PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Journal Name

RSCPublishing

ARTICLE

On the Dissolution of Lithium Sulfate in Water: Anion Photoelectron Spectroscopy and Density Functional Theory Calculations

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Gang Feng, Gao-Lei Hou, Hong-Guang Xu, Zhen Zeng, and Wei-Jun Zheng*

The initial dissolution steps of lithium sulfate (Li_2SO_4) in water were investigated by performing anion photoelectron spectroscopy and density functional theory calculations on the $Li_2SO_4(H_2O)_n^-$ (n = 0-5) clusters. The plausible structures of these clusters and the corresponding neutrals were obtained with LC-ωPBE/6-311++G(d,p) calculations by comparing the experimental and theoretical vertical electron detachment energies. Two types of structures for bare $Li_2SO_4^{-/0}$ were found: turtle-shaped structure and propeller-shaped structure. For $Li_2SO_4(H_2O)_n^-$ cluster anions with n = 1-3, two kinds of isomers derived from the turtle-shaped and propeller-shaped structures of bare $Li_2SO_4^-$ were identified. For n = 4-5, these two kinds of isomers become to present similar structural and energetic features and thus are not distinguishable. For the anionic clusters the water molecules prefer to firstly interact with one Li atom until fully coordinating it. While for neutral clusters, the water molecules interact with the two Li atoms alternately, therefore, show a pairwise solvation behavior. The Li-S distance increases smoothly as addition of water molecules one by one. Addition of five water molecules to Li_2SO_4 cannot induce the dissociation of one Li^+ because the water molecules are shared by two Li^+ ions.

Introduction

Dissolution of salts is a very fundamental process and is important for many chemical processes[1-8] and our daily life.[9, 10] However, a molecular level view on the nature of the initial steps of salt dissolution has not been well established, which could provide valuable details for understanding the behavior and the chemical fate of salt in the bulk and complex environment. In the initial steps of the dissolution, the solvent molecules interact with the anion and cation, firstly forming contact ion pair (CIP) due to the directly electrostatic attraction of the anion and cation, and then the structure is evolved into solvent-separated ion pair (SSIP) as the number of the interacting solvent molecules increases. This is the key step dominating the initial process of dissolution.[7, 11]

Theoretical[12-32] and experimental[33-42] efforts have been devoted to investigate the CIP to SSIP transition of salts under the effect of solvent molecules. Among them, alkali halides are the preferred models for this kind of purpose studies because of their simplicity and the important roles they play. Experimental techniques such as matrix-isolated infrared spectroscopy,[33] resonance enhanced two-photon ionization,[34, 35] attenuated total reflection infrared spectroscopy,[36] reaction equilibration measurement from mass spectrometry,[37, 38] Fourier transform microwave spectroscopy,[39, 40] and anion photoelectron spectroscopy (PES)[41, 42] have been used to disclose the fundamental aspect of salt dissolution.

The sulfates are widely used salts, which are critically important in industry and atmospheric aerosol chemistry.[43-45] However, their dissolutions in water are not well understood yet. Wang et al.[46] conducted PES studies on $NaSO_4^-(H_2O)_n$ (n = 0-4) clusters and found that the first three water molecules prefer to interact with SO_4^{2-} via three $OH\cdots O(SO_4^{2-})$ hydrogen bonds and with Na^+ via three $Na\cdots O(H_2O)$ interactions forming a pried apart $Na^+SO_4^{2-}$. Theoretical modeling of infrared photo dissociation(IRPD) spectra of $NaSO_4^-(H_2O)_n$ (n = 0-5) clusters were also performed by Jin et al. to provide structural information on the early stage of the dissolution.[47] Zhang et al. investigated the formation of $MgSO_4$ ion pairs in solution with ab initio calculations.[48] The structural and energetic features of $(NH_4)_2SO_4(H_2O)_n$ (n = 0-9) was reported by Liu et al.[49] Sulfate ion is a polyatomic group and has two negative charges distributing over four O atoms which can form strong hydrogen bond with water molecules, different from halide ions in nature.[50, 51] SO_4^{2-} has the strongest salting-out effect in the Hofmeister series,[52] very different from I^- anion in the case studied previously.[41] Detailed information, at molecular level, on the dissolution processes will be a great help to understand the nature of salt dissolution and to understand the chemical fate of sulfate salts in aerosol formation and their salt effect in the bulk. Lithium sulfate (Li_2SO_4) is a simply salt with high solubility in water and thus provides a desirable model to elucidate the microscopic aspect of the dissolution of sulfate salts. Here, we present the investigation of the $Li_2SO_4(H_2O)_n^-$ (n = 0-5) clusters using mass-selected anion PES and density functional theory (DFT) calculations to understand the initial dissolution steps of Li_2SO_4 in water.

Experimental

The experiments were performed on a home-built apparatus consisting of a time-of-flight mass spectrometer and a magnetic-bottle photoelectron spectrometer, which has been described elsewhere.[53] Briefly, the second harmonic light pulses of a Nd:YAG laser was used to ablate a rotating and translating Li_2SO_4 disc target, while helium with ~4 atm backing pressure seeded with water vapor was expanded through a pulsed valve to produce the $Li_2SO_4(H_2O)_n^-$ (n = 0-5) clusters. These cluster anions were mass analyzed by the time-of-flight mass spectrometer and were each mass-selected and decelerated before being photodetached. The photodetached electrons were energy analyzed by the magnetic-bottle photoelectron spectrometer. The photoelectron spectra were calibrated with the spectra of Cs^- and Bi^- taken at similar conditions. The instrumental resolution was ~40 meV for electrons with 1 eV kinetic energy.

Theoretical

Geometry optimizations of $Li_2SO_4(H_2O)_n^-$ (n = 0-5) clusters and the neutrals were carried out with DFT calculations employing the long-range corrected hybrid func-tional LC-ωPBE,[54-57] which has been proved very reliable for salt dissolution problems.[41] The Pople-type basis set 6-311++G(d, p)[58] was used for all the atoms. The starting structures of the $Li_2SO_4(H_2O)_{1-2}^-$ clusters were obtained by varying the positions of the water molecules with respect to Li_2SO_4. The structures of the larger clusters were generated from the smaller ones by adding water molecules to the Li atoms through Li-O interaction or to SO_4^{2-} and other water molecules through $OH^{\cdots}O(SO_4^{2-})$ and $OH^{\cdots}O(H_2O)$ hydrogen bonds, at different positions. In order to check the performance of LC-ωPBE functional, the structures of $Li_2SO_4(H_2O)^-$ were also optimized with M06-2X, ωB97XD and B3LYP functionals, which provide results agreeing with those of LC-ωPBE functional (Table S1). Harmonic vibrational frequencies were calculated to estimate the zero-point vibrational energies and to confirm that the optimized structures are real local minima. All the calculations were carried out with Gaussion09 suit of program package.[59]

Results and Discussions

Photoelectron Spectra

The photoelectron spectra of $Li_2SO_4(H_2O)_n^-$ (n = 0-5) recorded with 1064 and 532 nm photons are shown in Figure 1. The vertical detachment energies (VDEs) of the $Li_2SO_4(H_2O)_n^-$ (n = 0-5) clusters were measured from the peak apex of the corresponding spectrum while the adiabatic detachment energies (ADEs) were estimated by adding the instrumental resolution to the electron binding energy (EBE) at the crossing point of the leading edge of the first peak and the baseline (Table S2).

The 1064 and 532 nm spectra share similar features, showing very broad peaks. The 1064 nm spectrum of $Li_2SO_4^-$ shows one weak peak at 0.24 eV (labeled as X') and one strong peak centered at 0.75 eV (labeled as X). The spectra of $Li_2SO_4(H_2O)_n^-$ (n = 1-3) clusters have similar features as $Li_2SO_4^-$, except that the peaks shift to the high EBE. Peak X' centers at 0.32, 0.37 and 0.54 eV, while X centers at 1.03, 1.07 and 0.92 eV for $Li_2SO_4(H_2O)^-$, $Li_2SO_4(H_2O)_2^-$ and $Li_2SO_4(H_2O)_3^-$, respectively. The spectra of $Li_2SO_4(H_2O)_4^-$ and $Li_2SO_4(H_2O)_5^-$ show only one broad peak, center at 0.91 and 0.94 eV, respectively. The VDE of peak X' increases smoothly when n increases from 0 to 3 while the VDE of the peak X first increases when n changes from 0 to 2 and drops 0.15 eV at n = 3, then almost keeps constant for n = 4 and 5.

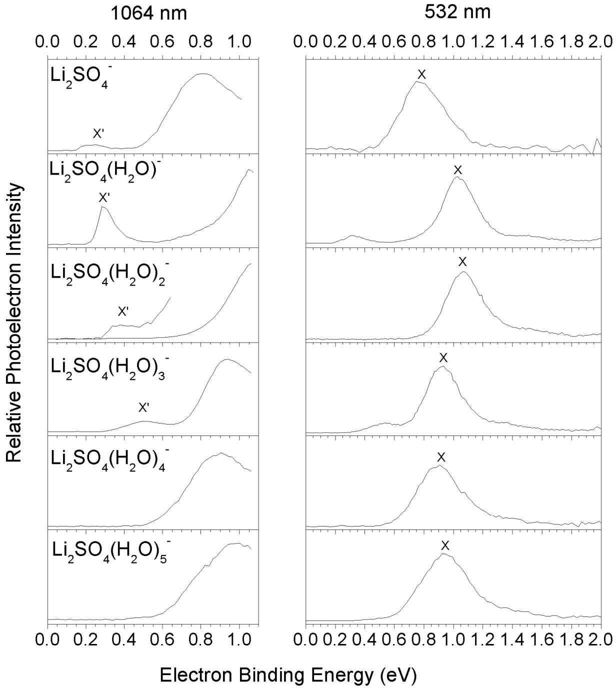

Figure 1. Photoelectron spectra of $Li_2SO_4(H_2O)_n^-$ (n = 0-5) recorded with 1064 and 532 nm photons.

Theoretical Results

Many low-lying isomers of $Li_2SO_4(H_2O)_n$ anions and neutrals were found by DFT calculations, especially for n = 4-5. In Figure 2, we show the typical low-lying isomers of $Li_2SO_4(H_2O)_n^-$ (n = 0-5) in the order of relative stability. The relative energies, VDEs and ADEs of these isomers are summarized in Table 1 and are compared to the experimental VDEs and ADEs. The isomers of the neutral clusters are shown in Figure 3. In all the isomers, the tetrahedral geometry of SO_4^{2-} moiety was preserved with the S atom at the center and four O atoms at the corners. The detailed geometries of isomers for the anion and the neutral are given in the supporting information. In order to distinguish the Li-O interaction between Li and SO_4^{2-} from that between Li and H_2O, in the followed paragraphs, we will use the notation "Li-O(SO_4^{2-})" to designate the Li-O interaction between Li and SO_4^{2-} and the notation "Li-O(H_2O)" to designate the Li-O interaction between Li and H_2O.

Two low-lying isomers 0a and 0b were found for $Li_2SO_4^-$. Isomer 0a can be viewed as a turtle-shaped structure with one O atom as the head, a S-O bond as the back of the body, two O atoms as the fore legs, and two Li atoms as the hind legs (Figure S2). Isomer 0b can be viewed as a propeller-shaped structure with two rhombuses sharing a S atom and perpendicular to each other (Figure S2). The turtle-shaped structure (0a) has C_s symmetry with one of the O atoms shared by two Li atoms and each Li atom interacting with two O atoms

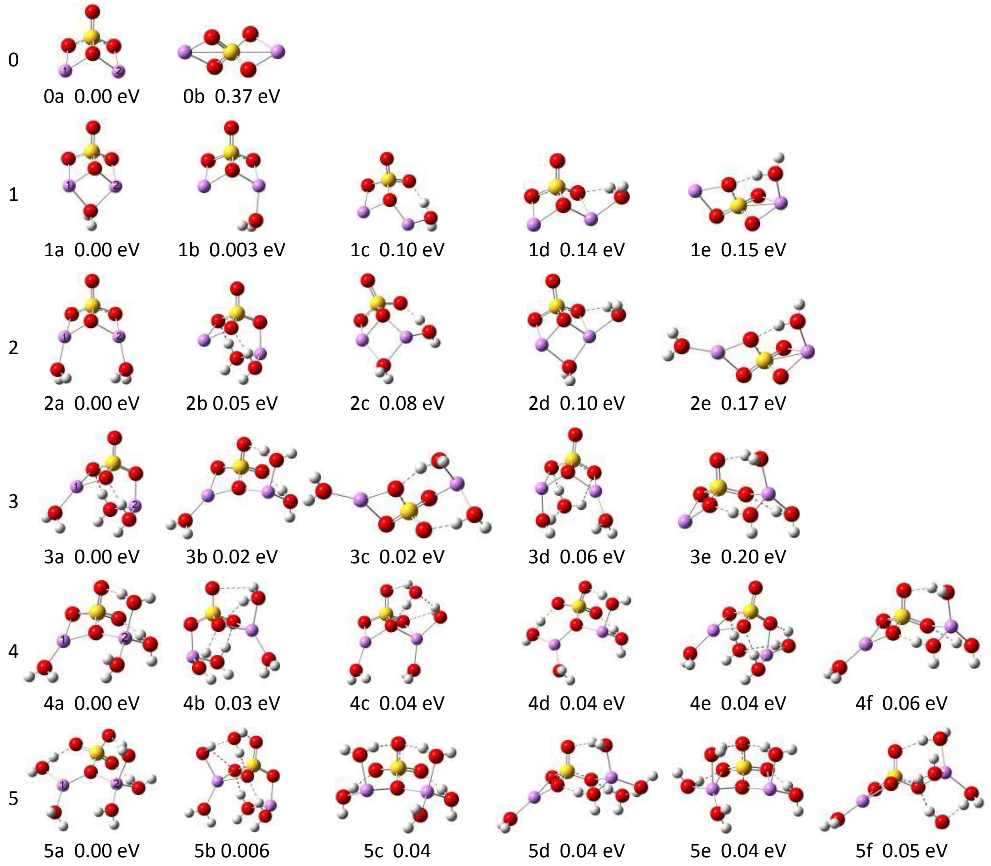

Figure 2. Structures and the relative stability of the typical low-lying isomers of $Li_2SO_4(H_2O)_n^-$ (n = 0-5) calculated at LC-ωPBE/6-311++G(d, p) level.

including the shared one. The theoretical VDE of this isomer (0.95 eV) is in agreement with that of the peak X (0.75 eV). The propeller-shaped structure (0b) is less stable than the turtle-shaped structure by 0.37 eV and has a linear Li-S-Li arrangement with D_{2d} symmetry. Its theoretical VDE is in reasonable agreement with peak X' (~0.24 eV). We suggest that the turtle-shaped and propeller-shaped structures coexist in our experimental condition with the propeller-shaped structure weakly populated. Although the propeller-shaped structure of $Li_2SO_4^-$ is much higher than the turtle-shaped structure in energy, it can still exist in the cluster beam because that its neutral counterpart is very stable and thereby able to obtain an electron to form the anion. More likely, there is a larger barrier between the propeller-shaped structure and turtle-shaped structure. Thus, they can coexist instead of transforming into the lower energy one. As shown in Figure 3, the neutral Li_2SO_4 has nearly identical structures as its anions except that the order of these two structures is switched, with the propeller-shaped structure being more stable than the turtle-shaped structure by 0.19 eV in energy. The Li-S distances in the neutral Li_2SO_4 are slightly shorter than those in their corresponding anionic counterparts. The similar structures of anionic and neutral states suggest that the electron is likely detached from a non-bonding orbital.

The first four low-lying isomers of $Li_2SO_4(H_2O)^-$ (1a-1d) are all derived from the turtle-shaped structure. Isomers 1a and 1b are almost degenerate in energy. Isomer 1a has C_s symmetry with the water molecule linking to two Li atoms through a bifurcated Li-O(H_2O) interaction. Isomer 1b has C_1 symmetry with the water molecule interacting with only one Li atom. The VDEs for isomers 1a and 1b are calculated to be 0.94 and 1.09 eV respectively, which are both quite close to the experimental value of 1.03 eV. Isomer 1c is higher in energy than 1a by 0.10 eV with the water molecule inserting into one Li-O(SO_4^{2-}) bond via Li-O(H_2O) interaction and an $OH^{\cdots}O$ hydrogen bond. Isomer 1d has a similar structure as 1c, but with no Li-O(SO_4^{2-}) bond being broken. The theoretical VDEs for isomer 1c and 1d are calculated to be 1.22 and 0.77 eV, respectively. They may also contribute to the peak X as the peak X spans from about 0.7 eV to 1.3 eV. Isomer 1e is derived from the propeller-shaped structure, in which the O atom of water molecule interacts with Li and one H atom of water molecule interacts with one O atom of SO_4^{2-} moiety that connects to another Li atom forming an $OH^{\cdots}O$ hydrogen bond. Its theoretical VDE (0.38 eV) is consistent with the low EBE peak (X'), suggesting the co-existence of this isomer in the cluster beam. In contrast to the case of $Li_2SO_4(H_2O)^-$ anion, the most stable isomer of neutral $Li_2SO_4(H_2O)$ (1a') is derived from the propeller-shaped structure similar to isomer 1e but with one O-H bond of the water molecule paralleling to one Li-O bond, forming an $OH^{\cdots}O(SO_4^{2-})$ hydrogen bond. Isomer 1b' is also derived from the propeller-shaped structure with the O atom of water linking to Li, which is slightly higher in energy than isomer 1a' by 0.01 eV. Isomers 1c', 1d' and 1e' are from the turtle-shaped structure with the water molecule located differently via Li-O(H_2O) and $OH^{\cdots}O$ hydrogen bond interactions.

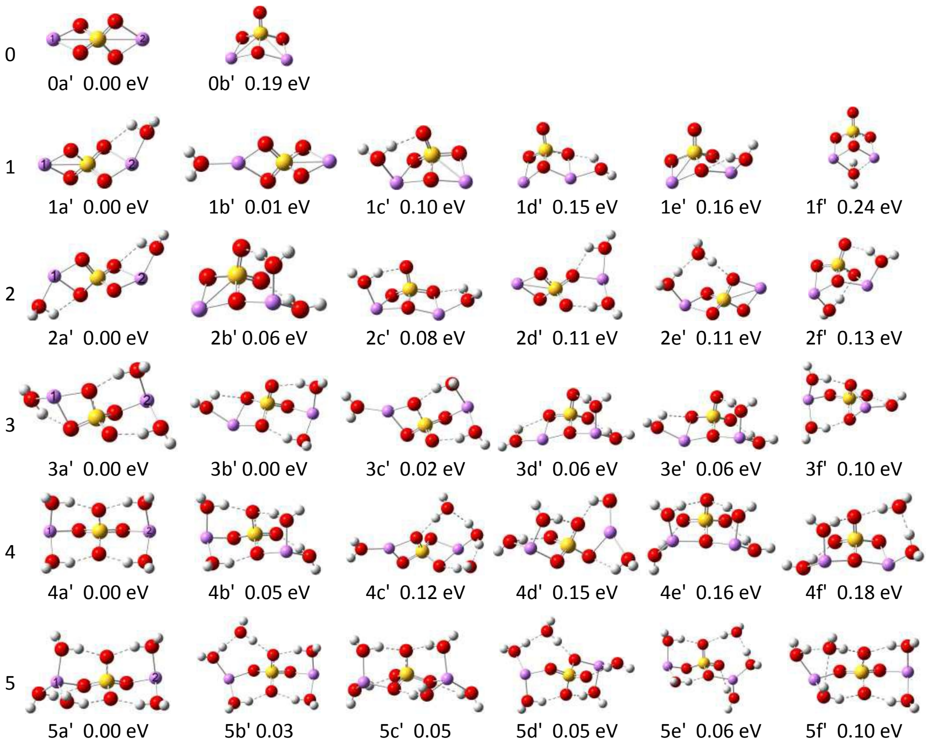

Figure 3. Structures and the relative stability of the typical low-lying isomers of $Li_2SO_4(H_2O)_n$, (n = 0-5) calculated at LC-ωPBE/6-311++G(d,p) level.

Table 1. Low energy isomers of $Li_2SO_4(H_2O)_n^-$ and the comparison of theoretical VDEs and ADEs to the experimental values, all energies are given in eV.

Cluster	Isomer	ΔE	Theor.		Expt.			
					X		X'	
			VDE	ADE	VDE	ADE	VDE	ADE
$Li_2SO_4^-$	0a	0.00	0.95	0.62	0.75	0.49		
	0b	0.37	0.08	0.07			0.24	0.13
$Li_2SO_4(H_2O)^-$	1a	0.00	0.94	0.60	1.03	0.84		
	1b	0.003	1.09	0.57				
	1c	0.10	1.22	0.44				
	1d	0.14	0.77	0.46				
	1e	0.20	0.38	0.26			0.32	0.24
$Li_2SO_4(H_2O)_2^-$	2a	0.00	1.09	0.49	1.07	0.80		
	2b	0.05	1.04	0.61				
	2c	0.08	1.14	0.42				
	2d	0.10	0.94	0.54				
	2e	0.17	0.34	0.30			0.37	0.27
$Li_2SO_4(H_2O)_3^-$	3a	0.00	0.90	0.48	0.92	0.69		
	3b	0.02	0.47	0.33				
	3c	0.02	0.33	0.29				
	3d	0.06	1.01	0.24				
	3e	0.20	0.54	0.31			0.54	0.28
$Li_2SO_4(H_2O)_4^-$	4a	0.00	0.83	0.42	0.91	0.56		
	4b	0.03	0.78	0.35				
	4c	0.04	1.07	0.51				
	4d	0.04	0.85	0.19				
	4e	0.04	0.91	0.51				
	4f	0.06	0.44	0.25				
$Li_2SO_4(H_2O)_5^-$	5a	0.00	1.04	0.36	0.94	0.58		
	5b	0.006	0.88	0.45				
	5c	0.04	0.65	0.30				
	5d	0.04	0.45	0.38				
	5e	0.04	0.84	0.21				
	5f	0.05	0.37	0.35				

Table 2. The energy differences (ΔE) and the NBO charge distributions of the most stable isomers derived from the turtle-shaped and propeller-shaped structures of bare Li_2SO_4.

Anion						Neutral					
		NBO charge distribution/*e*						NBO charge distribution/*e*			
Isomers	ΔE/eV	Turtle-shaped		Propeller-shaped		Isomers	ΔE/eV	Turtle-shaped		Propeller-shaped	
		Li1	Li2	Li1	Li2			Li1	Li2	Li1	Li2
0a/0b	0.37	0.39	0.39	0.40	0.40	0a'/0b'	0.19	0.89	0.89	0.89	0.89
1a/1e	0.20	0.62	0.62	-0.07	0.81	1a'/1c'	0.10	0.89	0.82	0.83	0.89
2a/2e	0.17	0.70	0.70	0.29	0.79	2a'/2b'	0.06	0.82	0.82	0.80	0.89
3a/3e	0.20	0.56	0.72	-0.08	0.71	3a'/3d'	0.06	0.82	0.80	0.82	0.80
4a/4f	0.06	0.64	0.63	0.28	0.70	4a'/4a'	0.00	0.81	0.81	-	-
5a/5d	0.04	0.70	0.64	0.30	0.69	5a'/5a'	0.00	0.71	0.81	-	-

Similar to $Li_2SO_4(H_2O)^-$, the first four low-lying isomers of $Li_2SO_4(H_2O)_2^-$ (2a-2d) are all derived from the turtle-shaped structure. The most stable structure of $Li_2SO_4(H_2O)_2^-$ (2a) has each water molecule connecting to different Li atoms. Its theoretical VDE (1.09 eV) is in good agreement with the experimental value of peak X (1.07 eV). Isomer 2b has two water molecules interacting with the same Li atom, therefore, breaking one Li-O(SO_4^{2-}) bond and forming two Li-O(H_2O) linkages and two $OH^{\cdots}O(SO_4^{2-})$ hydrogen bonds. The theoretical VDE of isomer 2b (1.04 eV) is also in excellent agreement with peak X. The calculated VDEs of isomers 2c and 2d are also very close to the experimental value of peak X. Thus it is reasonable to assign peak X to isomers 2a, 2b, 2c and 2d. Isomer 2e is evolved from the propeller-shaped structure and is less stable than isomer 2a by 0.17 eV, with the second water molecule interacting with another Li atom through its O atom. Its VDE (0.34 eV) is consistent with the peak X'. With these considerations, we suggest that all these five isomers co-exist with isomer 2e weakly populated. All the isomers of $Li_2SO_4(H_2O)_2$ neutral showed in Figure 3 fall in a small energy gap (0.13 eV). Isomers 2a', 2d' and 2e' belong to the propeller-shaped structure. Isomers 2b', 2c' and 2f' belong to the turtle-shaped structure. Isomer 2a' has each water molecule interacting with Li_2SO_4 via one Li-O(H_2O) and one $OH^{\cdots}O(SO_4^{2-})$ hydrogen bond. Isomer 2b' presents a similar structure as isomer 2b that the two water molecules interact with one Li and break one Li-O(SO_4^{2-}) bond.

Isomers 3a-3d are almost degenerate in energy. Isomers 3a, 3b, and 3d are evolved from the turtle-shaped structure, while isomers 3c and 3e can be derived from either turtle-shaped or propeller-shaped structures. Isomer 3a is derived from isomer 2b with two water molecules interacting with one Li atom and breaking one Li-O(SO_4^{2-}) bond while the third water molecule interacting with the bare Li atom. The theoretical VDE of this isomer is 0.90 eV, in good agreement with the experimental value (0.92 eV). Isomers 3b and 3c have similar structures as isomer 3a but with a different Li-O(SO_4^{2-}) bond being broken by inserting two water molecules. The VDEs of isomers 3b and 3c are calculated to be 0.47 and 0.33 eV respectively, consistent with the broad peak X' at ~0.54 eV. Isomer 3d is derived from isomer 2a by connecting the third water molecule via two $OH^{\cdots}O(SO_4^{2-})$ and one $OH^{\cdots}O(H_2O)$ hydrogen bonds. Its VDE is in reasonable agreement with the experimental value of peak X. Isomer 3e is less stable than isomer 3a by 0.20 eV, with three water molecules interacting with one Li atom via three Li-O(H_2O) bonds and three $OH^{\cdots}O(SO_4^{2-})$ hydrogen bonds. The VDE of this isomer is calculated to be 0.54 eV, in excellent agreement with the experimental value of peak X'. Thus we suggest that isomer 3a is the major one and isomers 3b, 3c, 3d and 3e are the minor ones contributing to the observed photoelectron spectrum of $Li_2SO_4(H_2O)_3^-$. The structural evolution of $Li_2SO_4(H_2O)_3$ neutral becomes less clear. Isomers 3a', 3b', 3c', and 3f' can be evolved from either turtle-shaped or propeller-shaped structures, while isomers 3d' and 3e' are the turtle-shaped structure. The most stable structure of $Li_2SO_4(H_2O)_3$ neutral has a similar configuration as isomer 3c but with one more $OH^{\cdots}O(SO_4^{2-})$ hydrogen bond. The structures of isomers 3b' and 3c' are similar to isomer 3a', but with the dangling water molecule pointing to different orientation.

The first five isomers of $Li_2SO_4(H_2O)_4^-$ (4a-4e) are all turtle-shaped structures while isomer 4f is a propeller-shaped structure. Isomer 4a is derived from isomer 3b, with three water molecules interacting with one Li atom and one water molecule interacting with another Li atom. Isomers 4b and 4e are derived from isomer 3a, with the fourth water molecule interacting with different Li atom. The water-water hydrogen bond interaction shows up in isomer 4c, similar to the case in isomer 3d. In isomer 4d, each Li atom interacts with two water molecules sharing one O atom of the SO_4^{2-} moiety, two Li-O(SO_4^{2-}) bonds are broken by the water molecules. The VDEs of 4a, 4b, 4c, 4d and 4e are calculated to be 0.83, 0.78, 1.07, 0.85 and 0.91 eV, respectively, agree with the experimental value (0.91 eV). We suggest that isomers 4a and 4b are the dominating structures and isomers 4c, 4d and 4e are the minor ones. For the $Li_2SO_4(H_2O)_4$ neutral, the propeller-shaped and turtle-shaped structures are indistinguishable because of the disturbance of water molecules to salt structure. Isomer 4a' has C_{2v} symmetry. It can be viewed as a tent-shaped structure with two Li atoms and two O atoms of the SO_4^{2-} moiety at the top while the four water molecules and the other two O atoms of SO_4^{2-} form the floor, each Li atom interacting with two water molecules and one O atom of the SO_4^{2-} moiety (Figure S2). The water molecules each forms a hydrogen bond with an O atom of the SO_4^{2-} moiety and interacts with a Li atom simultaneously, thus, two Li-O(SO_4^{2-}) bonds of Li_2SO_4 are broken due to the addition of four water molecules. Isomer 4b' has a similar structure as 4a', with each two water molecules breaking one Li-O(SO_4^{2-}) bond.

All the isomers of $Li_2SO_4(H_2O)_5^-$ shown in Figure 2 are almost degenerate in energy. Isomers 5a, 5b, 5c, and 5e are turtle-shaped structures, while isomers 5d and5f belongs to propeller-shaped structure. Isomer 5a is evolved from isomer 4a or 4d, with the fifth water molecule directly contacting to the Li atom. Its theoretical VDE (1.04 eV) is consistent with the experimental value of 0.94 eV. Isomer 5b is from isomer 4b, with the fifth water molecule attaching to the SO_4^{2-} moiety and interacting with one water molecule forming three hydrogen bonds. Only one Li-O(SO_4^{2-}) bond is broken. The theoretical

VDE of 5b (0.88 eV) is also in accordance with the experimental value. Isomer 5c is evolved from isomer 4d, with the fifth water molecule connected via a Li-O(H_2O) linkage and an OH···O(SO_4^{2-}) hydrogen bond. In isomers 5d and 5e, the fifth water molecule interacts with the SO_4^{2-} moiety and one water molecule. The theoretical VDEs of 5c and 5d (0.65 and 0.45 eV, respectively) are consistent with the front part of the broad peak in the experimental spectrum. The VDE of 5e are calculated to be 0.84 eV, which is in reasonable agreement with the experimental value. The VDE of 5f is 0.37 eV, far away from the experimental value. With these considerations, we suggest that isomers 5a and 5b are the major ones in our experiments and isomers 5c, 5d, and 5e are weakly populated. The low-lying isomers of neutral $Li_2SO_4(H_2O)_5$ cluster are also fall in a narrow energy gap. The propeller-shaped and turtle-shaped structures are indistinguishable. Isomer 5a' is formed by adding one water molecule to one Li atom of 4a' to fully coordinate it. Isomers 5c' and 5d' have one Li atom full coordinated. Isomers 5b', 5e' and 5f' are formed with the fifth water connected to SO_4^{2-} and one water molecule through OH···O hydrogen bonds.

Discussion

Bare $Li_2SO_4^-$ and its neutral both have turtle-shaped structure and propeller-shaped structure, but with reversed relative stabilities. The most stable isomers of $Li_2SO_4(H_2O)_n^-$ (n = 0-3) are turtle-shaped structures while those of the neutrals are propeller-shaped structures. The addition of water molecules reduces the energy difference between the turtle-shaped and propeller-shaped structures in both anionic and neutral states (Table 2). For the neutrals, three or more water molecules are able to eliminate the energy difference of the two types of structures. Addition of four or more water molecules to $Li_2SO_4^-$ makes these two types of structures energetically indistinguishable. This is consistent with the photoelectron spectroscopy observations that for $Li_2SO_4(H_2O)_n^-$ (n = 0-3) two peaks are attributed to turtle-shaped and propeller-shaped structures respectively. For $Li_2SO_4(H_2O)_n^-$ (n = 4-5) only one peak was detected because the EBE value of peak X' increases as the number of water molecule increases and likely reaches the onset of peak X and may also because that the intensity of feature X' is really weak thereby is difficult to be recognized. As shown in Figure 4, both the experimental and theoretical VDEs of the propeller-shaped structures approach those of the turtle-shaped structures with increasing number of water molecules. These results confirm that the evolution of photoelectron spectra with the cluster size provides valuable information on the structures of the corresponding clusters. We also note that the $Li_2SO_4(H_2O)_n$ cluster anions and neutrals tend to display similar structures as the number of water molecules increases.

The analysis of natural bond orbital (NBO) charge distributions (Table 2 and Figure S2) showed that the total charge on the two Li atoms of the $Li_2SO_4(H_2O)_n^-$ cluster anions is between +0.63 to +1.34 e depending on the structures and the number of water molecules involved, which is much smaller than that of the neutral clusters. This indicates that the excess electron mainly localizes on the Li atoms. In addition, the charges on the two Li atoms of the turtle-shaped $Li_2SO_4(H_2O)_n^-$ cluster anions are almost balanced with their charges ranging from +0.39 to +0.70 e with increasing number of water molecules. Whereas, for the propeller-shaped $Li_2SO_4(H_2O)_n^-$ cluster anions, the positive charge on one of the Li atoms (which interacts with more water) is much more than that on the other. This also implies that the excess electron localizes almost equally on the two Li atoms for the turtle-shaped structures but prefers to localize on the Li atom interacting with less water molecules for the propeller-shaped structures (Table 2). For the neutral $Li_2SO_4(H_2O)_n$ clusters, the charge on each Li atom is in the range of +0.71 to +0.89 e. The addition of five water molecules reduces the total charge on the two Li atoms from +1.78 e to +1.51 e whereas the charge carried by SO_4^{2-} moiety is reduced from -1.77 e to -1.64 e (Table 2). Thus the addition of water molecules weakens the Coulomb attraction between the Li^+ and SO_4^{2-} ions.

Table 3. The evolutions of Li-S distances (Å) in the most stable isomers of $Li_2SO_4(H_2O)_n^-$ (n = 0-5) and those of the neutrals.

Cluster	Anion		Neutral	
	Li1-S	Li2-S	Li1-S	Li2-S
Li_2SO_4	2.42	2.42	2.35	2.35
$Li_2SO_4(H_2O)$	2.41	2.41	2.35	2.42
$Li_2SO_4(H_2O)_2$	2.43	2.43	2.42	2.42
$Li_2SO_4(H_2O)_3$	2.45	2.82	2.43	2.77
$Li_2SO_4(H_2O)_4$	2.43	2.93	2.82	2.82
$Li_2SO_4(H_2O)_5$	3.03	2.92	2.93	2.81

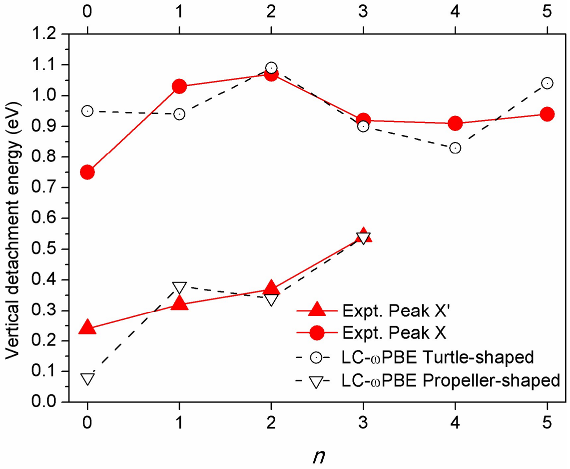

Figure 4. Experimental VDEs of $Li_2SO_4(H_2O)_n^-$ (n = 0-5) clusters compared to those of the most stable isomers of turtle-shaped and propeller-shaped structures obtained with LC-ωPBE method.

Table 3 shows the Li-S distance variation of the most stable isomers of $Li_2SO_4(H_2O)_n^-$ clusters and the corresponding neutrals. The Li-S distances in the $Li_2SO_4(H_2O)_n$ neutral are shorter than those in the anion due to the weakening of the Li^+-SO_4^{2-} Coulomb attraction in the anion by the excess electron. The Li-S distance does not increase when $Li_2SO_4^-$ interacts with one water molecule. The Li-S distances increase only slightly from 2.41 to 2.43 Å when $Li_2SO_4^-$ interacts with two water molecules. At n = 3, one Li-S bond distance increases significantly to 2.82 Å upon the addition of the third water molecule which forms an OH···O hydrogen bond and breaks one of the Li-O(SO_4^{2-}) bonds. This solvation effect also lowers the VDE of $Li_2SO_4(H_2O)_3^-$ by 0.15 eV comparing to that of $Li_2SO_4(H_2O)_2^-$. Addition of the fourth and fifth water molecules increases that Li-S distance further to 2.93 and 3.03 Å respectively. These structural variations are consistent with the experimental observation that the EBE of peak X first increases when the number of water molecules changes from 0 to 2, and drops by 0.15 eV at n = 3, and then keeps almost constant for n = 4 and 5.

For the $Li_2SO_4(H_2O)_n$ neutral clusters, the water molecules interact with the two Li atoms alternately, in which a newly added water molecule interacts with the Li atom different from that the previous water molecule interacting with, for example, the first and second water molecules interact with different Li atoms respectively. The modification of the two Li-S distances by the water molecules shows a property of a pairwise increase (Table 3). The first water molecule induces one of the Li-S distances to increase from 2.35 to 2.42 Å. The second water molecule increases the other Li-S distance to 2.42 Å. At $n = 3$, the interaction of two water molecules with one Li atom breaks one of the Li-O(SO_4^{2-}) bonds, thus elongates that Li-S distance considerably to 2.77 Å. Similarly, the addition of the fourth water molecule lengthens the Li-S distances to 2.82 Å. At $n = 5$, the maximum Li-S distance reaches 2.93 Å when three of the water molecules interact with one Li atom. For each Li atom, only one of its two Li-O bonds can be broken with up to 5 water molecules, implying that more water molecules are required to fully separate the Li^+-SO_4^{2-} CIP into SSIP.

In the $Li_2SO_4(H_2O)_n$ (n = 1-5) anion and neutral clusters, the water molecules prefer to stay close to the Li atoms rather than to the SO_4^{2-} moiety, which is different from the way water molecules interacting with $NaSO_4^-$ where water molecules first occupy the three O sites of SO_4^{2-} forming a solvation ring between Na^+ and SO_4^{2-}.[46, 47] This indicates that the Li-O(H_2O) interaction is stronger than $OH\cdots O(SO_4^{2-})$ hydrogen bond and water$\cdots$water hydrogen bond. The highest coordinate number of Li atom in $Li_2SO_4(H_2O)_n$ anion and neutral cluster is 4 (number of Li-O contacts), consistent with the teracoordination of Li^+ in bulk water.[60] The current study also confirms that the structure of salt-water cluster is valent-dependent. In the $Li_2SO_4(H_2O)_n^{-/0}$ (n = 1-5) clusters, the water molecules are shared by two Li^+ ions due to the bivalent nature of Li_2SO_4, and therefore the dissolution progress is different from that of monovalent salts such as $NaBO_2$,[61] LiI and CsI.[41]

Conclusions

We investigated the mass-selected $Li_2SO_4(H_2O)_n^-$ (n = 0-5) clusters with photoelectron spectroscopy. DFT calculations were performed to provide the energetic and structural information on bare and solvated Li_2SO_4 anions and neutrals. The most probable structures of $Li_2SO_4(H_2O)_n^-$ (n = 0-5) clusters were determined by comparing their theoretical VDEs to the experimental values. Bare $Li_2SO_4^-$ has two low-lying isomers coexisted, which are named as turtle-shaped and propeller-shaped structures respectively. These two types of structures are preserved in $Li_2SO_4(H_2O)_n^-$ (n = 1-3) in the cluster beam and thus two EBE features were observed, but tend to have similar energetic properties and only one EBE feature was observed for larger clusters. All of the 5 water molecules interact with the Li atoms and prefer to form $OH\cdots O(SO_4^{2-})$ hydrogen bond with the SO_4^{2-} moiety rather than with other water molecules, revealing that the Li-O and $OH\cdots O(SO_4^{2-})$ interactions are stronger than the water-water interaction. For the most stable structures of $Li_2SO_4(H_2O)_n$ (n = 1-5) neutrals, the water molecules interact with the two Li atoms alternately showing a pairwise solvation behaviour. The Li atoms can only be partially separated from the SO_4^{2-} moiety with up to 5 molecules, suggesting that more water molecules are required to form SSIP.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21403249 and 21273246). The theoretical calculations were conducted on the ScGrid and DeepComp 7000 of the Supercomputing Center, Computer Network Information Center of Chinese Academy of Sciences.

Notes and references

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
Email: zhengwj@iccas.ac.cn

Electronic Supplementary Information (ESI) available: [Completion of one Reference [59]; Table with VDEs of $Li_2SO_4(H_2O)^-$ with different functionals; Table with experimental VDEs and ADEs (eV) of $Li_2SO_4(H_2O)_n^-$ (n = 0-5) clusters; Figure of the mass spectrum of $Li_2SO_4(H_2O)_n^-$ (n = 0-5); Figure of the structures of most stable isomers belong to turtle-shaped, propeller-shaped and tent-shaped viewed from different points; NBO analysis of the most stable isomers; Cartesian atomic coordinates of the low-lying isomers of the $Li_2SO_4(H_2O)_n^{-/0}$ (n = 0-5)]. See DOI: 10.1039/b000000x/

1 M. P. Apse, G. S. Aharon, W. A. Snedden, and E. Blumwald, *Science,* 1999, **285**, 1256.
2 K. W. Oum, M. J. Lakin, D. O. DeHaan, T. Brauers, and B. J. Finlayson-Pitts, *Science,* 1998, **279**, 74.
3 E. E. Gard, M. J. Kleeman, D. S. Gross, and L. S. Hughes, J. O. Allen, B. D. Morrical, D. P. Fergenson, T. M. Dienes, E. Gäli, R. J. Johnson, G. R. Cass, and K. A. Prather, *Science*, 1998, **279**, 1184.
4 E. M. Knipping, M. J. Lakin, K. L. Foster, P. Jungwirth, D. J. Tobias, R. B. Gerber, D. Dabdub, and B. J. Finlayson-Pitts, *Science,* 2000, **288**, 301.
5 P. Neysens, W. Messens, and L. D. Vuyst, *Int. J. Food Microbiol.,* 2003, **88**, 29.
6 T. Cserháti, and E. Forgács, *Int. J. Pharmaceut.,* 2003, **254**, 189.
7 C. Dedonder-Lardeux, G. Grégoire, C. Jouvet, S. Martrenchard, and D. Solgadi, *Chem. Rev.,* 2000, **100**, 4023.
8 B. J. Finlayson-Pitts, *Chem. Rev.*, 2003, **103**, 4801.
9 L. E. de-Bashan and Y. Bashan, *Water Res.*, 2004, **38**, 4222.
10 N. Tsipouras, C. J. Rix, and P. H. Brady, *Clin. Chem.*, 1997, **43**, 290.
11 M. J. Blandamer and M. F. Fox, *Chem. Rev.*, 1970, **70**, 59.
12 P. Jungwirth, *J. Phys. Chem. A*, 2000, **104**, 145.
13 D. E. Woon and T. H. Dunning,. *J. Am. Chem. Soc.*, 1995, **117**, 1090.
14 G. H. Peslherbe, B. M. Ladanyi, and J. T. Hynes, *J. Phys. Chem. A*, 1998, **102**, 4100.
15 C. P. Petersen, and M. S. Gordon, *J. Phys. Chem. A*, 1999, **103**, 4162.
16 G. H. Peslherbe, B. M. Ladanyi, and J. T. Hynes, *J. Phys. Chem. A*, 2000, **104**, 4533.
17 S. Yamabe, H. Kouno, and K. Matsumura, *J. Phys. Chem. B*, 2000, **104**, 10242.
18 P. Jungwirth, and D. J. Tobias, *J. Phys. Chem. B*, 2001, **105**, 10468.
19 S. Godinho, P. C. do Couto, and B. J. C. Cabral, *Chem. Phys. Lett.*, 2006, **419**, 340.
20 A. C. Olleta, H. M. Lee, and K. S. Kim, *J. Chem. Phys.,* 2006, **124**, 024321.

21 C. Olleta, H. M. Lee, and K. S. Kim, *J. Chem. Phys.*, 2007, **126**, 144311.

22 G. Sciaini, R. Fernandez-Prini, D. A. Estrin, and E. Marceca, *J. Chem. Phys.*, 2007, **126**, 174504.

23 M. Pettitt, and P. J. Rossky, *J. Chem. Phys.,* 1986, **84**, 5836.

24 A. C. Belch, M. Berkowitz, and J. A. McCammon, *J. Am. Chem. Soc.*, 1986, **108**, 1755.

25 E. Smith, and L. X. Dang, *J. Chem. Phys.*, 1994, **100**, 3757.

26 T. Asada, and K. Nishimoto, *Chem. Phys. Lett.*, 1995, **232**, 518.

27 T. Asada, and K. Nishimoto, *Mol. Simul.*, 1996, **16**, 307.

28 C.-K. Siu, B. S. Fox-Beyer, M. K. Beyer, and V. E. Bondybey, *Chem.-Eur. J.*, 2006, **12**, 6382.

29 C. Krekeler, B. Hess, and L. D. Site, *J. Chem. Phys.*, 2006, **125**, 054305.

30 M. Koch, Q. K. Timerghazin, G. H. Peslherbe, B. M. Ladanyi, and J. T. Hynes, *J. Phys. Chem. A*, 2006, **110**, 1438.

31 D. M. Koch, and G. H. Peslherbe, *J. Phys. Chem. B*, 2008, **112**, 636.

32 C.W. Liu, F. Wang, L.-J. Yang, X.-Z. Li, W.-J. Zheng, and Y.-Q. Gao, *J. Phys. Chem. B*, 2014, **118**, 743.

33 B. S. Ault, *J. Am. Chem. Soc.*, 1978, **100**, 2426.

34 G. Gregoire, M. Mons, C. Dedonder-Lardeux and C. Jouvet, *Eur. Phys. J. D*, 1998, **1**, 5.

35 G. Gregoire, M. Mons, C. Dedonder-Lardeux, C. Jouvet, S. Martrenchard and D. Solgadi, *J. Chem. Phys.,* 2000, **112**, 8794.

36 J. J. Max and C. Chapados, *J. Chem. Phys.*, 2001, **115**, 2664.

37 Q. Zhang, C. J. Carpenter, P. R. Kemper and M. T. Bowers, J. *Am. Chem. Soc.*, 2003, **125**, 3341.

38 A. T. Blades, M. Peschke, U. H. Verkerk and P. Kebarle, *J. Am. Chem. Soc.*, 2004, **126**, 11995.

39 A. Mizoguchi, Y. Ohshima and Y. Endo, *J. Am. Chem. Soc.,* 2003, **125**, 1716.

40 A. Mizoguchi, Y. Ohshima and Y. Endo, *J. Chem. Phys*,. 2011, **135**, 064307.

41 R. Z. Li, C. W. Liu, Y. Q. Gao, H. Jiang, H. G. Xu and W. J. Zheng, *J. Am. Chem. Soc.*, 2013, **135**, 5190.

42 C. W. Liu, G. L. Hou, W. J. Zheng and Y. Q. Gao, *Theor. Chem. Acc.* 2014, **133**, 1550.

43 A. Albrecht, *Science*, 1989, **245**, 1227.

44 M. O. Andreae and P. J. Crutzen, *Science,* 1997, **276**, 1052.

45 M. C. Kido Soule, P. G. Blower and G. L. Richmond, *J. Phys. Chem. B* 2007, **111**, 13703.

46 X. B. Wang, H. K. Woo, B. Jagoda-Cwiklik, P. Jungwirth and L. S. Wang, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4294.

47 T. Jin, B. B. Zhang, J. Song, L. Jiang, Y. S. Qiu and W. Zhuang, *J. Phys. Chem. A,* 2014, **118**, 9157.

48 H. Zhang, Y. H. Zhang and F. Wang, *J. Comput. Chem.* 2009, **30**, 493.

49 W. W. Liu, X. L. Wang, S. L. Chen, Y. H. Zhang and Z. S. Li, *Ther. Chem. Acc.* 2012, **131**, 1103.

50 X. Yang, X. B. Wang and L. S. Wang, *J. Phys. Chem. A,* 2002, **106**, 7607.

51 B. Gao and Z. F. Liu, *J. Chem. Phys.*, 2004, **121**, 8299.

52 J. Tobias and J. C. Hemminger, *Science,* 2008, **319**, 1197.

53 H. G. Xu, Z.-G. Zhang, Y. Feng, J. Y. Yuan, Y. C. Zhao, and W. J. Zheng, *Chem. Phys. Lett.,* 2010, **487**, 204.

54 Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, *J. Chem. Phys.,* 2004, **120**, 8425.

55 A. Vydrov, J. Heyd, A. V. Krukau and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 074106.

56 A. Vydrov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 234109.

57 A. Vydrov, G. E. Scuseria and J. P. Perdew, *J. Chem. Phys.*, 2007, **126**, 154109.

58 R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.* 1971, **54**, 724.

59 M. J. Frisch, et al. Gaussian09; Gaussian Inc: Walling-ford, CT, 2009.

60 H. H. Loeffler and B. M. Rode, *J. Chem. Phys.* 2002, **117**, 110.

61 Y. Feng, M. Cheng, X. Y. Kong, H. G. Xu and W. J. Zheng, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15865.