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Evaluation of experimental alkali metal ion–ligand noncovalent bond strengths with DLPNO-CCSD(T) method

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ABSTRACT

We applied the domain based local pair natural orbital coupled cluster approach with single, double, and perturbative triple excitations, DLPNO-CCSD(T), to rationalize more than 130 experimental bond dissociation enthalpies collected in the work of Rodgers and Armentrout [Chem. Rev. 116, 5642–5687 (2016)] and involving alkali metal cations and versatile neutral organic and inorganic ligands ranging from common solvents to amino acids. In general, a remarkable agreement has been obtained between predicted and experimental alkali metal ion–ligand noncovalent bond strengths, highlighting a high degree of reliability of data assembled by Rodgers and Armentrout. In the case of some inconsistent experimental data given for some species, we pointed to a number for which best agreement with DLPNO-CCSD(T) calculations has been achieved. In addition, we refined a couple of ΔH_0 for which DLPNO-CCSD(T) values turned out to be significantly different from their experimental counterparts. We suggest an application of the DLPNO-CCSD(T) to derive the reference values to train/validate force field and neural network methods to be further applied in molecular dynamic simulations to unravel the mechanisms in biological systems and alkali metal ion batteries.

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I. INTRODUCTION

Noncovalent interactions^{1,2} of alkali metal cations with versatile ligands and solvent functional groups are at the heart of many biological and industrially appreciated processes.³ Due to its multiple effects on the nervous system and blood properties, lithium salts are active ingredients of many pharmaceuticals against mental disorders.^{4–7} Furthermore, Li^+ ions exhibit antiviral activity against DNA type viruses.⁸ Both sodium and potassium ions maintain the electrolyte balance in the body and are responsible for transportation of molecules across the cell membranes, a process known as the sodium-potassium pump.⁹ In addition, the K^+ ion acts as a cofactor for certain enzymes such as pyruvate kinase. Even if rubidium and cesium have no known biological roles, these can replace intracellular functions of K^+ ions.¹⁰ Besides, sodium and potassium salts serve as food preservatives. When it comes to

technological applications, alkali metal salts are used as components of glasses, ceramics, cement, soap, greases, stereoselective synthesis, nuclear reactors, nuclear fusion, and batteries and fuel cells.¹¹ Moreover, Li^+ is a driving force in Li-ion batteries¹² utilized in portable electronics, power tools, and electric vehicles.¹³ Like Li-ion batteries, remarkable progress has been made to develop Na-ion batteries.¹⁴

As the cation- π interaction is predicted to be the strongest among other noncovalent interactions,¹⁵ it plays an important role in many above-mentioned applications, particularly in protein structure, molecular recognition, and enzyme catalysis.^{16–18} Therefore, the study of the thermochemical properties of cation–neutral association reactions is one of prime importance in versatile fields of contemporary interest.^{17,18} The high interest in these systems has led to the determination of a large number of ligand–alkali metal noncovalent bond strengths over the years, as excellently summarized

by Rodgers and Armentrout recently.³ This kind of data collection represents a reference for years to come.

However, the reliability of compilations merging the data from a large number of sources is always questionable, unless each included experimental number is reconfirmed by a separate measurement carried out in a different scientific group (ideal situation). In reality, however, due to the complexity of the gas phase measurements often performed with custom-built equipment, and significant economic costs associated with experimental science in general, this is rarely the case. It is quite common that a physical observable is characterized either by a set of inconsistent values assembled from different sources or by a single number coming from the half-century-old measurement. In this scenario, electronic structure calculations can represent a powerful tool to validate databases assembled from different experimental sources. When keen attention is paid to inclusion of the effects arising from dispersion forces,^{19,20} subvalence and core-core correlation,^{20–26} basis set incompleteness and superposition errors,^{27,28} the results of chemical accuracy can be achieved.^{29–31} Until very recently, the only viable option for accurate calculations has been the canonical coupled cluster method with single, double, and perturbative triple excitations, CCSD(T),³² known as the “gold standard” in quantum chemistry. However, due to poor scaling with respect to the system size, N^7 , and slow convergence with respect to the basis set size, accurate CCSD(T) calculations are feasible only for small model systems with up to a dozen of atoms. Recently, its local alternative DLPNO-CCSD(T) approximation^{33–35} has been developed and shown to be applicable with the most strict criteria to the systems with up to dozens of atoms keeping the accuracy of the parent method.^{20,24,36–40} With this background, we rationalized experimentally measured noncovalent bond dissociation energies of ligands from alkali metal cations according to the reaction of the following equation:

II. COMPUTATIONAL DETAILS

A. Geometry optimization

All geometry optimizations and vibrational frequency calculations have been performed with long-range dispersion corrected hybrid density functional, ω B97xD⁴¹ as implemented in the Gaussian09 program package.⁴² The default values were adopted for the self-consistent field and geometry optimization convergence criteria. Numerical integration of the exchange-correlation (XC) terms was performed using the tighter-than-default “ultrafine” option (pruned, 99 radial shells, and 590 angular points per shell) to eliminate the potential numerical noise in energy second derivatives.^{43–45} For hydrogen, lithium, carbon, nitrogen, oxygen, fluorine, sodium, phosphorus, sulfur, and chlorine, we used nonrelativistic all electron correlation consistent polarized valence double- ζ basis set augmented with diffuse functions, aug-cc-pVDZ.^{46,47} Potassium, bromine, rubidium, and cesium were treated with pseudopotential based aug-cc-pVDZ-PP basis sets of Hill and Peterson.⁴⁸ All basis sets were collected from a correlation consistent basis set repository.⁴⁹ The 10 electrons of potassium and bromine, 28 electrons of rubidium, and 46 electrons of cesium were described

with fully relativistic Stuttgart/Köln pseudopotentials.⁵⁰ If several conformations/spatial structures could be possible for some molecules, the structure of the most stable one was found by geometry optimization of manually generated conformations/spatial structures. Harmonic force constants were computed at the optimized geometries to characterize the true energy minima. The ideal gas, rigid-rotor harmonic-oscillator approximation was applied to evaluate the thermal and entropic contribution terms, which are used to derive the total enthalpies at 298.15 K.

Noteworthy, most of the experimental bond dissociation energies are given as enthalpies at 0 K (ΔH_0) and others are enthalpies at 298.15 K (ΔH_{298}). To make the study consistent, all ΔH_{298} experimental values were converted to ΔH_0 via the following procedure. First, ZPE and enthalpy corrections were calculated at the ω B97xD/aug-cc-pVDZ-PP level. Then, the subtraction of the enthalpy correction from the experimental ΔH_{298} was followed by the addition of the ZPE correction to arrive at the final H_0 energy change.

B. Single-point energies evaluations

All single-point energy evaluations were performed with the DLPNO-CCSD(T) method^{33–35} as implemented in the ORCA suite of programs.⁵¹ Tighter than the default “TightPNO” DLPNO settings (TCutPairs = 10^{-5} , TCutPNO = 10^{-7} , and TCutMKN = 10^{-3}) were used, as recommended, for applications where the most accurate values are targeted.^{24,37,52}

The following triple and quadruple- ζ correlation consistent basis sets were used in the present work. Hydrogen, carbon, nitrogen, oxygen, fluorine, phosphorus, sulfur, and chlorine were described with the all electron correlation consistent polarized and diffuse augmenting functions aug-cc-pVnZ basis sets of Dunning and co-workers.^{46,53} Lithium and sodium were treated with all electron correlation consistent polarized core valence basis sets of Peterson and Dunning⁴⁷ augmented with diffuse functions, aug-cc-pwCVnZ. Potassium, rubidium, cesium, and bromine were described with the pseudopotential based diffuse augmented correlation consistent polarized core valence aug-cc-pwCVnZ-PP basis sets of Peterson and co-workers.^{48,54} The 10 core electrons of potassium and bromine, the 28 core electrons of rubidium, and the 46 core electrons of cesium were described with Stuttgart-type fully relativistic effective core potentials.^{50,55,56}

To eliminate the effects of basis set incompleteness (BSI) and basis set superposition error (BSSE), we used the extrapolation schemes for HF and correlation energies of individual species suggested by Helgaker *et al.*^{57–59} [see Eqs. (2) and (3)]. For two adjacent triple- and quadruple- ζ basis sets,

$$E_{\text{HF}}^n = E_{\text{HF}}^\infty + \alpha e^{-1.63n}, \quad (2)$$

$$E_{\text{corl}}^n = E_{\text{corl}}^\infty + \beta n^{-3}, \quad (3)$$

where $n = 3$ and 4 for triple- and quadruple- ζ basis sets, E_{HF}^∞ and E_{corl}^∞ are HF and correlation energies at the complete basis set (CBS) limit, respectively, and α and β are parameters to be obtained from a system of the two equations. The total ΔH_0 at the CBS limit for each reaction ($A + B \rightarrow C$) was evaluated via the following equation:

$$\Delta ZPE_{DLPNO-CCSD(T)} = E_{HF}^{\infty}(C) + E_{corr}^{\infty}(C) + ZPE_{corr}^{\omega B97xD}(C) - (E_{HF}^{\infty}(A) + E_{corr}^{\infty}(A) + ZPE_{corr}^{\omega B97xD}(A) + E_{HF}^{\infty}(B) + E_{corr}^{\infty}(B) + ZPE_{corr}^{\omega B97xD}(B)), \quad (4)$$

where $ZPE_{corr}^{\omega B97xD}$ is the H_0 correction at $\omega B97xD/aug-cc-pVDZ$.

An effect of the counterpoise (CP) correction on the dissociation enthalpies turned out to be of a few tenths of kJ/mol; see Table S1 in the [supplementary material](#). For these reasons, all enthalpies in this work are not corrected for CP.

III. RESULTS AND DISCUSSION

This section is organized into two parts. First, we assess the accuracy of the DLPNO-CCSD(T) method in reproducing the most reliable experimental alkali metal ions–ligand noncovalent bond dissociation ΔH_0 with the uncertainty of not greater than 4.0 kJ/mol. Second, as the method turned out to perform well, we applied it to rationalize the experimental energies corresponding to the dissociation of noncovalently bonded ligands from the systems M^+-L . The reactions of lithium, sodium, potassium, rubidium, and cesium cations are considered separately. Furthermore, we proceed to the simultaneous dissociation of the first ligands from the systems like $(L)M^+-L$.

A. Accuracy of the DLPNO-CCSD(T) method

Despite excellent performance of the DLPNO-CCSD(T) approach in reproducing coinage metals–noncovalently bonded ligands dissociation enthalpies,³⁹ reaction energies,^{20,24,40,76,77} gas phase heats of formation of inorganic³⁶ and organic substances,^{38,78,79} a few recent works revealed some limitations as well. Chen and co-workers found that DLPNO-CCSD(T) method significantly overestimated gas phase bond dissociation energies in proton bound organic dimers.⁸⁰ Similarly, DLPNO-CCSD(T) gas phase transition metal–ligand dissociation enthalpies in large organometallic complexes (WCCR10 dataset)⁸¹ were reported to be substantially larger compared to their experimental counterparts.⁸² As noncovalent interactions contribute significantly to the chemical bonds for which the above-mentioned failures were obtained, the DLPNO-CCSD(T) approximation has been carefully tested in reproducing 26 alkali metal ions–ligands bond ΔH_0 . Only Li^+-Cs^+ systems with the ΔH_0 uncertainty within ± 4 kJ/mol have been included in the validation set; see Table I.^{33,35} In case of a few experimental measurements, an average ΔH_0 has been taken. The overall mean unsigned error (MUE)/mean signed error (MSE) are 5.0 and -1.6 kJ/mol, respectively. A scatter plot based on experimental (x axis) and DLPNO-CCSD(T)/CBS (y axis) values is given in Fig. 1. The calculated squared Pearson correlation coefficient $R^2 = 0.94$ demonstrates good fit between experimental and theoretical values indicating the DLPNO-CCSD(T) method to be a reliable tool for calculation of alkali metal ions–ligands noncovalent bond dissociation energies.

For further validation of the method used for optimization, we have reoptimized aforementioned 26 species using $\omega B97xD/aug-cc-pVTZ(-PP)$ and $PBE/aug-cc-pVDZ(-PP)$ separately. Thereafter, those optimized geometries were used for single point calculations

TABLE I. Experimental and calculated gas phase bond dissociation ΔH_0 of selected complexes with an uncertainty not greater than 4.0 kJ/mol.

Systems	Expt.	Calculated
$(CO)Li^+-CO$	36.0 ± 4.0^{60}	44.3
$(NH_3)Na^+-NH_3$	99.6 ± 1.0^{61}	93.4
$Na^+-CH_3CO_2CH_3$	123.2 ± 3.0^{62}	130.8
Na^+-CH_3CHO	$113.0 \pm 3.0^{63-65}$	121.0
$Na^+-pyrazine$	107.0 ± 4.0^{66}	103.6
$Na^+-pyridine$	127.0 ± 3.0^{66}	132.1
$Na^+-pyrimidine$	103.0 ± 4.0^{66}	108.5
K^+-CH_3CN	101.3 ± 2.0^{67}	101.3
$(CH_3CN)K^+-CH_3CN$	89.2 ± 2.0^{67}	84.6
$K^+-n-C_3H_7OH$	83.0 ± 4.0^{68}	87.2
$K^+-C_2H_5COOH$	86.0 ± 4.0^{68}	96.1
$K^+-CH_3NH_2$	78.7 ± 4.0^{69}	81.1
$K^+-(CH_3)_2NH$	81.0 ± 4.0^{69}	81.5
$(H_2O)K^+-H_2O$	$67.0 \pm 4.0,^{70,71} 67.0^{72}$	61.2
$K^+-(C_2H_5)_2O$	92.0 ± 4.0^{69}	90.3
$K^+-CH_3COC_2H_5$	95.0 ± 4.0^{68}	105.0
$K^+-(CH_3)_3N$	85.4 ± 4.0^{73}	80.2
$K^+-(1-CH_3-pyrazole)$	94.0 ± 4.0^{74}	96.5
$K^+-pyrimidine$	69.0 ± 4.0^{66}	76.3
Rb^+-NH_3	75.1^{75}	69.4
$(NH_3)Rb^+-NH_3$	64.7^{75}	57.5
Rb^+-CH_3CN	86.6 ± 1.0^{67}	93.6
$(CH_3CN)Rb^+-CH_3CN$	77.6 ± 1.1^{67}	77.1
$(H_2O)Rb^+-H_2O$	57.8 ± 4.0^{70}	54.2
$Cs^+-(CH_3CN)$	79.7 ± 1.0^{67}	86.2
$(CH_3CN)Cs^+-CH_3CN$	71.3 ± 1.0^{67}	71.8

at the DLPNO-CCSD(T)/aug-cc-p(wC)VTZ(-PP) level. The detailed results are shown in Table S1 (in the [supplementary material](#)). The calculations reveal that the MUE of $\omega B97xD/aug-cc-pVTZ(-PP)$ and $PBE/aug-cc-pVDZ(-PP)$ optimized geometries with respect to the default $\omega B97xD/aug-cc-pVDZ(-PP)$ optimized geometries are 0.4 and 0.4 kJ/mol, respectively. Furthermore, to evaluate the effect of DLPNO approximation, single point calculations at the CCSD(T)/aug-cc-p(wC)VTZ(-PP) method have been performed. The MUE of 0.45 kJ/mol between the DLPNO-CCSD(T) and CCSD(T) methods indicates the reliability of DLPNO approximation.

B. Bond dissociation energies of M^+-L

We have collected a large number of systems including Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ ions binding various types of organic and inorganic ligands, including amino acids. For a number of species, the literature reports several experimental values along with a wide range of uncertainties. First, for each molecule, an average ΔH_0 has been obtained by averaging all available experimental numbers. Second, the experimental uncertainties for each averaged value have been calculated in the following way. By combination of

FIG. 1. Correlation between experimental and calculated DLPNO-CCSD(T)/CBS alkali metal cations–ligands dissociation enthalpies at 0 K (ΔH_0).

individual experimental values with corresponding uncertainties, the highest and the lowest possible numbers were obtained. Thereafter, the positive and negative deviations were calculated as a difference between the average enthalpy and the highest and lowest possible values, correspondingly.

1. Lithium ion

The average experimental $\text{Li}^+\text{-L}$ bond dissociation ΔH_0 with error bars along with their DLPNO-CCSD(T) counterparts are shown in Fig. 2. The majority of calculated dissociation ΔH_0 values have been found to be within the experimental error bars, indicating strong correlation between predicted and experimentally measured ΔH_0 . The overall MUE and MSE for $\text{Li}^+\text{-L}$ are 6.8 and 0.6 kJ/mol. The positive MSE indicates that theoretical values are generally overestimated. An examination identified only three exceptions as discussed herein. Thus, for the $\text{Li}^+\text{-HCO}_2\text{CH}_3$ complex, predicted dissociation ΔH_0 was found to be 189.2 kJ/mol which is 18.1 kJ/mol above the experimental value and out of an uncertainty bar.^{63,65,73,83} Similarly, $\text{Li}^+\text{-C}_2\text{H}_5\text{COOH}$ bond dissociation ΔH_0 of 180.4 kJ/mol is above the average of the two

FIG. 2. Experimental and DLPNO-CCSD(T) bond dissociation ΔH_0 s of 47 $\text{Li}^+\text{-L}$ complexes in kJ/mol.

available experimental numbers (165.0 ± 6.0^{25} and $168.0 \pm 11.0^{63-65}$) and 1.4 kJ/mol above the error bar. The DLPNO-CCSD(T) calculations also predict the Li^+ -Proline bond dissociation ΔH_0 to be 234.8 kJ/mol which is 18.2 kJ/mol below an average of the two experimental values of 255.0 ± 7.0^{84} and 253.0 ± 14.0 kJ/mol.⁸⁵ As the calculated number is 4.2 kJ/mol out of the uncertainty bar, we expect that another re-examination of the experimental data would be of interest.

Furthermore, we performed a detailed comparison of the calculated ΔH_0 and their experimental counterparts for some selected species with largest error bars (Table S3 in the [supplementary material](#) for details). Thus, an experimental uncertainty for Li^+ - H_2 of 35.0 kJ/mol results in formal experimental ΔH_0 ranging from -8.0 to 62.0 kJ/mol.⁸⁶ Predicted ΔH_0 for Li^+ - H_2 dissociation amounts to 19.0 kJ/mol, which is reasonably close to experimentally derived ΔH_0 of 27.0 kJ/mol. Hence, despite large experimental uncertainty tabulated in Ref. 86 for Li^+ - H_2 , ΔH_0 value turned out to be accurate. The experimental Li^+ - $^n\text{C}_4\text{H}_9\text{OH}$ bond dissociation ΔH_0 is presented by four separate measurements: 178.0 ± 8.0 ,⁸⁷ 169.0 ± 8.0 ,⁸⁸ 177.0 ± 8.0 ,⁸⁸ and 173.0 ± 11.0 kJ/mol.^{63,65,83} The DLPNO-CCSD(T) predicts ΔH_0 of 166.8 kJ/mol, which suggests the second experimental measurement to be the most accurate. Two separate ΔH^0 measurements of 207.0 ± 18.0^{74} and $179.0 \pm 11.0^{63,65,83}$ kJ/mol are reported for Li^+ -(1- CH_3 -pyrazole) resulting in overall uncertainty interval of 57.0 kJ/mol. The calculated value is 188.9 kJ/mol, which is 7.6 kJ/mol below the average of the two experimental quantities (Fig. 2, Table S3). The Li^+ affinity to imidazole has been measured in two separate experiments resulting in ΔH_0 of 211.0 ± 10.0^{89} and 195.0 ± 10.0 kJ/mol.⁶³⁻⁶⁵ The DLPNO-CCSD(T) prediction of 210.1 kJ/mol supports the former measurement. Similarly, out of two independent ΔH_0 measurements of 242.0 ± 20.0^{74} and 216.0 ± 11.0^{64} kJ/mol reported for Li^+ -(1- CH_3 -imidazole), our calculated value of 221.2 kJ/mol prefers the latter experimental number. We predict Li^+ -(1H-1,2,4-triazole) bond dissociation ΔH_0 of 177.7 kJ/mol supporting the lowest of the two available experimental measurements of 191.0 ± 8.0^{89} and 172.0 ± 11.0 kJ/mol.^{63,65,83} DLPNO-CCSD(T) ΔH_0 of 164.8 kJ/mol obtained for Li^+ -toluene dissociation agrees well with experimentally measured value of 158.0 ± 11.0 kJ/mol of Yanez and co-workers.⁹⁰ Whereas, other available experimental ΔH_0 of 183.0 ± 16.0^{91} kJ/mol is apparently too high. Two experimental dissociation ΔH_0 s for Li^+ -phenol are 179.0 ± 16.0^{92} and 162.0 ± 11.0 kJ/mol,^{63,65} which are considerably larger than our predicted value of 154.3 kJ/mol. The calculated dissociation ΔH_0 of 130.6 kJ/mol for Li^+ -(F-benzene) complex indicates that the experimental value of 147.0 ± 20.0 kJ/mol⁹³ might be overestimated. Calculated ΔH_0 dissociation for Li^+ -naphthalene of 165.1 kJ/mol is in good agreement with the experimental value of 165.0 ± 11.0^{90} kJ/mol, while other experimental ΔH_0 of 187.0 ± 16.0^{94} kJ/mol is apparently too high. A significant disagreement has been detected between two available experimental Li^+ - $\text{OP}(\text{OCH}_3)_3$ bond dissociation ΔH_0 s of 281.0 ± 15.0^{95} and 233.0 ± 11.0 kJ/mol.⁶⁴ Our predicted value of 240.7 kJ/mol supports the latter measurements and indicates the former to be too high. The dissociation ΔH_0 of 238.6 kJ/mol calculated by the DLPNO-CCSD(T) method for the Li^+ -glycine complex is significantly larger than any of the three available experimental measurements: 220.0 ± 8.0 ,²⁵ 224.0 ± 10.0 ,⁹⁶ and 230.0 ± 14.0 kJ/mol.⁸⁵ However, the last

one reported by Feng *et al.* is more close to our predicted value. For the Li^+ -alanine complex, our calculated bond dissociation ΔH_0 of 248.2 kJ/mol practically matches the larger of the two reported experimental values of 229.0 ± 20.0^{97} and 239.0 ± 17.0 kJ/mol.⁸⁵ Similarly, Li^+ -valine DLPNO-CCSD(T) ΔH_0 of 253.1 kJ/mol prefers the value of 247.0 ± 17.0 kJ/mol measured by Feng *et al.*⁸⁵ over another experimental value of 238.0 ± 20.0 kJ/mol.⁹⁷ The Li^+ -serine bond dissociation ΔH_0 of 281.0 ± 13.0 kJ/mol measured by Armentrout and co-workers⁹⁸ turned out to be reasonably close to our predicted value of 279.0 kJ/mol. Another experimental ΔH_0 of 261.0 ± 14.0 kJ/mol is apparently too low.⁸⁵ Predicted dissociation ΔH_0 of 311.0 kJ/mol for Li^+ -methionine agrees well with the value of 292.0 ± 12.0^{99} kJ/mol indicating another experimental value of 274.0 ± 14.0 kJ/mol⁸⁵ to be slightly underestimated. Finally, for the Li^+ -threonine complex, we predict dissociation ΔH_0 of 285.6 kJ/mol which is close to the highest of the two available experimental data: 285.0 ± 14.0^{98} and 272.0 ± 14.0 kJ/mol.⁸⁵

2. Sodium ion

In general, DLPNO-CCSD(T) predicted Na^+ -ligand noncovalent interaction energies are in good agreement with the experimental numbers as most of the calculated values are within the error bars; see Fig. 3. For Na^+ -L, the overall MUE and MSE are 6.8 and 0.6 kJ/mol. The positive MSE indicates that theoretical values are relatively higher than experimental measurements. A few systems having significant inconsistency between calculated and experimental dissociation ΔH_0 (Fig. 3, Table S4) shall be discussed in brief separately. For Na^+ - CH_3CHO , our predicted value of 121.0 kJ/mol is 5.0 kJ larger than the highest possible experimental value of 113.0 ± 3.0 kJ/mol.¹⁰⁰ Similar discrepancy has been revealed for Na^+ - $\text{CH}_3\text{CO}_2\text{CH}_3$ where the experimental ΔH_0 of 123.0 ± 3.0^{62} kJ/mol looks underestimated with respect to our predicted value of 130.8 kJ/mol.

Even if calculated ΔH_0 values strongly correlate with the average experimental values, some individual measurements show significant deviations and inconsistencies resulting in wide error bars for some species; see Table S3. Alike the previous discussion for the Li^+ -L systems, we have compared the calculated ΔH_0 with available individual experimental counterparts for Na^+ -L complexes. Predicted Na^+ -CO bond dissociation ΔH_0 of 29.1 kJ/mol is in good agreement with the experimental value of 32.0 ± 8.0 kJ/mol reported by Armentrout and co-workers.⁶⁰ Other experimental value of 55.0 kJ/mol measured by Castleman *et al.* is apparently too high.¹⁰¹ For Na^+ - CH_3OH , all experimental dissociation ΔH_0 values are ranging from 86.0 to 111.0 kJ/mol.^{62,102-105} Calculated ΔH_0 of 104.8 kJ/mol suggests the experimental value of 110.0 ± 1.0 kJ/mol obtained by Castleman and co-workers to be more accurate over other four reports.¹⁰⁴ Our predicted ΔH_0 of 113.7 kJ/mol for Na^+ - $\text{C}_2\text{H}_5\text{OH}$ supports strongly the value of 110.0 ± 6.0 kJ/mol measured by Amicangelo and Armentrout.¹⁰⁶ Other experimental values 102.0 ± 4.0^{102} and 106.0 ± 3.0^{62} kJ/mol available in the literature are probably less accurate. For Na^+ - $^n\text{C}_3\text{H}_7\text{OH}$, the computed ΔH_0 of 118.0 kJ/mol is in favor of the experimental number of 114.0 ± 6.0 kJ/mol obtained by Amicangelo and Armentrout.¹⁰⁶ The DLPNO-CCSD(T) results in 120.5 and 116.1 kJ/mol for Na^+ - $^n\text{C}_4\text{H}_9\text{OH}$ and Na^+ - $^i\text{C}_4\text{H}_9\text{OH}$ bond dissociation ΔH_0 . Even if both values are close to the identical number of 116.0 ± 6.0 kJ/mol measured by Amicangelo and

FIG. 3. Experimental and DLPNO-CCSD(T) bond dissociation ΔH_0 s of 41 $\text{Na}^+\text{-L}$ complexes in kJ/mol.

Armentrout¹⁰⁶ for $\text{Na}^+\text{-}^n\text{C}_4\text{H}_9\text{OH}$ and $\text{Na}^+\text{-}^i\text{C}_4\text{H}_9\text{OH}$, the relative difference of 4.4 between the two ΔH_0 s is not reproduced in the experiment. $\text{Na}^+\text{-}^n\text{C}_4\text{H}_9\text{OH}$ and $\text{Na}^+\text{-}^i\text{C}_4\text{H}_9\text{OH}$ bond dissociation ΔH_0 s of 110.0 ± 3.0 and 111.0 ± 3.0 kJ/mol reported by

McMahon and Ohanessian⁶² incorrectly describe the relative bond strengths. Only ΔH_0 of 109.0 ± 5.0 and 105.0 ± 6.0 kJ/mol measured by the same group of Armentrout at the very first report¹⁰² reproduced stronger $\text{Na}^+\text{-ligand}$ bonding in $\text{Na}^+\text{-}^n\text{C}_4\text{H}_9\text{OH}$ comparing to that in $\text{Na}^+\text{-}^i\text{C}_4\text{H}_9\text{OH}$. In the case of $\text{Na}^+\text{-CH}_3\text{OCH}_3$, the calculated value of 106.7 kJ/mol is in good agreement with the experimental measurement of 101.0 ± 6.0 ¹⁰³ kJ/mol, while the other two experimental values of 92.0 ± 5.0 ¹⁰⁷ and 100.0 ± 3.0 ⁶² kJ/mol are somewhat low. Predicted dissociation ΔH_0 of $\text{Na}^+\text{-CH}_3\text{NH}_2$ of 114.2 kJ/mol supports the threshold collision-induced dissociation experiment value of 113.0 ± 6.0 kJ/mol reported by El Aribi *et al.*¹⁰⁸ Other two available experimental measurements of 132.0¹⁰⁴ and 108.0 ± 1.0 ¹⁰⁵ kJ/mol are somewhat larger and smaller, respectively. For $\text{Na}^+\text{-indole}$, experimental bond dissociation energy of 138.0 ± 14.0 kJ/mol¹⁰⁹ is overestimated compared to the DLPNO-CCSD(T) predicted value of 124.4 kJ/mol, while the other experimental number 121.0 ± 3.0 kJ/mol¹¹⁰ is closer to our prediction. Similarly, for the $\text{Na}^+\text{-Cl-benzene}$ complex, the two independent experimental dissociation ΔH_0 s of 74.0 ± 3.0 ¹¹¹ and 80.0 ± 8.0 ⁶² kJ/mol are available, whereas the latter is relatively more supported by our prediction of 83.5 kJ/mol. For $\text{Na}^+\text{-glycine}$, the calculated ΔH_0 of 163.8 kJ/mol suggests the that the most accurate experimental value is 164.0 ± 6.0 kJ/mol.¹¹² Three experimental ΔH_0 s reported in the literature for $\text{Na}^+\text{-cysteine}$ are 177.0 ± 5.0 ,¹¹³ 177.0 ± 12.0 ,¹¹⁴ and 174.0 ± 8.0 kJ/mol.¹¹⁵ The first two values are in good agreement with the DLPNO-CCSD(T) value of 181.1 kJ/mol. The predicted dissociation ΔH_0 of 198.4 kJ/mol for $\text{Na}^+\text{-serine}$ supports the number of 200.0 ± 8.0 ⁹⁸ kJ/mol by Armentrout and co-workers in favor of other reported values of 185.0 ± 12.0 kJ/mol by Gapeev and Dunbar¹¹⁴ and 189.0 ± 8.0 kJ/mol by Wesdemiotis.¹¹⁵ Similarly, for $\text{Na}^+\text{-phenylalanine}$, our predicted ΔH_0 of 206.4 kJ/mol supports the experimental value of 206.0 ± 7.0 kJ/mol¹¹⁶ over other two reports of 195.0 ± 12.0 ¹¹⁴ and 196.0 ± 8.0 kJ/mol.¹¹⁵ In the case of $\text{Na}^+\text{-histidine}$, the dissociation ΔH_0 is presented by four separate measurements: 222.0 ± 11.0 ,¹¹⁷ 184.0 ± 12.0 ,¹¹⁴ 217.0 ± 8.0 ,¹¹⁵ and 225.0 ± 8.0 kJ/mol.¹¹⁸ The DLPNO-CCSD(T) predicted ΔH_0 of 212.6 kJ/mol, insisting on the third experimental measurement by Wesdemiotis and co-workers, is within the uncertainty of the first value, while the fourth value is overestimated, and the second one is apparently too low. There are many experimental bond dissociation energies reported for $\text{Na}^+\text{-glycine}_2$: 209.0 ± 13.0 ,¹¹⁹ 179.0 ± 10.0 ,¹²⁰ 184.0 ± 16.0 ,¹²¹ 201.0 ± 8.0 ,¹²² and 175.0 ± 10.0 kJ/mol.⁶⁷ The DLPNO-CCSD(T) predicted value of 186.5 kJ/mol is closest to ΔH_0 of 184.0 ± 16.0 kJ/mol reported by Feng *et al.*¹²¹

3. Potassium ion

For all but 6 species, predicted $\text{K}^+\text{-L}$ bond dissociation ΔH_0 s are within experimental error bars suggesting a strong correlation between calculated and experimental values; see Fig. 4 (Table S5). The MUE for $\text{Rb}^+\text{-L}$ is 4.9 kJ/mol, and the positive MSE of 0.3 kJ/mol indicates the theoretical ΔH_0 values are in general higher than experimental findings. The discrepancies have been found for $\text{K}^+\text{-CH}_3\text{OH}$, $\text{K}^+\text{-CH}_3\text{COC}_2\text{H}_5$, $\text{K}^+\text{-C}_2\text{H}_5\text{COOH}$, $\text{K}^+\text{-pyrazole}$, $\text{K}^+\text{-pyridine}$ and $\text{K}^+\text{-pyrimidine}$. The single experimental value available for $\text{K}^+\text{-CH}_3\text{OH}$ ΔH_0 of 90.8 kJ/mol¹²³ is 13.4 kJ/mol higher than the DLPNO-CCSD(T) predicted value of 77.4 kJ/mol. In contrast, for $\text{K}^+\text{-CH}_3\text{COC}_2\text{H}_5$, the predicted dissociation ΔH_0

FIG. 4. Experimental and DLPNO-CCSD(T) bond dissociation ΔH_0 s of 25 K^+ -L complexes in kJ/mol.

is 105.0 kJ/mol which is larger than the experimental value by 10.0 kJ/mol and 6.0 kJ/mol upper bound than the error bar.⁶⁸ Similarly, K^+ -C₂H₅COOH ΔH_0 of 86.0 $\pm$ 4.0 kJ/mol measured by Moision and Armentrout⁶⁸ is lower than the predicted value of 96.1 kJ/mol. Calculated dissociation ΔH_0 s of K^+ -pyrazole and K^+ -pyridine are 92.2 and 97.0 kJ/mol, respectively; those are higher than the respective experimental values by 10.7 and 8.1 kJ/mol (Fig. 4, Table S5).^{66,69,74,124} For K^+ -pyrimidine, the

experimental dissociation energy of 69.0 $\pm$ 4.0⁶⁶ kJ/mol is in reasonable agreement with our predicted value of 76.3 kJ/mol.

Four individual complexes of K^+ -L for which individual experimental measurements are not consistent are discussed herein. For the K^+ -CH₃OCH₃ complex, our predicted bond dissociation ΔH_0 of 78.8 kJ/mol is in between two reported experimental values of 73.0 $\pm$ 4.0¹²⁵ and 86.0 $\pm$ 4.0¹²⁶ kJ/mol. Our predicted value of 92.2 kJ/mol for K^+ -pyrazole supports the experimental number of 84.0 $\pm$ 3.0 kJ/mol measured by Huang and Rodgers⁷⁴ and indicates the other reported value 80.0 $\pm$ 4.0 kJ/mol to be slightly underestimated.¹²⁴ Similarly, K^+ -pyridine dissociation ΔH_0 is represented by the two experimental values of 90.0 $\pm$ 4.0⁶⁶ and 87.7 $\pm$ 4.0 kJ/mol.⁶⁹ Our predicted ΔH_0 of 97.0 kJ/mol supports the former measurement. The DLPNO-CCSD(T) predicted value of 98.3 kJ/mol for K^+ -aniline is higher than both the experimental measurements of 83.0 $\pm$ 3.0¹²⁷ and 95.0 $\pm$ 4.0 kJ/mol.⁶⁹ However, the latter one is closer to our predicted ΔH_0 .

4. Rubidium and cesium ions

Finally, the DLPNO-CCSD(T) method has been utilized to rationalize the available experimental measurements for noncovalent bond dissociation in Rb^+ and Cs^+ complexes (see Fig. 5 and Table S5). The MUEs for Rb^+ -L and Cs^+ -L are 4.6 and 7.0 kJ/mol, and the respective MSEs are 0.0 and 3.7 kJ/mol. The positive MSEs in both cases indicate theoretical values are generally overestimated. In case of Rb^+ -NH₃, our predicted dissociation ΔH_0 of 69.4 kJ/mol is a bit smaller than the experimental value of 75.1 kJ/mol.⁷⁵ Similarly, for Rb^+ -CH₃CN, the experimental value of 86.6 $\pm$ 1.0⁶⁷ kJ/mol looks slightly underestimated comparing to our predicted value of 93.6 kJ/mol. Cs^+ -CH₃CN complex also shows the same trend where experimental value of 79.7 $\pm$ 1.0⁶⁷ kJ/mol is smaller than the DLPNO-CCSD(T) predicted value of 86.2 kJ/mol. However, in all cases, the discrepancy between the experimental and DLPNO-CCSD(T) values is within 6.0 kJ/mol, indicating an

FIG. 5. Experimental and DLPNO-CCSD(T) bond dissociation ΔH_0 s of Rb^+ -L (3 complexes) and Cs^+ -L (2 complexes) in kJ/mol.

FIG. 6. Experimental and DLPNO-CCSD(T) bond dissociation ΔH_0 s of 15 $(L)M^+-L$ complexes in kJ/mol.

excellent performance of the DLPNO-CCSD(T) method and/or good quality of the measurements. For the Cs^+-H_2O complex, the two ΔH_0 experimental measurements of 54.4 ± 4.0 ⁷⁰ and 47.5 ± 4.0 ¹²⁸ kJ/mol reported in the literature are in good agreement with our predicted value of 58.4 kJ/mol.

C. Noncovalent bond dissociation energies of $(L)M^+-L$

In this section, we focus on selected species with two ligands bound to the metal cation, $(L)M^+-L$ shown in Fig. 6 (refer to Table S6 in the supplementary material for more details). Similarly to previous results, DLPNO-CCSD(T) predicted first ligand dissociation ΔH_0 values agree reasonably well with the reported experimental measurements. The calculated MUEs for $(L)M^+-L$ ($M = Li, Na, K, Rb,$ and Cs) are 6.6, 3.1, 5.7, 3.8, and 2.6 kJ/mol, and the respective MSEs are 1.4, -0.2, -5.7, -3.8, and -2.1 kJ/mol. All the negative values of MSE except for $(L)Li^+-L$ indicate that theoretical values are mostly lower than those of the experiment. For the $(NH_3)Li^+-NH_3$ complex, the dissociation ΔH_0 of 130.7 kJ/mol was predicted which is slightly lower than the available experimental value of 138.6 ± 5.0 kJ/mol reported by Castleman *et al.*⁶¹ In contrast, for $(CO)Li^+-CO$, the experimental measurement of 36.0 ± 4.0 ⁶⁰ kJ/mol turned out to be slightly lower comparing to DLPNO-CCSD(T) calculated ΔH_0 of 44.3 kJ/mol. In the case of $(NH_3)Na^+-NH_3$, our protocol provides the ΔH_0 of 93.4 kJ/mol which is 6.2 kJ/mol smaller than experimental findings of 99.6 ± 1.0 kJ/mol and 5.2 kJ/mol smaller than the error bar.⁶¹ The first NH_3 dissociation ΔH_0 of $(NH_3)K^+-NH_3$ species is 72.2 ± 5.0 kJ/mol as measured experimentally.^{75,129} This value is higher by 6.0 kJ/mol than our predicted number of 66.2 kJ/mol. For $(NH_3)Rb^+-NH_3$, the experimental value of 64.7 kJ/mol turned out to be 7.2 kJ/mol larger comparing DLPNO-CCSD(T) predicted value of 57.5 kJ/mol.⁷⁵ In contrast, for $(CH_3CN)Rb^+-CH_3CN$ our calculated ΔH_0 of 77.1 kJ/mol is strongly supported by the experimental value of 77.6 ± 1.0 kJ/mol measured by Davidson and Kebarle.⁶⁷

As for some species, the experimental ΔH_0 s are in disagreement with each other, and we applied the DLPNO-CCSD(T) method to rationalize the measurements. Thus, for $(H_2O)Li^+-H_2O$ species, the two separate experimental values of 113.0 ± 10.0 and 107.0 ± 4.0 kJ/mol have been reported by Rodgers and Armentrout¹³⁰ and Dzidic and Kebarle.⁷⁰ Our calculated value of 116.7 kJ/mol strongly supports the former measurement. Similarly, for $(CO)Na^+-CO$ species, our predicted ΔH_0 of 27.1 kJ/mol is in good agreement with the experimental value of 24.0 ± 3.0 kJ/mol,⁶⁰ while the other measurements of 34.0 kJ/mol is somewhat overestimated.¹⁰¹ Between two experimental dissociation ΔH_0 s of 102.0 ± 4.0 ⁶⁷ and 109.0 ± 8.0 ¹³¹ kJ/mol for $(CH_3CN)Na^+-CH_3CN$, our predicted value of 111.0 kJ/mol indicates the second measurement to be more accurate over the first one.

IV. CONCLUSIONS

We utilized the DLPNO-CCSD(T) approach to evaluate the experimentally measured dissociation energies collected for alkali metal ions and a wide set of noncovalently bonded organic (olefins, N- and O-donors, amino acids, etc.) and inorganic ligands (H_2 , H_2O , H_2S , etc.). In general, good to excellent agreement has been found between predicted and experimental H_0 -corrected energies has been found indicating a high degree of reliability for the data compilation of Rodgers and Armentrout, assembled by extracting values from different experimental papers.³ In the case of some inconsistent experimental data given for some species, we pointed to a number for which best agreement with DLPNO-CCSD(T) calculations has been achieved. Furthermore, we refined a few dissociation energies for which our predicted numbers turned out to be significantly different from their experimental counterparts. We suggest use of the DLPNO-CCSD(T) derived thermochemical parameters for alkali metal reactions as reference values to train/validate force field and neural network methods,¹³²⁻¹⁴⁰ to be further applied in

molecular dynamic simulations to unravel the mechanisms in biological systems and alkali-metal ion batteries. Finally, the DLPNO-CCSD(T) reaction enthalpies can be further utilized for derivation of the gas phase heats of formation of alkali metal ion-ligand complexes following our recent study on silver compounds.¹⁴¹

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for experimental and calculated dissociation ΔH_0 in gas phase of all species studied in this report (shown in Table S1–S6), Cartesian coordinates (Å), ZPE and enthalpic corrections, and DLPNO-CCSD(T) energies with different basis sets of all species (tabulated in Table S7).

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The authors declare no competing financial interest.

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