

Comparative calculations of alkali metal cation basicities of some Lewis bases

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Abstract. Lithium, sodium, and potassium cation basicities were calculated for some Lewis bases using the DFT B3LYP/6-311+G**, G2, G2(MP2), G3, and CBS-QB3 methods and compared with corresponding experimental values. The best results for lithium cation basicities (LCB) were obtained with the G2, G2(MP2), and CBS-QB3 methods. So, the G2(MP2) method seems to be the best compromise between speed and accuracy for the calculations of LCBs. Also the quicker DFT B3LYP/6-311+G** level of theory can be used for quantitative prediction of LCBs, if the systematic error is taken into account. For sodium cation basicities (SCB) both G2 and G2(MP2) methods gave excellent correlation and mean absolute deviation (0.6–0.7 kcal/mol), thus G2(MP2) can be suggested for calculation of SCB. The less expensive DFT B3LYP/6-311+G** method gave also good correlation with the experiment. Potassium cation affinities can be calculated with equal accuracy using three methods: G2, G2(MP2), and B3LYP/6-311+G**.

Key words: lithium cation basicity, sodium cation basicity, potassium ion basicity.

INTRODUCTION

Alkali metal ions were the first metal cations studied in the gas phase for their Lewis acid properties. This was due to their relatively easy production under vacuum. In contrast with transition metal ions, alkali metal cations reactivity towards ligands is simple: they form adducts, or clusters, which can be considered as ions 'solvated' by one or several ligands. Moreover, the possibility of measuring accurate alkali metal cation affinities with high accuracy by means of different experimental techniques (equilibrium constant determination by high pressure mass spectrometry (HPMS) [1–4] or ion cyclotron resonance (ICR) [5–9], unimolecular dissociation – Cook's kinetic method [4, 10, 11], energy resolved collision-induced dissociation (CID) [12–14], photodissociation and radiative association kinetics [15, 16]), has stimulated a growing interest in the

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study of these interactions [17–19]. Such measurements generate data that help understand the fundamental interactions important in analytical mass spectrometry, organic synthesis, catalysis, lithium battery electrochemistry [20], and cation transport in living systems ion channels [21].

The gas-phase lithium, sodium, and potassium cation basicities (LCB, SCB, and PCB, respectively) are defined as the Gibbs free energies associated with the thermodynamic equilibria:



where e.g. $\Delta G_{Li^+} = -RT \ln K_1$ and $LCB = -\Delta G_{Li^+}$. In the similar manner, the gas-phase lithium, sodium, and potassium cation affinities (LCA, SCA, and PCA, respectively) are defined as the negative values of the enthalpy changes of reaction (1), e.g. $LCA = -\Delta H_{Li^+}$.

Numerous computational studies [22–43] have been carried out to study the structure and energetics of interactions between alkali metal cations and different Lewis bases. Such studies have usually been limited to a small number of similar bases, and limited relationships have been established between experimental and theoretically calculated cation basicity (or affinity) values.

Burk et al. calculated lithium cation basicities for 37 compounds at G2 and G2(MP2) levels of theory and for 63 compounds at DFT B3LYP/6-311+G** level of theory [44]. It was concluded that G2 and G2(MP2) methods estimate the LCB values with equal accuracy so that there is no need to use a computationally more demanding G2 method for predicting LCBs. A similar conclusion was reached for sodium cation basicities by Remko & Šarišsky [30]. The DFT method had a somewhat larger average error, but was also found to give adequate LCB values. It was noted that in the LCB region above 36 kcal/mol the discrepancies between calculated and experimental values were considerably greater.

Good agreement between experimental (HPMS) and computational (MP2/6-31+G*) SCBs was found by Hoyau et al. for 40 bases [45]. Similar results were obtained by Rodgers & Armentrout, who used MP2(full)/6-311G** level of calculation [46]. In 2000 McMahon & Ohanessian studied sodium binding to 50 molecules and put together an extensive affinity scale [47]. Experiments were done using FT-ICR and calculations using the MP2(full)/6-31G* method. A SCA scale from 6 to 45 kcal/mol was put together. A good agreement was found between the experimental and theoretical values. In 2001 Petrie studied the SCA of 38 molecules using the CPd-G2thaw and c-SLW3 methods [48]. Calculated values were systematically ca 0.7 kcal/mol higher than the experimental values. At the same time these values are 0.5 to 0.7 kcal/mol lower than obtained in previous works. Bloomfield et al. used the high-level ab initio CP-dG2thaw method to recalculate the sodium affinity scale for 22 bases in 2006 [49]. The results were in good agreement with the experiment (± 0.3 kcal/mol) and ensured the addition of 97 new ligands to the scale.

Siu et al. studied the BSSE corrections for the G2 and G3 methods in 2001 [50]. A detailed analysis is given on Li^+ , Na^+ , and K^+ complexes with Lewis

bases (small chain alcohols and amines). It was found that applying the full BSSE often gives misleading results. This can be corrected by taking into account the geometry effect. For potassium complexes the geometry effect is negligible but for lithium and sodium ion complexes the value is large and of similar magnitude but opposite sign to the core size effect.

In 2004 Tsang et al. looked into the theoretical potassium and sodium affinities of amides in order to validate these values experimentally using the kinetic method [51]. The theoretical calculations were done at the G2(MP2,SVP) theory. The results for relative and absolute affinities were in good agreement with the experimental values. Several earlier inconsistencies in sodium and potassium affinity scales were resolved.

Lau et al. made the most thorough calculations of the potassium cation basicity scale in 2003 [52]. The calculations carried out using the DFT B3LYP/6-311+G(3df,2p) method and 136 ligands were considered. Experimental PCA values for 70 bases were used for comparison. The experimental and theoretical values were in good agreement with the mean average error of 1.1 kcal/mol.

In 2000 Ma et al. suggested the use of a smaller core size for potassium ion when calculating its complexes [53]. Short chain alcohols were used for a test and differences between Li^+ , Na^+ , and K^+ were noted. Calculations were made using the G2(MP2,SVP) and G3 methods. The nature of interactions between cations and bases was also discussed.

There are a large number of publications about sodium and potassium cation binding to the amino acids and peptides. In 2003 Kish et al. studied SCAs of the amino acids experimentally by collision activated dissociation and converted their results to the ladder of sodium affinities via Cooks's kinetic method [54]. The SCA scale was verified with calculations at MP2(full)/6-31G*. A similar experimental method was used by Gapeev & Dunbar, who also obtained a satisfactory affinity scale for amino acids [55]. However, a large uncertainty remains about the anchoring of the scale to the SCA value of glycine. Potassium bindings to dipeptides and corresponding structures were determined theoretically by Wong et al. in 2002 using the DFT method B3LYP/6-31G* [56]. In 2007 Wang et al. studied experimentally and theoretically (MP2(full)/6-311+G**) the sodium ion affinities of simple di-, tri-, and tetrapeptides [57]. The experimental sodium affinities agreed excellently with the theoretical predictions.

In the current paper we study the ability of DFT B3LYP/6-311+G** and high level G2, G2(MP2), G3, and CBS-B3 methods to predict the affinities of different bases towards alkali metal (lithium, sodium, and potassium) cations.

METHODS

All calculations were carried out with the Gaussian 03 program package [58]. The DFT B3LYP functional [59–62] with 6-311+G** basis, G2 [63], G2(MP2) [64], G3 [65], and CBS-QB3 [66, 67] methods were used. Geometries were optimized and the frequencies calculated at respective levels. All stationary points

were found to be true minima (number of imaginary frequencies, NImag = 0). The calculated (unscaled) frequencies were also used for the calculations of the enthalpies and free energies using standard procedures [68]. No corrections for the basis set superposition error were made.

RESULTS AND DISCUSSION

Lithium cation basicities

In the current work we calculated LCB values using the high-level G2, G3, and CBS-QB3 methods. The calculated LCB values are reported in Table 1 along

Table 1. Experimental and calculated at different levels lithium cation basicities (LCB) and differences between the experimental [44] and calculated LCBs (Δ). MAD is the mean absolute difference between the experimental and calculated LCBs at the given level of theory. All values are in kcal/mol

Base	Exp.	B3LYP		G2		G2(MP2)		G3		CBS-QB3	
		LCB	Δ	LCB	Δ	LCB	Δ	LCB	Δ	LCB	Δ
CH ₃ SH	20.3	22.5	2.2	20.8	0.5	20.8	0.5	21.3	1.0	19.6	0.7
CH ₃ CH ₂ SH	21.4	24.8	3.4	22.4	1.0	22.4	1.0	22.9	1.5	21.1	-0.3
i-CH ₃ CH ₂ CH ₂ SH	22.4	25.8	3.4	23.5	1.1	23.5	1.1	24.4	2.0	22.5	0.1
(CH ₃) ₂ S	23.4	26.5	3.1	24.6	1.2	24.6	1.2	25.2	1.8	23.2	-0.2
H ₂ O	24.7	29.7	5.0	26.4	1.7	26.1	1.4	27.4	2.7	26.3	1.6
H ₂ CO	25.4	30.6	5.2	28.0	2.6	28.0	2.6	28.8	3.4	27.8	2.4
HCN	25.9	27.7	1.8	25.4	-0.5	25.5	-0.4	26.7	0.8	25.6	-0.3
CH ₃ OH	28.5	32.4	3.9	29.1	0.6	29.0	0.5	30.4	1.9	29.0	0.5
NH ₃	30.2	34.2	4.0	30.2	0.0	29.9	-0.3	31.4	1.2	30.3	0.1
CH ₃ CH ₂ OH	30.4	35.0	4.6	30.9	0.5	30.8	0.4	32.2	1.8	31.0	0.6
CH ₃ NH ₂	31.3	34.8	3.5	32.0	0.7	31.8	0.5	33.1	1.8	31.9	0.6
CH ₃ CHO	31.8	36.5	4.7	33.0	1.2	33.0	1.2	35.1	3.3	32.8	1.0
(CH ₃) ₃ N	32.0	34.1	2.1	32.4	0.4	32.2	0.2	33.5	1.5	32.0	0.0
(CH ₃) ₂ NH	32.1	34.8	2.7	32.5	0.4	32.3	0.2	33.7	1.6	32.3	0.2
i-CH ₃ CH ₂ CH ₂ OH	32.3	36.8	4.5	33.5	1.2	33.4	1.1	34.8	2.5	33.3	1.0
HCO ₂ CH ₃	32.4	36.3	3.9	33.2	0.8	33.2	0.8	34.2	1.8	32.8	0.4
CH ₃ CH ₂ CHO	32.8	37.6	4.8	34.1	1.3	34.1	1.3	35.1	2.3	33.9	1.1
Pyrazol	33.6	38.5	4.9	35.3	1.7	35.2	1.6	36.7	3.1	35.0	1.4
CH ₃ CN	34.0	39.2	5.2	35.5	1.5	35.5	1.5	36.6	2.6	35.4	1.4
(CH ₃) ₂ CO	35.3	40.9	5.6	36.7	1.4	36.7	1.4	38.0	2.7	36.7	1.4
CH ₃ CH ₂ CH ₂ CN	35.7	41.0	5.3	37.7	2.0	37.7	2.0	39.7	4.0	38.6	2.9
4-Methylpyrazole	35.7	41.0	5.3	37.5	1.8	37.4	1.7	38.9	3.2	38.2	2.5
HCONH ₂	36.4	43.7	7.3	40.0	3.6	39.9	3.5	41.3	4.9	40.5	4.1
CH ₃ CO ₂ CH ₂ CH ₃	36.0	42.1	6.1	37.6	1.6	37.6	1.6	39.7	3.7	37.5	1.5
Imidazole	38.1	45.0	6.9	42.0	3.9	41.9	3.8	43.4	5.3	41.9	3.8
CH ₃ CONH ₂	39.3	47.0	7.7	43.5	4.2	43.5	4.2	45.0	5.7	43.0	3.7
HCONCH ₃	39.6	47.4	7.8	44.0	4.4	44.0	4.4	45.3	5.7	44.2	4.6
(CH ₃) ₂ SO	41.8	53.6	11.8	47.0	5.2	47.1	5.3	48.0	6.2	46.9	5.1
HCON(CH ₃) ₂	41.5	49.2	7.7	46.0	4.5	46.0	4.5	47.5	6.0	46.2	4.7
MAD			4.6		1.5		1.4		2.7		1.6

with our earlier B3LYP/6-311+G** and G2(MP2) values. The results of correlation analysis (squares of correlation coefficients, slopes, and intercepts of correlation lines) are given in Table 2 and the correlations are graphically represented in Fig. 1.

Comparison of the experimental and calculated LCBs indicates that practically in all cases the calculated LCBs are greater than the experimental ones. This trend is most pronounced in the case of LCBs above 36 kcal/mol as noted earlier [44]. Comparison of the mean absolute deviations (MAD) of the calculated LCBs from experimental ones for the high level G2, G3, and CBS-QB3 methods used indicates that the G2(MP2), G2, and CBS-QB3 methods are practically of the same quality, while the performance of the G3 method is somewhat worse. So, there is no need to calculate LCBs at the more expensive G2 or CBS-B3 levels as the improvement of the results compared to G2(MP2) is negligible. The MAD of B3LYP/6-311+G** calculations are worse than of the other methods used.

The correlations between experimental and calculated LCBs are also of high quality: R^2 values are 0.97 or higher, but the slopes of correlation lines are all greater than one and intercepts are not zeroes (slope one and zero intercept correspond to ideal correlation, free of systematic errors). However, note that in

Table 2. Results of the regression analysis of the correlation between the calculated and experimental alkali metal cation basicities: equations of the correlation lines and squares of correlation coefficients (R^2)

Method	Equation of the correlation line	R^2
Lithium cation basicities		
B3LYP	$LCB_{\text{calc}} = (1.27 \pm 0.04) \cdot LCB_{\text{exp}} - 3.61 \pm 1.42$	0.969
B3LYP*	$LCB_{\text{calc}} = (1.12 \pm 0.05) \cdot LCB_{\text{exp}} - 0.37 \pm 1.35$	0.968
G2	$LCB_{\text{calc}} = (1.16 \pm 0.03) \cdot LCB_{\text{exp}} - 3.60 \pm 1.11$	0.977
G2*	$LCB_{\text{calc}} = (1.028 \pm 0.03) \cdot LCB_{\text{exp}} - 0.22 \pm 0.97$	0.981
G2(MP2)	$LCB_{\text{calc}} = (1.17 \pm 0.04) \cdot LCB_{\text{exp}} - 3.72 \pm 1.15$	0.975
G2(MP2)*	$LCB_{\text{calc}} = (1.027 \pm 0.03) \cdot LCB_{\text{exp}} - 0.25 \pm 1.00$	0.979
G3	$LCB_{\text{calc}} = (1.21 \pm 0.03) \cdot LCB_{\text{exp}} - 3.66 \pm 1.02$	0.982
G3*	$LCB_{\text{calc}} = (1.09 \pm 0.03) \cdot LCB_{\text{exp}} - 0.33 \pm 1.03$	0.980
CBS-QB3	$LCB_{\text{calc}} = (1.22 \pm 0.03) \cdot LCB_{\text{exp}} - 5.53 \pm 1.07$	0.981
CBS-QB3*	$LCB_{\text{calc}} = (1.11 \pm 0.04) \cdot LCB_{\text{exp}} - 2.59 \pm 1.11$	0.978
Sodium cation basicities		
B3LYP	$SCB_{\text{calc}} = (1.03 \pm 0.05) \cdot SCB_{\text{exp}} + 2.39 \pm 1.02$	0.942
G2	$SCB_{\text{calc}} = (0.99 \pm 0.04) \cdot SCB_{\text{exp}} + 0.91 \pm 0.78$	0.963
G2(MP2)	$SCB_{\text{calc}} = (0.99 \pm 0.04) \cdot SCB_{\text{exp}} + 0.66 \pm 0.77$	0.964
G3	$SCB_{\text{calc}} = (1.02 \pm 0.05) \cdot SCB_{\text{exp}} + 3.23 \pm 1.10$	0.936
Potassium cation basicities		
B3LYP	$PCB_{\text{calc}} = (1.11 \pm 0.05) \cdot PCB_{\text{exp}} - 1.57 \pm 0.87$	0.958
G2	$PCB_{\text{calc}} = (0.96 \pm 0.05) \cdot PCB_{\text{exp}} + 1.04 \pm 0.74$	0.959
G2(MP2)	$PCB_{\text{calc}} = (0.97 \pm 0.05) \cdot PCB_{\text{exp}} + 0.86 \pm 0.76$	0.959

* Correlation analysis results with bases that have LCBs below 36 kcal/mol.

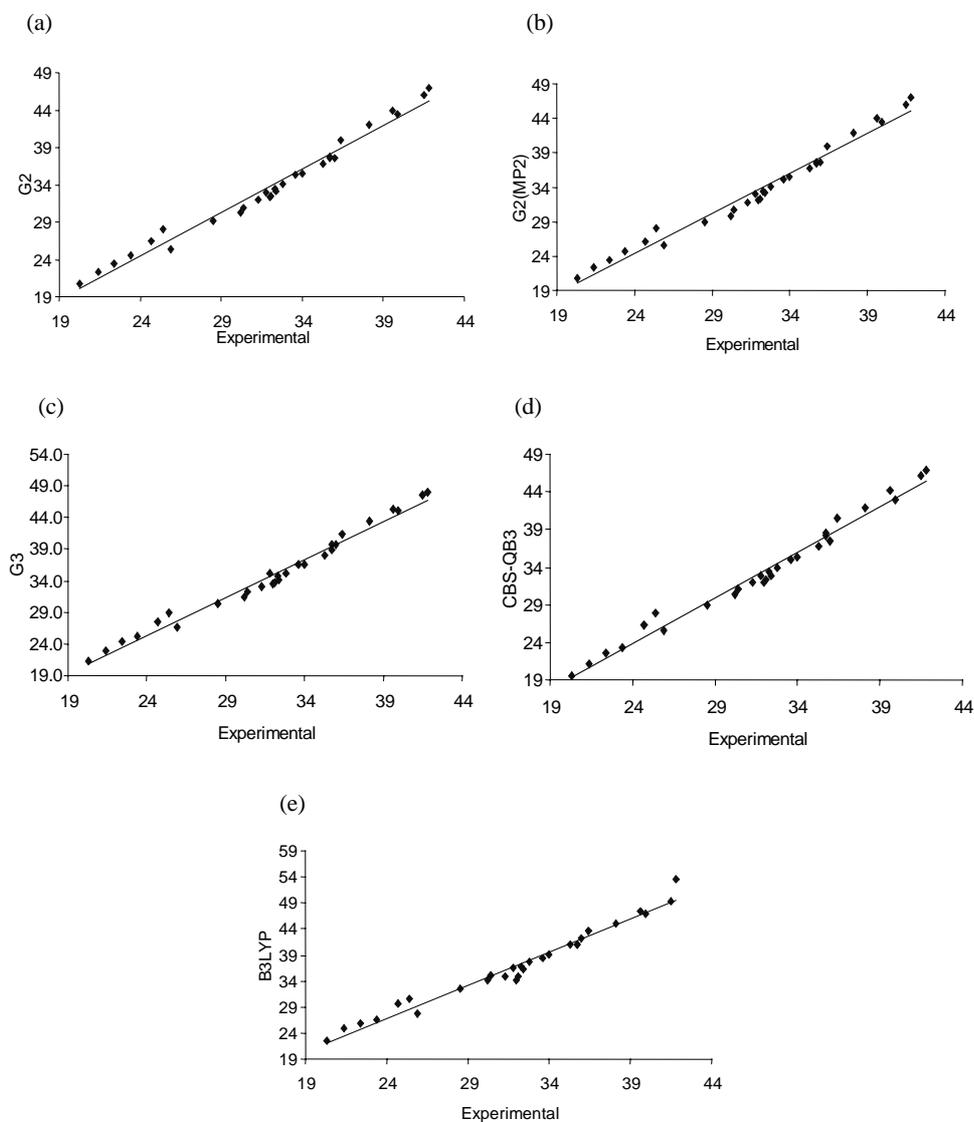


Fig. 1. Correlations between experimental and calculated lithium cation basicities calculated at the G2 (a), G2(MP2) (b), G3 (c), CBS-B3 (d), and DFT B3LYP/6-311+G** (e) levels. All LCB values are in kcal/mol.

the region of bases with $LCB_{\text{exp}} < 36$ kcal/mol the statistical characteristics of the fit are significantly better: the slopes and intercepts are now appreciably closer to their ideal values (1.0 and 0.0) and in some cases (G2 and G2(MP2)) statistically indistinguishable from perfect values. We note, however, that the standard deviation of the points from the correlation line (calculated vs. experimental LCBs) of the fastest method used – B3LYP/6-311+G** – was close to that of

other methods, and the correlation coefficient was only slightly lower than in the other cases. So, the DFT B3LYP/6-311+G** level of theory can be used for quantitative prediction of LCBs, if the systematic error is taken into account.

In an earlier study we observed that in the LCB region above 36 kcal/mol the discrepancies between calculated and experimental values are considerably larger than in a region of lower basicities [15]. Possible explanations of this observation include insufficient accuracy of the computational methods used, experimental errors due to unsystematic build-up of the absolute LCB scale, and some possible incorrect equilibrium measurements.

We tried to check for the insufficient accuracy of computational methods used by applying a recent W1 methodology [69, 70], which is claimed to yield energies within 0.3 kcal/mol accuracy [69, 70]. As the W1 methodology is computationally quite demanding we used it only for the smallest base in the high LCB region – dimethylsulphoxide. The calculated LCB was 48.3 kcal/mol, by 8.1 kcal/mol higher than the experimental value (40.2 kcal/mol). This indicates that the discrepancy between experimental and computational LCBs is not due to insufficient accuracy of the computational methods used. New experimental measurements in the high LCB (>36 kcal/mol) region are needed to clarify the origin of the discrepancy between the experiment and calculations.

Sodium cation basicities

In the current work we calculated SCB values using the high-level G2, G2(MP2), and G3 methods. The DFT B3LYP/6-311+G** method was also tested. The calculated SCB values are reported in Table 3, the results of correlation analysis (squares of correlation coefficients, slopes, and intercepts of correlation lines) are given in Table 2 and the correlations are graphically represented in Fig. 2.

Again, the experimental SCB values are consistently smaller than the G3 or DFT calculated ones. However, at variance with LCBs, the G2 and G2(MP2) methods provide excellent correlations (slopes are practically 1 and intercepts 0) between calculated and experimental SCBs, with small random deviations. Comparison of the MAD of the calculated SCBs with experimental ones for the high level G2(MP2), G2, and G3 methods used shows that the G2(MP2) and G2 methods are practically of equal excellent quality, while the performance of the G3 method is somewhat worse. So, again there is no need to calculate SCBs at the more expensive G2 level as the improvement of the results compared to G2(MP2) is negligible. The MAD of B3LYP/6-311+G** calculations are worse than of the other methods used, but the correlation coefficient is high, so that this method can provide SCB values fast and accurately, if empirical corrections are taken into account.

Table 3. Experimental and calculated at different levels sodium cation basicities (SCB) and the differences between the experimental [45, 47] and calculated SCBs (Δ). MAD is the mean absolute difference between the experimental and calculated SCBs at the given level of theory. All values are in kcal/mol

Base	Exp.	B3LYP		G2		G2(MP2)		G3	
		SCB	Δ	SCB	Δ	SCB	Δ	SCB	Δ
CH ₃ SH	10.5	13.3	2.8	11.9	1.4	11.8	1.3	13.9	3.4
n-C ₄ H ₉ Br	12.2	14.3	2.1	12.2	0.0	12.2	0.0	–	–
(CH ₃) ₂ S	14.2	16.0	1.8	14.4	0.2	14.4	0.2	17.0	2.8
Pyrrole	14.4	21.1	6.7	18.2	3.8	18.0	3.6	21.7	7.3
H ₂ O	15.7	18.4	2.7	15.6	–0.1	15.5	–0.2	18.3	2.6
C ₆ H ₆	15.7	17.4	1.7	17.0	1.3	16.7	1.0	19.5	3.8
C ₆ H ₅ OH	16.7	18.4	1.7	16.9	0.2	16.8	0.1	20.4	3.7
3-Methylpyrrole	16.8	22.6	5.8	18.7	1.9	18.5	1.7	23.6	6.8
CH ₃ OH	17.3	20.0	2.7	17.5	0.2	17.4	0.1	20.0	2.7
H ₂ CO	17.4	19.1	1.7	17.1	–0.3	17.2	–0.2	19.4	2.0
(CH ₃) ₂ O	17.6	21.8	4.2	18.1	0.5	18.1	0.5	20.4	2.8
NH ₃	18.6	21.4	2.8	18.5	–0.1	18.3	–0.3	20.8	2.2
CH ₃ CH ₂ OH	19.0	21.8	2.8	19.3	0.3	19.3	0.3	21.5	2.5
(CH ₃) ₃ N	19.0	20.3	1.3	19.1	0.1	18.9	–0.1	22.1	3.1
CH ₃ NH ₂	19.5	21.8	2.3	19.5	0.0	19.4	–0.1	22.0	2.5
(CH ₃) ₂ NH	19.6	21.3	1.7	19.5	–0.1	19.4	–0.2	22.2	2.6
i-CH ₃ (CH ₂) ₂ OH	20.4	23.1	2.7	20.4	0.0	20.4	0.0	23.6	3.2
Pyridine	20.4	25.5	5.1	23.4	3.0	23.4	3.0	26.1	5.7
Pyrazole	21.0	24.5	3.5	22.2	1.2	22.1	1.1	25.0	4.0
(CH ₃ CH ₂) ₂ O	21.3	23.4	2.1	21.0	–0.3	21.0	–0.3	24.7	3.4
4-Methylpyrazole	21.5	26.3	4.8	23.9	2.4	23.9	2.4	26.9	5.4
CH ₃ CO ₂ CH ₃	23.3	25.5	2.2	23.3	0.0	23.4	0.1	26.0	2.7
CH ₃ CN	23.6	26.1	2.5	24.1	0.5	24.1	0.5	26.4	2.8
(CH ₃) ₂ CO	24.1	26.8	2.7	23.8	–0.3	23.8	–0.3	26.4	2.3
Imidazole	27.3	30.2	2.9	27.9	0.6	27.8	0.5	30.7	3.4
CH ₃ CONH ₂	27.4	31.5	4.1	28.7	1.3	28.8	1.4	31.7	4.3
CH ₃ CONHCH ₃	29.2	34.2	5.0	30.3	1.1	30.3	1.1	33.4	4.2
HCON(CH ₃) ₂	30.1	33.0	2.9	30.6	0.5	30.7	0.6	35.1	5.0
CH ₃ CON(CH ₃) ₂	31.3	34.6	3.3	32.1	0.8	32.2	0.9	35.5	4.2
MAD			3.1		0.7		0.6		3.6

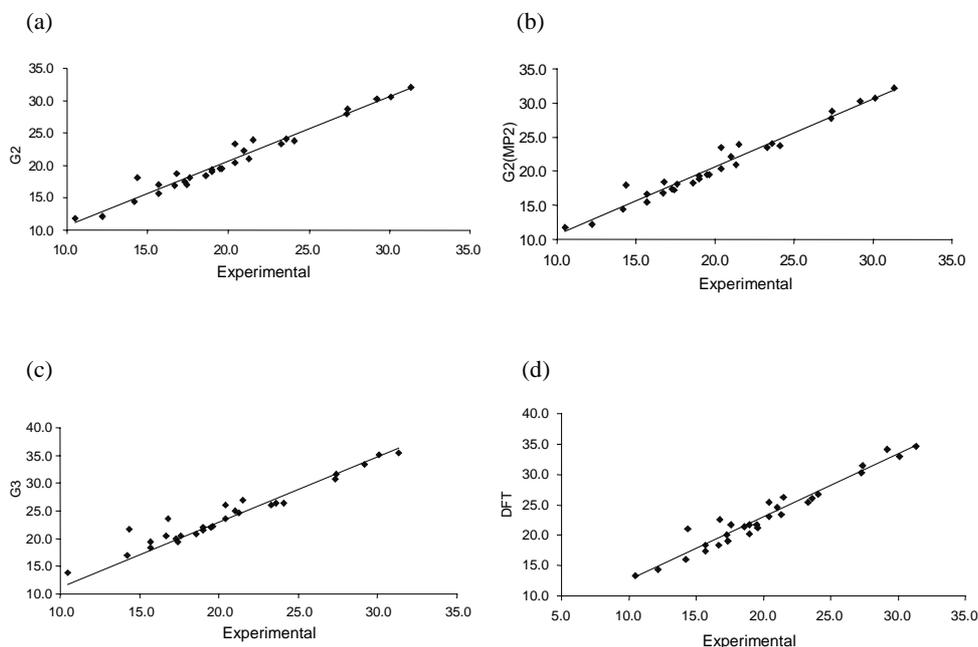


Fig. 2. Correlations between the experimental and calculated sodium cation basicities calculated at the G2 (a), G2(MP2) (b), G3 (c), and DFT B3LYP/6-311+G** (d) levels. All SCB values are in kcal/mol.

Potassium cation basicities

In the current work we calculated PCB values using the high-level G2, G2(MP2), and G3 methods. The DFT B3LYP/6-311+G** method was also tested. The calculated PCB values are reported in Table 4, the results of correlation analysis (squares of correlation coefficients, slopes, and intercepts of correlation lines) are given in Table 2 and the correlations are graphically represented in Fig. 3.

The calculated PCB values are in an excellent correlation with the experimental ones – for all methods used the MAD is 0.7–0.8 kcal/mol, R^2 are 0.96, and the correlation lines have slopes and intercepts close to ideal, in the case of G2(MP2) even equal with those within statistical error. So, the DFT B3LYP/6-311+G** method seems to be the best compromise between speed and accuracy for the calculation of PCBs.

Table 4. Experimental and calculated at different levels potassium cation basicities (PCB) and the differences between the experimental [52] and calculated PCBs (Δ). MAD is the mean absolute difference between the experimental and calculated PCBs at the given level of theory. All values are in kcal/mol

Base	Exp. PCB	B3LYP		G2		G2(MP2)	
		PCB	Δ	PCB	Δ	PCB	Δ
C ₆ H ₅ OH	11.0	10.9	-0.1	12.9	1.9	12.9	1.9
H ₂ O	11.5	12.2	0.7	10.8	-0.7	10.8	-0.7
NH ₃	11.8	12.9	1.1	12.1	0.3	12.0	0.2
C ₆ H ₆	11.9	9.2	-2.7	13.8	1.9	13.9	2.0
CH ₃ NH ₂	12.7	13.0	0.3	12.9	0.2	12.9	0.2
(CH ₃) ₃ N	13.0	11.6	-1.4	12.9	-0.1	12.9	-0.1
Pyrrrole	13.0	12.9	-0.1	13.9	0.9	13.9	0.9
(CH ₃) ₂ NH	13.1	12.4	-0.7	13.1	0.0	13.1	0.0
(CH ₃) ₂ O	13.4	13.6	0.2	12.9	-0.5	12.9	-0.5
Pyrazole	13.9	15.3	1.4	15.5	1.6	15.6	1.7
n-CH ₃ (CH ₂) ₂ NH ₂	14.2	14.1	-0.1	14.4	0.2	14.4	0.2
(CH ₃ CH ₂) ₂ O	14.9	14.6	-0.3	14.8	-0.1	14.9	0.0
Pyridine	15.2	16.4	1.2	16.6	1.4	16.6	1.4
4-Methylpyrazole	16.2	17.3	1.1	17.0	0.8	17.1	0.9
2-Methylpyridine	16.7	16.0	-0.7	16.5	-0.2	16.6	-0.1
CH ₃ CN	18.0	17.8	-0.2	17.8	-0.2	17.9	-0.1
(CH ₃) ₂ CO	19.0	18.5	-0.5	18.0	-1.0	18.1	-0.9
Imidazole	20.0	20.2	0.2	20.4	0.4	20.4	0.4
HCON(CH ₃) ₂	23.0	23.6	0.6	23.6	0.6	23.8	0.8
CH ₃ CON(CH ₃) ₂	24.0	25.4	1.4	25.1	1.1	25.3	1.3
(CH ₃) ₂ SO	25.0	27.1	2.1	24.3	-0.7	24.5	-0.5
MAD			0.8		0.4		0.4

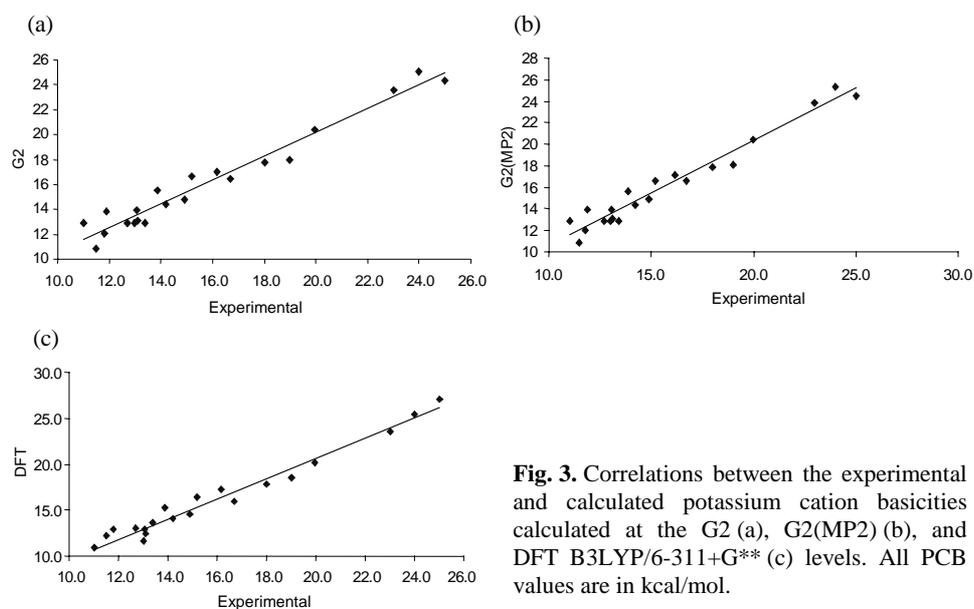


Fig. 3. Correlations between the experimental and calculated potassium cation basicities calculated at the G2 (a), G2(MP2) (b), and DFT B3LYP/6-311+G** (c) levels. All PCB values are in kcal/mol.

CONCLUSIONS

We compared the ability of the B3LYP/6-311+G**, G2(MP2), G2, G3, and CBS-QB3 methods to predict the gas-phase complexation free energies of lithium, sodium, and potassium cations with Lewis bases.

The best results for lithium cation basicities were obtained with the G2, G2(MP2), and CBS-QB3 methods. So, the G2(MP2) method seems to be the best compromise between speed and accuracy for the calculations of LCBs. Also the quicker DFT B3LYP/6-311+G** level of theory can be used for quantitative prediction of LCBs, if the systematic error is taken into account. Calculations of dimethylsulphoxides LCB at the W1 level suggest that the discrepancy between experimental and calculated values in the high LCB region might originate from the accumulation of experimental errors and new experimental measurements in the high LCB (>36 kcal/mol) region are needed to clarify the origin of the discrepancy [44] between the experiment and calculations.

SCB and PCB values seem to be much easier to predict. For SCB both G2 and G2(MP2) methods give excellent correlation and small MAD (0.6–0.7 kcal/mol) so that G2(MP2) can be suggested for the calculation of SCB. The less expensive DFT B3LYP/6-311+G** method gave also good correlation with the experiment. Potassium cation affinities can be calculated with equal accuracy using the G2, G2(MP2), and B3LYP/6-311+G** methods.

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Lewisi aluste leelismetallikatiooni aluselised: mõnede arvutuskeemia meetodite võrdlus

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Mõnede Lewisi aluste aluselised liitium-, naatrium- ja kaaliumkatioonide suhtes on välja arvatud meetoditega DFT B3LYP/6-311+G**, G2, G2(MP2), G3 ning CBS-QB3 ja võrreldud vastavate eksperimentaalsete väärtustega. Parimad tulemused liitiumkatiooni aluseliste jaoks on saadud G2, G2(MP2) ja CBS-QB3-ga. G2(MP2) pakub seega parima kompromissi arvutuste täpsuse ja kiiruse osas. Ka DFT B3LYP/6-311+G** on kasutatav, kui arvestada süsteemataolist viga. Naatriumkatiooni aluseliste arvutamisel annavad nii G2 kui G2(MP2) hea korrelatsiooni eksperimendiga ja keskmine absoluutne viga on väike (0,6–0,7 kcal/mol). Seega on ka naatriumkatiooni aluseliste arvutamiseks sobivaim G2(MP2). Ka kiirem B3LYP/6-311+G** on kasutatav. Kaaliumkatiooni aluseliste arvutamiseks on G2, G2(MP2) ja B3LYP/6-311+G** sarnase kvaliteediga.