarce, and generally focus on very specific examples.⁴⁸⁻⁵⁰ The two studies that do take a more general approach were conducted in the early days of alkalide and electride research and use experimental data to estimate thermodynamic values for the few existing and many hypothetical alkalide materials^{51,52} (at the time). The present work uses theoretical methods (and the benefit of hindsight) to quantify the typical energy changes required for the formation of alkalide and electride materials.

The organic alkalides and electrides are synthesised by first dissolving an alkali metal in an appropriate solvent to form a solvated-electron solution. Ring- and cage-like ligands are then added to the solution and coordinate to the alkali metal cations. The ligand molecules used in the synthesis of alkalides and electrides are typically complex, with long IUPAC names. In this work we have used abbreviations consistent with previous publications.^{28,29,31,33,38,41,43,49,50,53-58} Once the alkali cation-ligand complex has formed, solvent is then removed via evaporation and addition of less favourable solvents.^{36,52,59} Alternatively a saturated solution of the alkali metal-ligand complex can be cooled to crystallize the desired material.^{36,52,59} As crystallisation occurs, the solvated electrons do not recombine with the parent alkali metal atoms, which are stabilised by the coordinating ligands. Rather, the electrons localise on the excess alkali metals atoms or within the voids of the resulting crystal structure.^{42,50}

The alkali metal-ligand complexes are the building blocks of the alkalide and electride materials. These neutral complexes possess a very diffuse valence state and were coined ‘expanded atoms’ by Wagner and Dye in 1993. Early attempts to understand the energetic

changes governing the formation of the alkalides and electrides focussed on the relative energies of these complexes, their cations, and the component ligands, metal atom, or ion. Thermodynamic cycles were constructed relying on known or estimated data,^{51,52} or measurements that had been taken between synthetic steps,⁴⁸ to assess the stability of the existing and potentially new alkalide or electride materials. A general form of this thermodynamic cycle is given in Figure 1. Specifically we calculate the values ΔE_a , ΔE_b , ΔE_c and ΔE_d :

$$\Delta E_a = E_{[ML]^+} - E_{ML} \quad (1)$$

$$\Delta E_b = E_{M^+} - E_M \quad (2)$$

$$\Delta E_c = (E_{M^+} + E_L) - E_{[ML]^+} \quad (3)$$

$$\Delta E_d = (E_M + E_L) - E_{ML} \quad (4)$$

where E_{ML} is the energy for the alkali metal-ligand complex, $E_{[ML]^+}$ is the energy of the alkali cation-ligand complex and E_L is the energy of the ligand molecule. E_M and E_{M^+} are the energies of the alkali metal atom and cation, respectively.

The specific thermodynamic data to which Dye had access was the electron affinities of the elemental atoms,⁶⁰⁻⁶² energy differences between the solid and gaseous elements,⁶³ and statistical-thermodynamic calculations of the entropies of gaseous species.⁶⁴ In some cases, calorimetric measurements of the binding energies of the complexing ligands to the alkali metal cations were available.⁶⁵ The remaining thermodynamic values had to be estimated. The free energies and enthalpies of formation of Cl^- , Br^- , and I^- in ammonia,⁶⁶ along with the appropriate gas-phase data was used to estimate the solvation energies of the alkali-metal anions based on the anion radius, analogous to the Born equation.⁶⁷ The alkali-metal anion radii were estimated by subtracting the radii of the alkali-metal cations from the interatomic distance of equivalent alkali-metal atoms in the metallic phase⁶⁸ (or in the case of Cs, the interatomic distance of Cs-Au in the ionic compound CsAu ⁶⁹). Lattice energies of the resulting ionic solids were estimated using the Kapustinskii equation.⁷⁰ This analysis successfully predicted the stability of the alkali metal-ligand complexes that form the known alkalides and electrides (at the time).^{51,52} Expansion of this analysis to hypothetical alkali metal-ligand complexes predicted potential new alkalide and electride materials.^{51,52} However, Dye commented that even small errors in the energy differences between each state

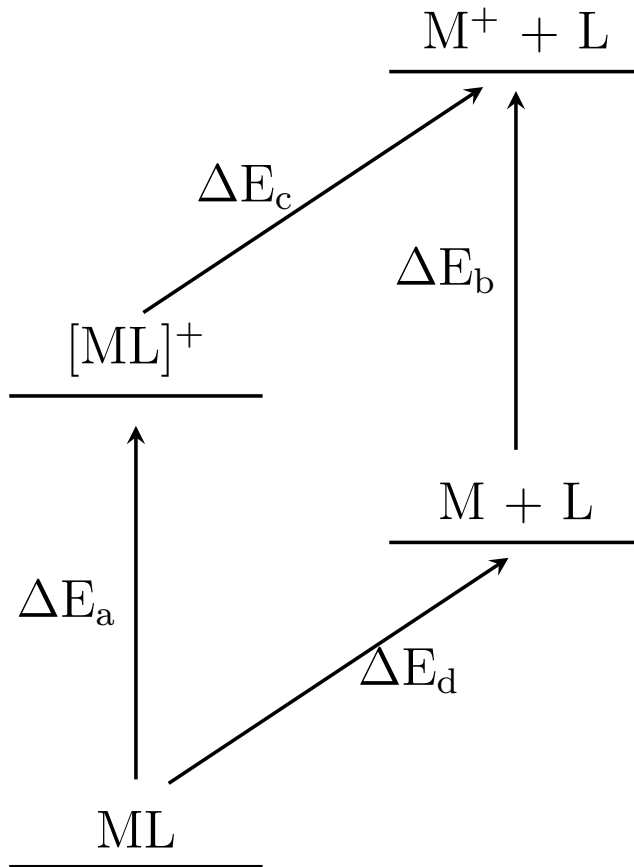


FIG. 1: A general thermodynamic cycle used to display the relative stabilities of the alkalide and electride complexes, relative to the reagents from which they are formed. M, L and ML refer to the alkali metal, ligand molecule, and alkali metal-ligand complex, respectively.

would make this method of analysis almost useless.⁵¹

The thermodynamic quantities estimated by Dye can be calculated using computational methods. However, there have been relatively few attempts to predict these energy differences as the vast majority of computational studies focus on either verifying the existence of the localised electron in the electride crystals^{49,53,71–85} or linking macroscopic properties of these materials to their electronic structure.^{81,86–94} There are only three studies that discuss the energetics of the alkali metal-ligand complexes in the context of alkalide and electride formation and even they retain different primary goals. The earliest example of this, by Rencsok *et al.* was specifically interested in justifying the depletion of electron spin-density experimentally observed at the Cs nucleus of $Cs^+(15C5)_2e^-$ and $Cs^+(18C6)_2e^-$ (the two electrides of known crystal structure then available).⁴⁹ However, with the smallest of these complexes containing 275 electrons, the computational resources available at the time re-

stricted the modelling of these alkali metal-ligand complexes to a single electron contained within two spherical charged shells surrounding a caesium core.⁴⁹ So that a detailed, all-electron analysis could still be conducted, an alternative, hypothetical alkali metal-ligand complex was proposed, $\text{Li}(9\text{C}3)_2$, this time containing 183 electrons. By taking advantage of symmetry and a modest basis set size (6-31G, specifically no diffuse orbitals) it was possible to conduct calculations on this system.⁴⁹ This analysis found a positive highest-occupied molecular orbital (HOMO) energy which was, as noted by the authors, probably due to the lack of diffuse orbitals in the basis set. A subsequent study revisited the $\text{Li}(9\text{C}3)_2$ complex using expanded basis sets (up to 6-31++G**) and identified a bound ‘Rydberg-type’ HOMO.⁵³ Further, Rencsok *et al.* noted a significant decrease in the ionisation potential of the complex compared to the bare lithium atom and argued that the complex was thermodynamically stable.⁵³

The only other study to examine directly the alkali metal-ligand complexes was the first to use computational methods to help design an alkalide and electride, and also the first to produce a room-temperature-stable organic electride, $\text{Na}^+(\text{tri-pip-aza-2.2.2})\text{e}^-$.⁵⁰ In this study, Redko *et al.* calculated the binding energies for a set of complexant ligands to the sodium cation; this corresponds to ΔE_c in Figure 1. From this set, the ligand with the highest predicted binding energy was chosen as the synthesis target. This ligand was then used to produce the first room-temperature-stable organic electride. In the present work, we calculate the full thermodynamic cycle for this, and other, alkali metal-ligand complexes to provide a more complete picture of the energy changes governing alkalide and electride formation. Direct comparison between the calculations conducted by Redko *et al.* and the present results is made in Section III B.

More recently, a new class of materials related to the alkalides and electrides has emerged: the molecular electrides (sometimes called superalkalies).^{56,57,95–112} The molecular electrides are an entirely theoretical construct based on substituting known complexant ligands of the alkalide and electride materials with new, untested ligands.⁵⁶ Studies of the molecular electrides have widely varied the type of complexant ligand, from very simple (NH_3),⁹⁷ to very complex (calix[4]pyrrole).⁵⁶ The primary requirement to be called a molecular electride is for the HOMO to be highly diffuse, similar to the Rydberg-like state observed by Rencsok *et al.*⁵³ Alternatively, if an extra alkali-metal atom is included, the highly-diffuse HOMO will localise primarily on the extra alkali metal, giving it a negative charge and forming

an alkalide-like molecule. The highly-diffuse HOMO gives these materials remarkable non-linear optical properties; in particular, the calculated hyperpolarisabilities are exceptionally high.^{95–100,102,104,105,111,112} However, both the energetic analysis of how these complexes might form and experimental investigation of these materials is still limited. We include some of the molecular electride species in this work to assess whether the synthetic methods used for the alkalide and electride materials might be transferable.

This article uses density-functional theory (DFT) to perform the first rigorous investigation of the thermodynamic cycles for the alkali metal-ligand complexes. The present work benefits from the past three decades of research, which provides an extensive set of alkali metal-ligand complexes that form the building blocks of the stable alkalide and electride materials. Structural analogues of these complexes, made by systematically varying the identity of the metal atom within the group, are also considered in order to study periodic trends. The existence of the Rydberg-like ground state for the neutral alkali-metal complexes, identified by Rencsok *et al.*, is verified.⁵³ The DFT analysis of the thermodynamic cycle reveals that the electron-rich ligands uniformly lower the IP of the complex to ca. 1-2 eV, providing a new design criteria for electride formation. A combination of the weakly-bound HOMO of the neutral complex and strong ligand coordination to the alkali cation constitute the thermodynamic driving force behind alkalide or electride formation. Finally, we construct a second thermodynamic cycle for the lattice energy of the simplest electride crystal, $\text{Cs}^+(\text{15C5})_2\text{e}^-$, and verify that the stabilisation of the electride complex predicted by the gas-phase calculations is comparable to the stabilisation observed in the solid state.

II. COMPUTATIONAL METHODS

The molecular geometries of the alkali metal-ligand complexes, alkali cation-ligand complexes and independent ligand molecules were optimized using the B3LYP¹¹³ functional with 6-31+G* basis set¹¹⁴ and the exchange-hole dipole (XDM)¹¹⁵ dispersion model. Rb and Cs were assigned the Def2-TZVP basis set and accompanying ECP.¹¹⁶ Single-point energy calculations were performed on the isolated alkali metal atoms and cations using identical theoretical methods. All calculations were conducted using the Gaussian 09¹¹⁷ and postg programs.¹¹⁸ The results of these calculations were then used to determine the energy differences for the thermodynamic cycle shown in Figure 1. Table I gives a full summary of

the alkali metal-ligand complexes for which calculations were conducted. The Cambridge Structural Database¹¹⁹ (CSD) codes for alkalide and electrone crystal structures containing the alkali metal-ligand complexes are given, where applicable.

The unit-cell geometry of the simplest electrone, $\text{Cs}^+(\text{15C5})_2\text{e}^-$, was taken directly from its experimental crystal structure.³⁴ Full relaxation of the atomic positions and cell dimensions, under periodic boundary conditions, was performed using the B86bPBE functional¹²⁰ and the XDM dispersion model,^{121,122} with the Quantum Espresso program.¹²³ This calculation used the planewave/pseudopotentials (PW/PS) approach and the Projector Augmented Wave (PAW) formalism,¹²⁴ with a plane-wave cut-off energy of 50 Ry, a $4\times 4\times 4$ \mathbf{k} -point mesh, and cold smearing¹²⁵ at a temperature of 0.01 Ry. An initial ferromagnetic bias was assigned to $\text{Cs}^+(\text{15C5})_2\text{e}^-$, consistent with our previous work.⁹³ An analogous relaxation calculation was performed on the isolated $\text{Cs}(\text{15C5})_2$ complex in a super-cell (with 10\AA of vacuum added on all sides) using a Γ -centered $1\times 1\times 1$ \mathbf{k} -point mesh. The caesium atom was then removed from the final, relaxed geometries and a single-point energy calculation performed for each case, with all other calculation parameters remaining constant. The resulting caesium binding energies were used to construct the thermodynamic cycle shown in Figure 5, discussed further in Section III C.

Of particular interest, as in many previous studies regarding electrone materials, is the behaviour of the single unpaired electron of the alkali metal-ligand complex. We report spin-density difference plots for four of the alkali metal-ligand complexes, shown in Figure 2, which provide an effective method for visualising the character of the highest-energy valence state, while remaining invariant with respect to unitary orbital transformations. We also provide plots of the HOMO and electron localisation function (ELF)^{126–128} in the Supporting Information. Finally, we use non-covalent interaction (NCI) plots^{129–131} to visualise the binding between the ligand molecules and the alkali-metal cations in the alkali cation-ligand complexes. The ELF and NCI plots were generated using the `critic2`¹³² and `nciplot`¹³³ programs, respectively.

TABLE I: The alkali metal-ligand complexes for which calculations were conducted in this work. The CSD code and source of the original structural representation is also given where available.¹¹⁹ The relative energies represented in Figure 1, the HOMO energies of the alkali metal-ligands (H_{ML}) and bare alkali metal atoms (H_M), are reported (in eV).

CSD Code	Expanded Atom	Ref	ΔE_a	ΔE_b	ΔE_c	ΔE_d	H_{ML}	H_M
Electrides								
ROGDAS	Li(cryptand-2.1.1)	41	1.99	5.62	5.62	1.98	-1.39	-3.65
DAWCIO	Na(tri-pip-aza-2.2.2)	50	1.14	5.41	5.10	0.84	-1.32	-3.51
GAVFIS	K(cryptand-2.2.2)	29	1.24	4.50	4.33	1.06	-1.28	-2.90
EBEWOX	Rb(cryptand-2.2.2)	43	1.61	4.33	3.41	0.70	-1.13	-2.80
TAGFEM*	Cs(15C5) ₂	33	1.40	4.01	3.56	0.95	-1.16	-2.60
DUBCIM†	Cs(18C6) ₂	28	1.26	4.01	4.20	1.45	-1.14	-2.60
WIHFIC	Cs(15C5)(18C6)	38	1.36	4.01	3.93	1.29	-1.15	-2.60
Alkalides								
COJDIO	Li(18C6)(CH ₃ N ₂) ₂	54	2.01	5.62	6.61	2.06	-1.35	-3.65
REGCAH	K(12C4) ₂	55	1.31	4.50	4.36	1.16	-1.29	-2.90
JEPMIA‡	Rb(15C5) ₂	33	1.44	4.33	3.98	1.10	-1.13	-2.80
REGCIP	Rb(18C6)(CH ₃ N ₂)	55	2.08	4.33	3.35	1.11	-1.25	-2.80
JAPVOL	Rb(18C6)	31	2.40	4.33	2.86	0.93	-1.30	-2.80
Additional Complexes								
	Li(9C3) ₂	49	2.16	5.62	5.52	2.06	-1.44	-3.65
	Na(cryptand-2.2.2)		1.60	5.41	4.79	0.98	-1.30	-3.51
	Na(15C5) ₂		1.42	5.41	5.33	1.35	-1.28	-3.51
	K(15C5) ₂		1.15	4.50	4.89	1.56	-1.26	-2.90
	K(tri-pip-aza-2.2.2)		1.04	4.50	4.13	0.67	-1.31	-2.90
	Rb(tri-pip-aza-2.2.2)		1.52	4.33	2.81	0.01	-1.26	-2.80
	Cs(tri-pip-aza-2.2.2)		1.51	4.01	2.84	0.35	-2.48	-2.60
	Cs(cryptand-2.2.2)		1.51	4.01	1.94	-0.56	-2.26	-2.60
Molecular Electrides								
	Li@B ₁₀ H ₁₄	58	6.25	5.62	-0.09	0.54	-4.93	-3.65
	Li-HCN	56	4.36	5.62	1.58	0.31	-2.56	-3.65
	Li@Calix	58	3.43	5.62	3.05	0.70	-2.48	-3.65
	Na@Calix	58	3.30	5.41	2.68	0.32	-2.26	-3.51

* Cs(15C5)₂ is the alkali metal-ligand complex of both an electride with CSD code TAGFEM³³ and an alkalide with CSD code JEPMEW.³³

† Cs(18C6)₂ is the alkali metal-ligand complex an electride with CSD code DUBCIM²⁸ and two alkalides with CSD codes FABMAW³² and FUJCUI.¹³⁴

‡ Rb(15C5)₂ is the alkali metal-ligand complex two alkalides with CSD codes JEPMIA³³ and FABMEA.³²

III. RESULTS AND DISCUSSION

A. The valence state

We begin by visualising the highest-energy valence state for a sample of the alkali metal-ligand complexes using spin-density difference plots, shown in Figure 2. In every case, a highly-diffuse Rydberg-like state is observed. This is consistent with the work of Rencsok *et al.* when examining the $\text{Li}(\text{9C3})_2$ complex⁵³ and reinforces that this is a consistent feature of the alkali metal-ligand complexes that form the alkalide and electride materials. Plots of the HOMO and ELF lead to the same conclusions and are provided in the Supplementary Information.

A thermodynamic cycle, related to those used by Kuchenmeister and Dye,^{48,51,52} was modeled to understand the energy changes required to synthesise alkalide and electride materials. Figure 1 shows this general thermodynamic diagram with the energies ΔE_a , ΔE_b , ΔE_c and ΔE_d calculated as described in Section I and reported in Table I. ΔE_b is simply the calculated ionisation potential of the alkali metal atom and hence has multiple identical entries.

We first note that, with the exceptions of the metal-ligand binding energy for Cs(cryptand-2,2,2) and the cation-ligand binding energy for $\text{Li}@\text{B}_{10}\text{H}_{14}$, all of the energies reported in Table I are positive, validating the rough energy ordering given in Figure 1. Additionally, neither of these exceptions come from complexes derived from known alkalides or electrides. We also note that the molecular electrides are exceptions to the trends discussed in the remainder of this section and this class of compounds will be discussed separately, in Section III D.

The most striking trend observed in Table I is that the ionisation potentials (IP) of the alkali metal-ligand complexes (ΔE_a) are consistently between 1 and 2 eV. The exceptions to this trend all either involve coordination to, and hence stabilisation by, a single crown ether molecule; are complexes of Li, which possesses the highest atomic IP; or both. The extent of ligand-induced IP lowering, relative to the free atom values, decreases down the alkali-metal group. This matches the trends in both the alkali metal-ligand and cation-ligand binding energies to be discussed in Section III B. Further, the HOMO energies found for all of the alkali metal-ligand complexes reported in Table I are almost uniformly -1.3

eV. The HOMO energies of the alkali metal-ligand complexes are consistently higher than the corresponding values for the free metal atoms. This indicates that the electron lone-pairs from the coordinating ligands destabilise the HOMO and cause the valence electron of the metal to become more weakly bound. This is reflected by the very diffuse excess-spin densities seen for the alkali metal-ligand complexes in Figure 2. Additionally, the change in the HOMO energy, relative to the free-metal atom, is again largest for the smallest alkali metals and decreases down the group, consistent with the observed changes in IPs. Taken together with the strong cation-ligand binding energies, the results indicate that the ligand molecules bind to and stabilise the alkali cation directly, while destabilising the HOMO of the alkali metal.

The lowering of the IP and raising of the HOMO energies to almost uniform values suggests that an IP of ca. 1-2 eV is essential to the formation of the alkalide and electride materials. The IP is an effective energy penalty that must be offset by the stabilisation gained from the crystal lattice to make formation of the bulk electrides favourable, and this will be discussed further in Section III C. While the particular energy values calculated might differ based on the level of theory, or the addition of solvent corrections, it is clear that the consistency of the IP/HOMO could make an excellent design criterion for future alkalide or electride materials.

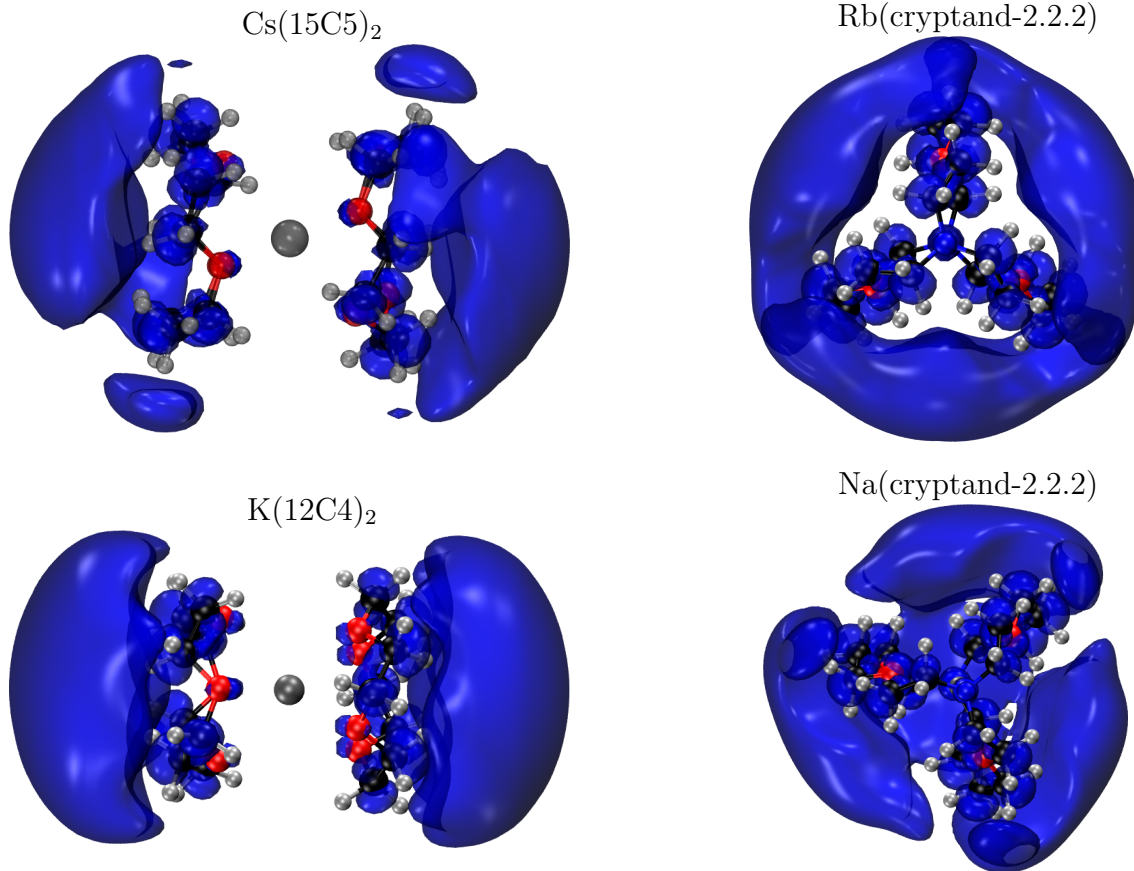


FIG. 2: Spin-density difference plots for four of the alkali metal-ligand complexes, plotted using a 0.001 a.u. isosurface.

B. Binding energies

The binding energies of the ligand molecules to the alkali metal atoms (ΔE_d) and cations (ΔE_c) are reported in Table I. The binding energies are, satisfyingly, consistently positive for the complexes derived from real alkalide and electride materials. For the ligand molecules tri-pip-aza-2.2.2, cryptand-2.2.2, and 15C5, if there was no known complex with the alkali metals Na through Cs, one was constructed from a known complex by changing the identity of the alkali-metal atom. The resulting binding energies are plotted in Figure 3. In general, the highest binding energies are reported for the smallest alkali metals and vice-versa, consistent with well understood electro-negativity trends. There are a few exceptions to this rule for the neutral complexes. For example, the binding energy of Na(cryptand-2.2.2) is 0.98 eV and lower than that of K(cryptand-2.2.2) at 1.06 eV. We propose that this is due to Na only having access to the p-shell for coordination to neighbouring atoms. This limits the coordination number of Na to 6, while K has access to the d-shell and can coordinate

to 8 neighbouring atoms, providing additional stabilisation. Additionally, we note that the neutral metal-ligand binding energy for Cs(cryptand-2.2.2) is negative due to poor size matching between the large Cs atom and the small cage of the cryptand. The Cs–O distances of 2.98Å predicted for this complex are significantly smaller than the sum of the atomic radii (3.2Å)¹³⁵ or the Cs–O distances of 3.12–3.23Å seen for Cs(15C5)₂.

The binding energies are consistently much stronger for the alkali cation-ligand complexes than for the alkali metal-ligand complexes. This makes sense as the ligand molecules generally have inward facing lone-pairs that stabilise the alkali cation; strong cation-ligand binding has previously been used as a criterion for stable electrone formation.⁵⁰ We have visualised the alkali cation-ligand interactions using NCI plots, shown in Figure 4. In each case, interaction between the oxygen or nitrogen lone pairs and the alkali cations is clearly identifiable as small circular disks. Specifically, 10 small disks are observed for Cs⁺(15C5)₂, 8 for Rb⁺(cryptand-2.2.2) and K⁺(12C4)₂, and 6 for Na⁺(cryptand-2.2.2). This is consistent with the p-shell coordination discussed above for the Na(cryptand-2.2.2) complex.

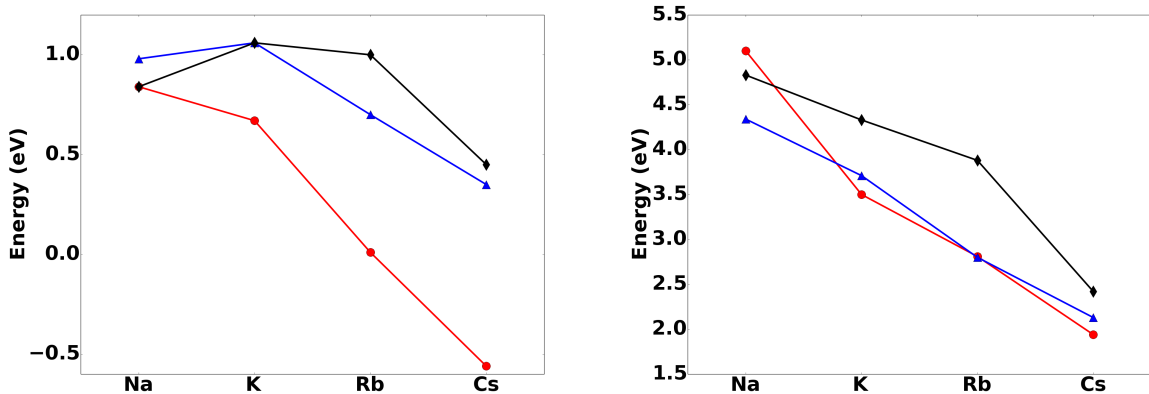


FIG. 3: Plots of the binding energy of the alkali metal atoms(left) and cations(right) to the ligands tri-pip-aza-2.2.2(●), cryptand-2.2.2(▲) and 15C5(◆).

The estimated, gaseous binding energies of the alkali metal cations to the cryptand-2.2.2 ligand (cryptand-2.1.1 for Li) were reported relative to Na⁺(cryptand-2.2.2) by Dye.⁵¹ If we equivalently report binding energies relative to our calculated value for Na⁺(cryptand-2.2.2), direct comparison can be made between these results. This comparison is summarised in Table II. In every case, the relative binding energies are in fairly good agreement. Further, Redko *et al.* calculated the binding energies of the Na⁺(cryptand-2.2.2) and Na⁺(tri-pip-aza-2.2.2) complexes as 4.33 and 4.06 eV, respectively. Our results compare well with these

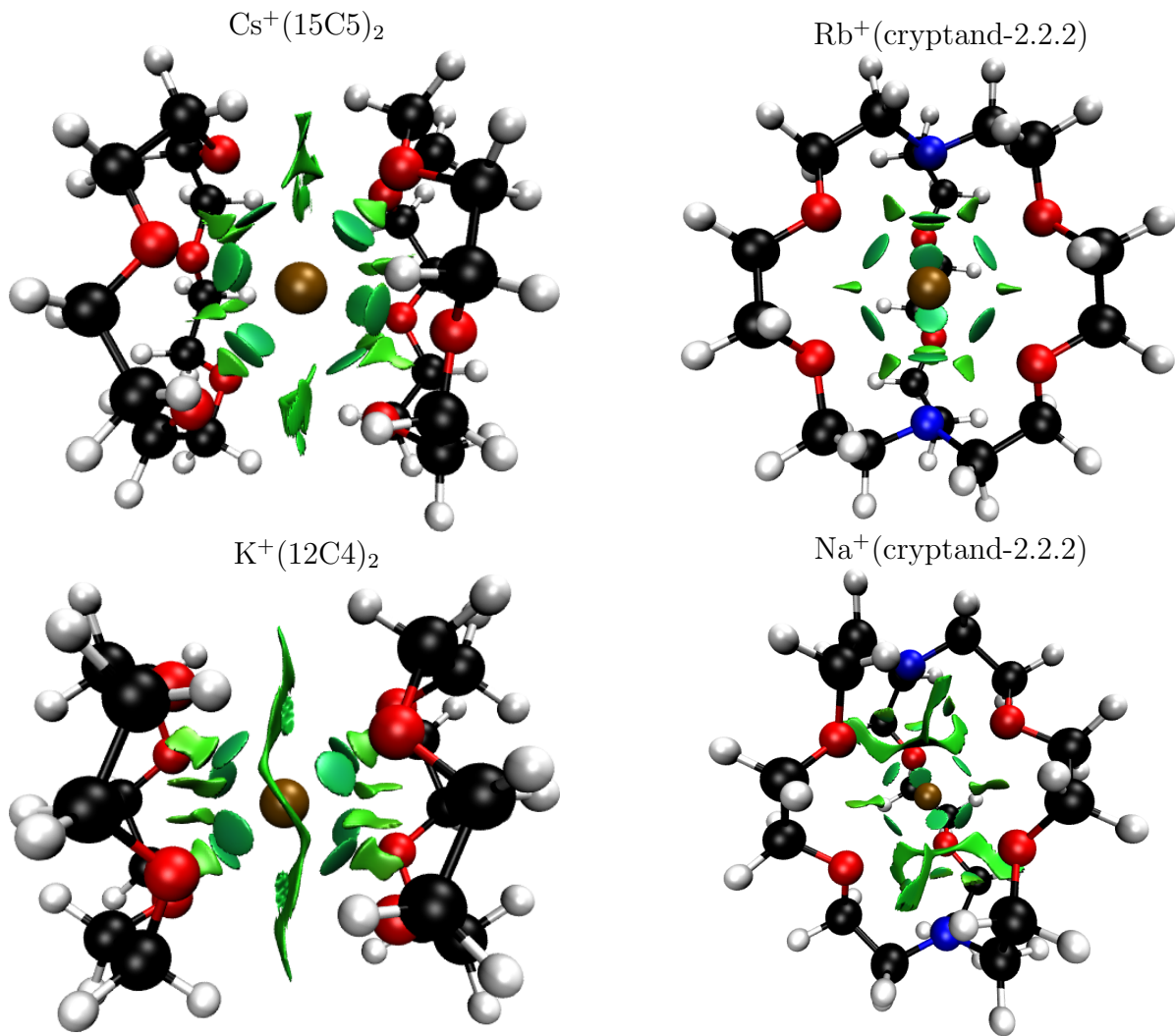


FIG. 4: NCI plots showing the metal ligand interactions for four of the alkali cation-ligand complexes using a 0.5 a.u. isosurface.

values, but are somewhat higher at 4.79 and 5.10 eV. This is to be expected as the inclusion of the XDM dispersion correction in our calculations will increase the binding energies relative to equivalent calculations that do not include dispersion physics.

C. Periodic-Boundary Calculations

To this point, all of the calculations presented in this work have used Gaussian basis sets and are limited to the gas-phase complexes. In this section, we report calculations for the simplest electrone crystal, $\text{Cs}^+(\text{15C5})_2\text{e}^-$, using PW/PS methods and construct a new thermodynamic cycle. This cycle, shown in Figure 5, involves metal-ligand binding

TABLE II: Selected alkali cation-ligand complex binding energies (in eV). Values calculated in this work are compared with those estimated by Dye.⁵¹ All values are expressed relative to the binding energy of the $\text{Na}^+(\text{cryptand-2.2.2})$ complex.

Expanded Atom	Estimated	Calculated
$\text{Li}^+(\text{cryptand-2.1.1})$	-0.96	-0.83
$\text{Na}^+(\text{cryptand-2.2.2})$	-	-
$\text{K}^+(\text{cryptand-2.2.2})$	0.65	0.46
$\text{Rb}^+(\text{cryptand-2.2.2})$	0.93	1.38
$\text{Cs}^+(\text{cryptand-2.2.2})$	1.63	1.95

energies, similar to those in Section III B, as well as lattice energies for the crystalline solid. To construct it, full DFT geometry relaxations were performed for the electrified crystal, and for the isolated alkali metal-ligand complex in a large super-cell ($\text{Cs}^+(\text{15C5})_2\text{e}^-_{(s)}$ and $\text{Cs}(\text{15C5})_{2(g)}$ in Figure 5, respectively). Subsequent single-point energy calculations were performed with the caesium atom removed from the relaxed geometries of either the lattice or complex ($(\text{15C5})_{2(s)}$ and $(\text{15C5})_{2(g)}$ in Figure 5, respectively) in order to determine the metal-ligand binding energies. We note that these periodic-boundary calculations are much more computationally intensive than the finite-molecule ones presented in the previous sections. For this reason, only the simplest electrified crystal is analysed in this manner and presented as an illustrative link between the solid-state and gas-phase calculations.

Both thermodynamic cycles presented in this work provide a direct measurement of the binding energy of the neutral alkali metal ligand-complex, 0.95 eV according to Table I and 1.45 eV according to Figure 5. The 0.50 eV energy difference is quite reasonable given the different functionals and basis sets used (viz. B3LYP-XDM/6-31+G* for the finite-molecule case and B86bPBE-XDM with an effectively-complete planewave basis set for the periodic-boundary case). The use of a hybrid functional and especially a much smaller basis set in the Gaussian calculations are both expected to decrease the binding. Additional differences between these calculations, specifically using the fixed geometry of the complex for the isolated ligands in the PW/PS calculations, are estimated to contribute only 0.07 eV and hence are negligible. With this in mind, the metal-ligand binding energies are quite comparable between the two different calculation styles.

The electrified crystal is expected to be predominately ionic, with the caesium complexes auto-ionising and taking on cationic character, while the ejected electrons localise in the crystal voids. In practise, our previous DFT calculations reveal that the complexes are

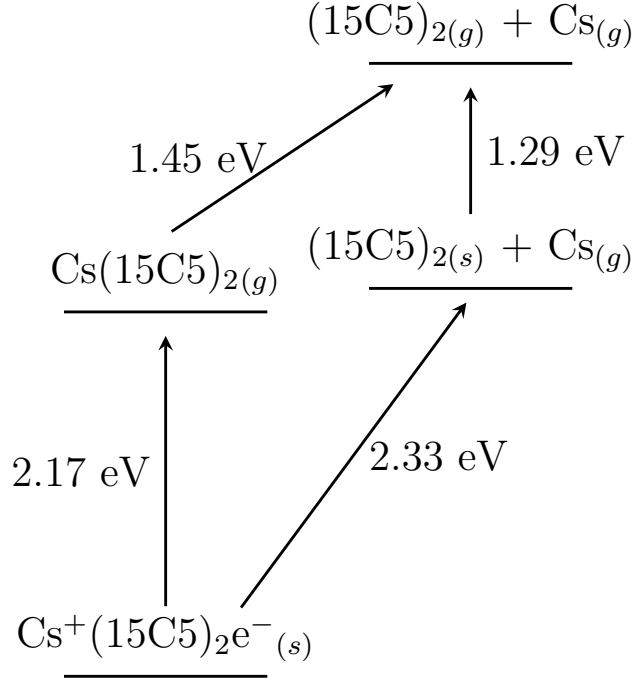


FIG. 5: A thermodynamic cycle of the simplest electride, $\text{Cs}^+(\text{15C5})_2\text{e}^-$, as it is dissociated into its gaseous components.

only partially ionised, with 0.36 of an electron localised within the interstitial, obtained from integration of the electron density regions corresponding to non-nuclear maxima.⁹³ Consequently, the binding energies of the caesium cation and neutral atom to the ligand molecules, reported in Table I as 3.56 and 0.95 eV, respectively, should act as upper and lower bounds to the caesium binding energy in the electride crystal. The calculated binding energy in Figure 5 is 2.33 eV, which is satisfyingly between these two limits.

Finally, the results in Figure 5 display the direct energy benefit of electride formation. The lattice energy for the electride is 2.17 eV, which is much higher than the analogous lattice energy of 1.29 eV for only the ligand molecules, without the caesium atoms present. The 0.88 eV decrease in the lattice energy upon removal of caesium is far more than would be expected from the loss of dispersion energy due to the absence of the metal atoms. Similarly, the metal-ligand binding energy increases by the same amount of 0.88 eV, going from the isolated complex to the solid state. We propose this additional stabilisation of the $\text{Cs}(\text{15C5})_2$ lattice is due to electride formation. In Section III A, we suggested that the stabilisation gained from the lattice energy must exceed the IP of the alkali metal-ligand complex in order to form a stable bulk electride. The calculated IP of 1.40 eV for $\text{Cs}(\text{15C5})_2$ in Table I is

on par with the 1.29 eV lattice energy obtained without caesium, but is significantly lower than the 2.17 eV lattice energy obtained for the full electride crystal, consistent with this conjecture. Thus, it is this extra stabilisation of the lattice that is the driving force for electride formation.

D. Molecular electrides

The molecular electrides are the exception to every trend discussed so far in this work. As shown in Table I, the IPs do not lie between 1 and 2 eV and, in the case of $\text{Li}@B_{10}H_{14}$, the IP and HOMO actually increase compared to the bare Li atom. Also, the binding energies of the alkali metal-ligand complexes are consistently larger than for the equivalent cation complexes. Indeed, the complex $\text{Li}^+@B_{10}H_{14}$ is predicted to be unstable.

It is clear, based on these breaks from the trends identified for the known alkalide and electride materials, that the molecular electrides represent a distinctly different class of materials. The deviation from the observed alkalide/electride trends may actually be necessary for the formation of the molecular electrides. The desirable hyperpolarisability properties of the molecular electrides rely on the highly diffuse, but still bound Rydberg-like state. For this to occur, a larger binding energy and more stable neutral molecular state is reasonable. In contrast, the alkalide and electride materials rely on the low IP and stable ionic complexes to allow the valence electron to dissociate from the alkali cation-ligand complex, first in solution and then in the crystalline state.

IV. CONCLUSIONS

Thermodynamic cycles are a well-established tool for understanding the relative energetics that allow the formation of alkalides and electrides. Density-functional calculations were used to perform the first rigorous investigation of the thermodynamic cycles for the alkali metal-ligand complexes that are the building blocks of these materials. A new, related class of materials, the molecular electrides, was also included in this analysis.

For the complexes derived from alkalides and electrides of known crystal structure, strong binding energies between the alkali cation and the surrounding ligands are predicted. NCI plots show that this binding is primarily due to stabilisation of the cation by oxygen and

nitrogen lone electron pairs, as expected. These findings are consistent with the design requirement proposed by Redko *et al.*⁵⁰ that a strong ligand-cation binding energy is necessary to synthesise an alkalide or electride material.

By plotting the spin-density difference for a sample of the alkali metal-ligand complexes, we identify Rydberg-like states. This is consistent with the hypothetical $\text{Li}(\text{9C3})_2$ complex analysed by Renscok *et al.*⁵³ and the diffuse HOMO states that enable the exceptional hyperpolarisability properties of the molecular electrides. This state is clearly a constant feature of the components of the alkalide and electride materials. With the exception of the Rydberg-like state, we identify no consistent trends between the alkali metal-ligand complexes derived from the known alkalide and electride materials and the theoretically-derived molecular electrides. While the molecular electrides clearly draw inspiration from the electrides, the design philosophy required for their synthesis must differ from the design philosophy highlighted in this work.

Finally, the ionisation potential is calculated to be almost uniformly 1-2 eV for all of the alkali metal-ligand complexes derived from known alkalide and electride crystal structures. Using illustrative periodic-boundary calculations for the $\text{Cs}^+(\text{15C5})_2\text{e}^-$ crystal, we link the IP to the stabilisation of the lattice caused by electride formation. This is a new observation and suggests that a specific IP of the alkali metal-ligand complexes is central to the formation of the alkalide and electride materials. Computational screening of the IP and can be added to the criterion of strong ligand-cation binding energy proposed by Redko *et al.* to inform design of new alkalides and electrides.

V. ACKNOWLEDGEMENTS

The authors would like to acknowledge Dr. Alberto Otero-de-la-Roza for helpful discussions and technical support when using the critic2 program. We also thank the National Sciences and Engineering Research Council of Canada (NSERC) for financial support and the Multi-Environment Computer for Exploration and Discovery (MERCED), as well as Compute Canada (ACEnet and Westgrid), for computational time.

REFERENCES

- ¹S. Watanabe, T. Watanabe, K. Ito, N. Miyakawa, S. Ito, H. Hosono, and S. Mikoshiba, *Sci. Technol. Adv. Mat.* **12**, 034410 (2011).
- ²H. Yanagi, K.-B. Kim, I. Koizumi, M. Kikuchi, H. Hiramatsu, M. Miyakawa, T. Kamiya, M. Hirano, and H. Hosono, *J. Phys. Chem. C* **113**, 18379 (2009).
- ³Y. Toda, H. Hirayama, N. Kuganathan, A. Torrisi, P. V. Sushko, and H. Hosono, *Nat. Commun.* **4**, (2013).
- ⁴M. Kitano, Y. Inoue, Y. Yamazaki, F. Hayashi, S. Kanbara, S. Matsuishi, T. Yokoyama, S.-W. Kim, M. Hara, and H. Hosono, *Nat. Chem.* **4**, 934 (2012).
- ⁵M. Kitano, S. Kanbara, Y. Inoue, N. Kuganathan, P. V. Sushko, T. Yokoyama, M. Hara, and H. Hosono, *Nat. Commun.* **6**, (2015).
- ⁶Y. Lu, J. Li, T. Tada, Y. Toda, S. Ueda, T. Yokoyama, M. Kitano, and H. Hosono, *J. Am. Chem. Soc.* **138**, 3970 (2016).
- ⁷J. Li, B. Yin, T. Fuchigami, S. Inagi, H. Hosono, and S. Ito, *Electrochem. Commun.* **17**, 52 (2012).
- ⁸X. Z. Chen, J. L. Dye, H. A. Eick, S. H. Elder, and K.-L. Tsai, *Chem. Mater.* **9**, 1172 (1997).
- ⁹Z. Grobelny, A. Stolarzewicz, B. Morejko-Buz, R. A. Bartsch, K. Yamato, F. A. Fernandez, and A. Maercker, *J. Org. Chem.* **67**, 7807 (2002).
- ¹⁰Z. Grobelny, A. Stolarzewicz, B. Morejko-Buż, and A. Maercker, *J. Organomet. Chem.* **660**, 6 (2002).
- ¹¹J. A. Nelson and M. J. Wagner, *Chem. Mater.* **14**, 915 (2002).
- ¹²J. A. Nelson and M. J. Wagner, *Chem. Mater.* **14**, 4460 (2002).
- ¹³J. A. Nelson and M. J. Wagner, *Chem. Mater.* **14**, 1639 (2002).
- ¹⁴J. A. Nelson, E. L. Brant, and M. J. Wagner, *Chem. Mater.* **15**, 688 (2003).
- ¹⁵J. A. Nelson and M. J. Wagner, *J. Am. Chem. Soc.* **125**, 332 (2003).
- ¹⁶J. A. Nelson, L. H. Bennett, and M. J. Wagner, *J. Mater. Chem.* **13**, 857 (2003).
- ¹⁷K. E. Mooney, J. A. Nelson, and M. J. Wagner, *Chem. Mater.* **16**, 3155 (2004).
- ¹⁸Z. Grobelny, A. Stolarzewicz, B. Morejko, W. Pisarski, A. Maercker, A. Skibinski, S. Krompiec, and J. Rzepa, *Macromolecules* **39**, 6832 (2006).
- ¹⁹Z. Grobelny, A. Stolarzewicz, and A. Maercker, *Curr. Org. Chem.* **11**, 1126 (2007).

- ²⁰H. Buchammagari, Y. Toda, M. Hirano, H. Hosono, D. Takeuchi, and K. Osakada, *Org. Lett.* **9**, 4287 (2007).
- ²¹O. Zivkovic, K. E. Mooney, and M. J. Wagner, *Chem. Mater.* **19**, 3419 (2007).
- ²²O. Zivkovic and M. J. Wagner, *J. Mater. Chem.* **18**, 2540 (2008).
- ²³O. Zivkovic, C. Yan, and M. J. Wagner, *J. Mater. Chem.* **19**, 6029 (2009).
- ²⁴S. Choi, Y. J. Kim, S. M. Kim, J. W. Yang, S. W. Kim, and E. J. Cho, *Nat. Commun.* **5**, (2014).
- ²⁵Y. J. Kim, S. M. Kim, H. Hosono, J. W. Yang, and S. W. Kim, *Chem. Comm.* **50**, 4791 (2014).
- ²⁶Y. J. Kim, S. M. Kim, E. J. Cho, H. Hosono, J. W. Yang, and S. W. Kim, *Chem. Sci.* **6**, 3577 (2015).
- ²⁷S. B. Dawes, D. L. Ward, R. H. Huang, and J. L. Dye, *J. Am. Chem. Soc.* **108**, 3534 (1986).
- ²⁸S. B. Dawes, A. S. Ellaboudy, and J. L. Dye, *J. Am. Chem. Soc.* **109**, 3508 (1987).
- ²⁹D. L. Ward, R. Huang, and J. L. Dye, *Acta Crystallogr. C* **44**, 1374 (1988).
- ³⁰R. Huang, M. Faber, K. Moeggenborg, D. Ward, and J. Dye, *Nature* **331**, 599 (1988).
- ³¹R. H. Huang, D. Ward, and J. Dye, *J. Am. Chem. Soc.* **111**, 5707 (1989).
- ³²S. B. Dawes, D. L. Ward, O. Fussa-Rydel, R. H. Huang, and J. L. Dye, *Inorg. Chem.* **28**, 2132 (1989).
- ³³D. L. Ward, R. Huang, and J. L. Dye, *Acta Crystallogr C* **46**, 1838 (1990).
- ³⁴S. B. Dawes, J. L. Eglin, K. J. Moeggenborg, J. Kim, and J. L. Dye, *J. Am. Chem. Soc.* **113**, 1605 (1991).
- ³⁵K. J. Moeggenborg, J. Papaioannou, and J. L. Dye, *Chem. Mater.* **3**, 514 (1991).
- ³⁶M. J. Wagner and J. L. Dye, *Annu. Rev. Mater.* **25**, 223 (1994).
- ³⁷M. J. Wagner, R. H. Huang, and J. L. Dye, *J. Phys. Chem.* **97**, 3982 (1993).
- ³⁸M. J. Wagner, R. H. Huang, J. L. Eglin, and J. L. Dye, *Nature* **368**, 726 (1994).
- ³⁹M. Wagner and J. Dye, *J. Solid State Chem.* **117**, 309 (1995).
- ⁴⁰J. Kim, J. L. Eglin, A. S. Ellaboudy, L. E. McMills, S. Huang, and J. L. Dye, *J. Phys. Chem.* **100**, 2885 (1996).
- ⁴¹R. H. Huang, M. J. Wagner, D. J. Gilbert, K. A. Reidy-Cedergren, D. L. Ward, M. K. Faber, and J. L. Dye, *J. Am. Chem. Soc.* **119**, 3765 (1997).

- ⁴²J. Kim, A. S. Ichimura, R. H. Huang, M. Redko, R. C. Phillips, J. E. Jackson, and J. L. Dye, *J. Am. Chem. Soc.* **121**, 10666 (1999).
- ⁴³Q. Xie, R. H. Huang, A. S. Ichimura, R. C. Phillips, W. P. Pratt, and J. L. Dye, *J. Am. Chem. Soc.* **122**, 6971 (2000).
- ⁴⁴D. Smith, B. Williamson, and P. Schatz, *Chem. Phys. Lett.* **131**, 457 (1986).
- ⁴⁵J. L. Dye and M. G. DeBacker, *Annu. Rev. Phys. Chem.* **38**, 271 (1987).
- ⁴⁶M. Y. Redko, R. H. Huang, J. E. Jackson, J. F. Harrison, and J. L. Dye, *J. Am. Chem. Soc.* **125**, 2259 (2003).
- ⁴⁷Z. Grobelny, A. Stolarzewicz, M. Szczepanski, and M. Sokol, *Curr. Org. Chem.* **12**, 1040 (2008).
- ⁴⁸M. E. Kuchenmeister and J. L. Dye, *J. Am. Chem. Soc.* **111**, 935 (1989).
- ⁴⁹R. Rencsok, T. Kaplan, and J. Harrison, *J. Chem. Phys.* **93**, 5875 (1990).
- ⁵⁰M. Y. Redko, J. E. Jackson, R. H. Huang, and J. L. Dye, *J. Am. Chem. Soc.* **127**, 12416 (2005).
- ⁵¹J. L. Dye, *J. Chem. Educ* **54**, 332 (1977).
- ⁵²J. L. Dye, *Angew. Chem. Int. Edit.* **18**, 587 (1979).
- ⁵³R. Rencsok, T. A. Kaplan, and J. F. Harrison, *J. Chem. Phys.* **98**, 9758 (1993).
- ⁵⁴J. L. Dye and R. H. Huang, *Pure Appl. Chem.* **65**, 435 (1993).
- ⁵⁵R. H. Huang, S. Z. Huang, and J. L. Dye, *J. Coord. Chem.* **46**, 13 (1998).
- ⁵⁶W. Chen, Z.-R. Li, D. Wu, Y. Li, C.-C. Sun, and F. L. Gu, *J. Am. Chem. Soc.* **127**, 10977 (2005).
- ⁵⁷W. Chen, Z.-R. Li, D. Wu, Y. Li, C.-C. Sun, F. L. Gu, and Y. Aoki, *J. Am. Chem. Soc.* **128**, 1072 (2006).
- ⁵⁸M. Garcia-Borrás, M. Solá, J. M. Buis, and B. Kirtman, *J. Chem. Theor. Comput.* **8**, 2688 (2012).
- ⁵⁹J. L. Dye, *Accounts Chem. Res.* **42**, 1564 (2009).
- ⁶⁰T. Patterson, H. Hotop, A. Kasdan, D. Norcross, and W. Lineberger, *Phys. Rev. Lett.* **32**, 189 (1974).
- ⁶¹E. Chen and W. Wentworth, *J. Chem. Educ* **52**, 486 (1975).
- ⁶²H. Hotop and W. C. Lineberger, *Journal of Physical and Chemical Reference Data* **4**, 539 (1975).
- ⁶³J. A. Dean, in *Lange's Handbook of Chemistry. 11th Edit* (McCirdw-Hill., 1973).

- ⁶⁴S. Glasstone, in *Textbook of Physical Chemistry. 2nd Edit* (Van Nostrand, 1946) p. 874.
- ⁶⁵J. J. Christen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.* **74**, 351 (1974).
- ⁶⁶W. M. Latimer and W. L. Jolly, *J. Am. Chem. Soc.* **75**, 4147 (1953).
- ⁶⁷E. A. Moelwyn-Hughes, in *Physical Chemistry. 2nd Edit.* (Pergamon Press., 1961) p. 882.
- ⁶⁸S. Matalon, S. Golden, and M. Ottolenghi, *J. Phys. Chem.* **73**, 3098 (1969).
- ⁶⁹W. Spicer, A. Sommer, and J. White, *Phys. Rev.* **115**, 57 (1959).
- ⁷⁰A. Kapustinskii, *Rev. Chem. Soc.* **10**, 283 (1956).
- ⁷¹G. Allan, M. De Backer, M. Lannoo, and I. Lefebvre, *Europhys. Lett.* **11**, 49 (1990).
- ⁷²S. Golden and T. R. Tuttle Jr, *Phys. Rev. B* **45**, 13913 (1992).
- ⁷³D. Singh, H. Krakauer, C. Haas, and W. Pickett, *Nature* **365**, 39 (1993).
- ⁷⁴T. Kaplan, R. Rencsok, and J. Harrison, *Phys. Rev. B* **50**, 8054 (1994).
- ⁷⁵S. Golden and T. R. Tuttle Jr, *Phys. Rev. B* **50**, 8059 (1994).
- ⁷⁶J. L. Dye, M. J. Wagner, G. Overney, R. H. Huang, T. F. Nagy, and D. Tomanek, *J. Am. Chem. Soc.* **118**, 7329 (1996).
- ⁷⁷J. L. Dye, *Inorg. Chem.* **36**, 3816 (1997).
- ⁷⁸P. V. Sushko, A. L. Shluger, K. Hayashi, M. Hirano, and H. Hosono, *Phys. Rev. Lett.* **91**, 126401 (2003).
- ⁷⁹Z. Li, J. Yang, J. Hou, and Q. Zhu, *Angew. Chem. Int. Edit.* **43**, 6479 (2004).
- ⁸⁰P. V. Sushko, A. L. Shluger, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **129**, 942 (2007).
- ⁸¹S. G. Dale, A. Otero-de-la Roza, and E. R. Johnson, *Phys. Chem. Chem. Phys.* **16**, 14584 (2014).
- ⁸²B. G. Janesko, G. Scalmani, and M. J. Frisch, *J. Chem. Phys.* **141**, 144104 (2014).
- ⁸³M.-S. Miao and R. Hoffmann, *Accounts Chem. Res.* **47**, 1311 (2014).
- ⁸⁴M.-S. Miao and R. Hoffmann, *J. Am. Chem. Soc.* **137**, 3631 (2015).
- ⁸⁵Y. Zhang, Z. Xiao, T. Kamiya, and H. Hosono, *J. Phys. Chem. Lett.* **6**, 4966 (2015).
- ⁸⁶Z. Li, J. Yang, J. G. Hou, and Q. Zhu, *J. Am. Chem. Soc.* **125**, 6050 (2003).
- ⁸⁷J. E. Medvedeva and A. J. Freeman, *Appl. Phys. Lett.* **85**, 955 (2004).
- ⁸⁸J. E. Medvedeva, A. J. Freeman, M. I. Bertoni, and T. O. Mason, *Phys. Rev. Lett.* **93**, 016408 (2004).
- ⁸⁹I. G. Ryabinkin and V. N. Staroverov, *Phys. Chem. Chem. Phys.* **13**, 21615 (2011).
- ⁹⁰S. Guan, S. A. Yang, L. Zhu, J. Hu, and Y. Yao, *Sci. Rep.* **5**, (2015).

- ⁹¹Y. He, *J. Alloy. Compd.* **654**, 180 (2016).
- ⁹²L. E. Johnson, P. V. Sushko, Y. Tomota, and H. Hosono, *P. Natl. Acad. Sci. USA* **113**, 10007 (2016).
- ⁹³S. G. Dale and E. R. Johnson, *Phys. Chem. Chem. Phys.* **18**, 27326 (2016).
- ⁹⁴W. Ming, M. Yoon, M.-H. Du, K. Lee, and S. W. Kim, *J. Am. Chem. Soc.* **138**, 15336 (2016).
- ⁹⁵Y. Li, Z.-R. Li, D. Wu, R.-Y. Li, X.-Y. Hao, and C.-C. Sun, *J. Phys. Chem. B* **108**, 3145 (2004).
- ⁹⁶W. Chen, Z.-R. Li, D. Wu, F.-L. Gu, X.-Y. Hao, B.-Q. Wang, R.-J. Li, and C.-C. Sun, *J. Chem. Phys.* **121**, 10489 (2004).
- ⁹⁷Y.-Q. Jing, Z.-R. Li, D. Wu, Y. Li, B.-Q. Wang, F. L. Gu, and Y. Aoki, *ChemPhysChem* **7**, 1759 (2006).
- ⁹⁸F. Ma, Z.-R. Li, H.-L. Xu, Z.-J. Li, Z.-S. Li, Y. Aoki, and F. L. Gu, *J. Phys. Chem. A* **112**, 11462 (2008).
- ⁹⁹F.-F. Wang, Z.-R. Li, D. Wu, B.-Q. Wang, Y. Li, Z.-J. Li, W. Chen, G.-T. Yu, F. L. Gu, and Y. Aoki, *J. Phys. Chem. B* **112**, 1090 (2008).
- ¹⁰⁰Z.-J. Li, Z.-R. Li, F.-F. Wang, C. Luo, F. Ma, D. Wu, Q. Wang, and X.-R. Huang, *J. Phys. Chem. A* **113**, 2961 (2009).
- ¹⁰¹S. Muhammad, H. Xu, Y. Liao, Y. Kan, and Z. Su, *J. Am. Chem. Soc.* **131**, 11833 (2009).
- ¹⁰²Z.-B. Liu, Z.-J. Zhou, Y. Li, Z.-R. Li, R. Wang, Q.-Z. Li, Y. Li, F.-Y. Jia, Y.-F. Wang, Z.-J. Li, *et al.*, *Phys. Chem. Chem. Phys.* **12**, 10562 (2010).
- ¹⁰³H.-L. Xu, F.-F. Wang, W. Chen, and G.-T. Yu, *Int. J. Quantum Chem.* **111**, 3174 (2011).
- ¹⁰⁴H.-L. Xu, S.-L. Sun, S. Muhammad, and Z.-M. Su, *Theor. Chem. Acc.* **128**, 241 (2011).
- ¹⁰⁵W.-M. Sun, D. Wu, Y. Li, and Z.-R. Li, *Dalton T.* **43**, 486 (2014).
- ¹⁰⁶Z.-J. Zhou, H. Li, X.-R. Huang, Z.-J. Wu, F. Ma, and Z.-R. Li, *Comp. Theor. Chem.* **1023**, 99 (2013).
- ¹⁰⁷A. K. Srivastava and N. Misra, *New J. Chem.* **38**, 2890 (2014).
- ¹⁰⁸W.-M. Sun, L.-T. Fan, Y. Li, J.-Y. Liu, D. Wu, and Z.-R. Li, *Inorg. Chem.* **53**, 6170 (2014).
- ¹⁰⁹V. Postils, M. Garcia-Borràs, M. Solà, J. M. Luis, and E. Matito, *Chem. Comm.* **51**, 4865 (2015).

- ¹¹⁰A. Kumar and S. R. Gadre, *Phys. Chem. Chem. Phys.* **17**, 15030 (2015).
- ¹¹¹J.-J. Wang, Z.-J. Zhou, H.-M. He, D. Wu, Y. Li, Z.-R. Li, and H.-X. Zhang, *J. Phys. Chem. C* **120**, 13656 (2016).
- ¹¹²W.-M. Sun, X.-H. Li, Y. Li, B.-L. Ni, J.-H. Chen, C.-Y. Li, D. Wu, and Z.-R. Li, *ChemPhysChem* **17**, 1 (2016).
- ¹¹³A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ¹¹⁴V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern, and L. A. Curtiss, *J. Comput. Chem.* **22**, 976 (2001).
- ¹¹⁵A. D. Becke and E. R. Johnson, *J. Chem. Phys.* **127**, 154108 (2007).
- ¹¹⁶F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- ¹¹⁷M. 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, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, . Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, "Gaussian 09 Revision A.1," Gaussian Inc. Wallingford CT 2009.
- ¹¹⁸A. Otero-de-la Roza and E. R. Johnson, *J. Chem. Phys.* **138**, 204109 (2013).
- ¹¹⁹F. H. Allen, *Acta Crystall. B-Stru.* **58**, 380 (2002).
- ¹²⁰A. D. Becke, *J. Chem. Phys.* **84**, 4524 (1986).
- ¹²¹A. Otero-de-la Roza and E. R. Johnson, *J. Chem. Phys.* **136**, 174109 (2012).
- ¹²²A. Otero-de-la Roza and E. R. Johnson, *J. Chem. Phys.* **137**, 054103 (2012).
- ¹²³P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. Chiarotti, M. Cococcioni, I. Dabo, *et al.*, *J. Phys. Condens. Mat.* **21**, 395502 (2009).
- ¹²⁴P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).

- ¹²⁵N. Marzari, D. Vanderbilt, A. De Vita, and M. C. Payne, *Phys. Rev. Lett.* **82**, 3296 (1999).
- ¹²⁶A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.* **92**, 5397 (1990).
- ¹²⁷A. Savin, O. Jepsen, J. Flad, O. K. Andersen, H. Preuss, and H. G. von Schnering, *Angew. Chem. Int. Edit.* **31**, 187 (1992).
- ¹²⁸B. Silvi and A. Savin, *Nature* **371**, 683 (1994).
- ¹²⁹E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen, and W. Yang, *J. Am. Chem. Soc.* **132**, 6498 (2010).
- ¹³⁰J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J. P. Piquemal, D. N. Beratan, and W. Yang, *J. Chem. Theor. Comput.* **7**, 625 (2011).
- ¹³¹A. Otero-de-la Roza, E. R. Johnson, and J. Contreras-García, *Phys. Chem. Chem. Phys.* **14**, 12165 (2012).
- ¹³²A. Otero-de-la-Roza, E. R. Johnson, and V. Luña, *Comput. Phys. Commun.* **185**, 1007 (2014).
- ¹³³E. R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-García, A. J. Cohen, and W. Yang, *J. Am. Chem. Soc.* **132**, 6498 (2010).
- ¹³⁴R. H. Huang, D. L. Ward, M. E. Kuchenmeister, and J. L. Dye, *J. Am. Chem. Soc.* **109**, 5561 (1987).
- ¹³⁵J. C. Slater, *J. Chem. Phys.* **41**, 3199 (1964).