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On the dissolution of lithium sulfate in water: anion photoelectron spectroscopy and density functional theory calculations†

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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 neutral clusters were obtained using 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: a turtle-shaped structure and a 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 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 the neutral clusters, the water molecules interact with the two Li atoms alternately, therefore, showing a pairwise solvation behavior. The Li–S distance increases smoothly upon addition of water molecules one by one. Addition of five water molecules to Li_2SO_4 cannot induce the dissociation of one Li^+ ion 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 salts in the bulk and complex environment. In the initial steps of dissolution, the solvent molecules interact with the anion and the cation, firstly forming a contact ion pair (CIP) due to the direct electrostatic attraction of the anion and the cation, and then the structure evolves into a solvent-separated ion pair (SSIP) as the number of 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 these kinds of 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 measurements 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 dissolution in water is 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 photodissociation (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) were reported by Liu *et al.*[49] The sulfate ion is a polyatomic group and has two negative charges distributing over

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† Electronic supplementary information (ESI) available: Complete ref. 59; a table with VDEs of $Li_2SO_4(H_2O)^-$ with different functionals; a table with experimental VDEs and ADEs (eV) of $Li_2SO_4(H_2O)_n^-$ (n = 0–5) clusters; a figure of the mass spectrum of $Li_2SO_4(H_2O)_n^-$ (n = 0–5); a figure of the structures of the most stable isomers of turtle-shape, propeller-shape and tent-shape viewed from different points; NBO analysis of the most stable isomers; and Cartesian atomic coordinates of the low-lying isomers of $Li_2SO_4(H_2O)_n^{-/0}$ (n = 0–5). See DOI: 10.1039/c4cp05698a

four O atoms which can form strong hydrogen bonds 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 the I^- anion in the case studied previously.[41] Detailed information, at the molecular level, on the dissolution processes will be of great help to understand the nature of salt dissolution and the chemical fate of sulfate salts in aerosol formation and their salt effect on the bulk. Lithium sulfate (Li_2SO_4) is a simple 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 using 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 were used to ablate a rotating and a 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 using the time-of-flight mass spectrometer and were each mass-selected and decelerated before being photodetached. The photodetached electrons were energy analyzed using the magnetic-bottle photoelectron spectrometer. The photoelectron spectra were calibrated with the spectra of Cs^- and Bi^- taken under 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 neutral clusters were carried out using DFT calculations employing the long-range corrected hybrid functional 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···O(SO_4^{2-}) and OH···O(H_2O) hydrogen bonds, at different positions. In order to check the performance of the 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 the LC-ωPBE functional (Table S1, ESI†). 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 using the Gaussion09 suit of program package.[59]

Results and discussion

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 Fig. 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, ESI†).

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 higher 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, centered 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 peak X first increases when n changes from 0 to 2 and drops to 0.15 eV at n = 3, then almost keeps constant for n = 4 and 5.

Theoretical results

Many low-lying isomers of $Li_2SO_4(H_2O)_n$ anions and neutral clusters were found using DFT calculations, especially for n = 4–5. In Fig. 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,

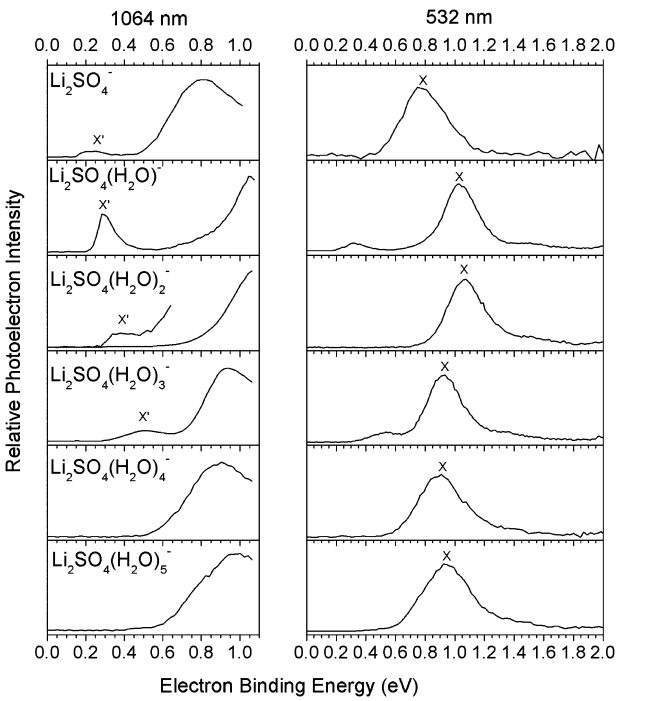

Fig. 1 Photoelectron spectra of $Li_2SO_4(H_2O)_n^-$ (n = 0–5) recorded with 1064 and 532 nm photons.

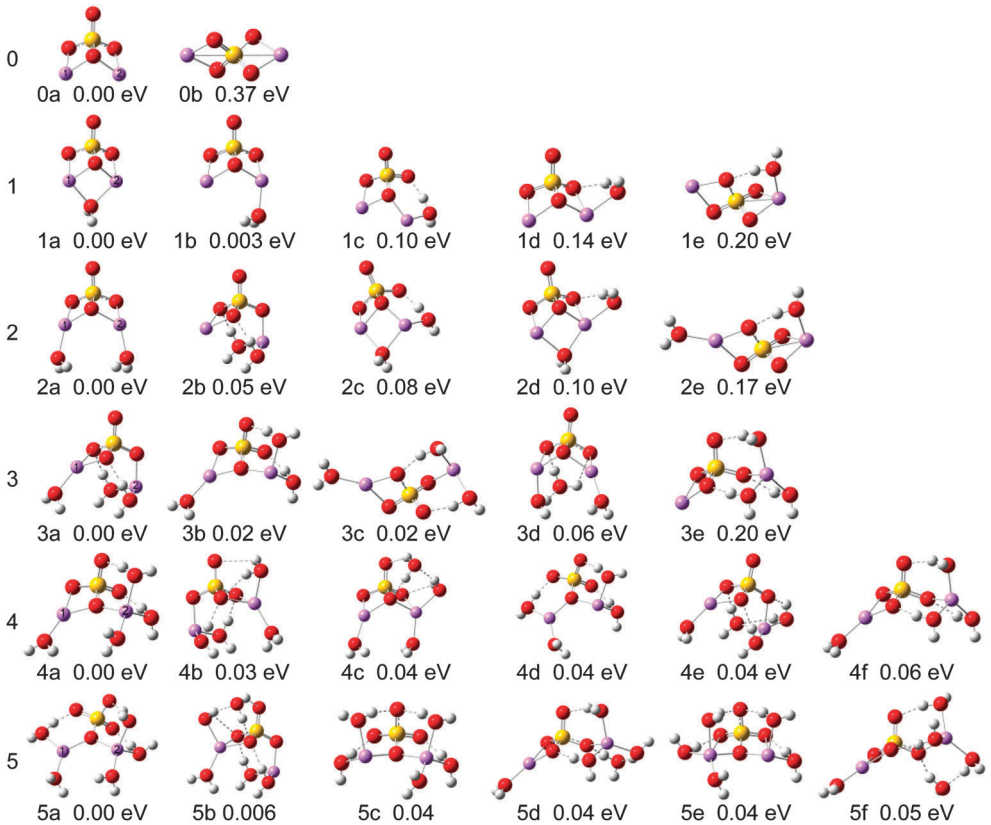

Fig. 2 Structures and the relative stability of the typical low-lying isomers of $Li_2SO_4(H_2O)_n^-$ (n = 0–5) calculated at the LC-ωPBE/6-311++G(d,p) level.

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 Fig. 3. In all the isomers, the tetrahedral geometry of the 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 cluster are given in the ESI.† In order to distinguish the Li–O interaction between Li and SO_4^{2-} from that between Li and H_2O, in the following 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, an S–O bond as the back of the body, two O atoms as the fore legs, and two Li atoms as the hind legs (Fig. S2, ESI†). Isomer **0b** can be viewed as a propeller-shaped structure with two rhombuses sharing an S atom and perpendicular to each other (Fig. S2, ESI†). 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 including the shared one. The theoretical VDE of this isomer (0.95 eV) is in agreement with that of 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 under our experimental conditions 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 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 the turtle-shaped structure. Thus, they can coexist instead of transforming into the lower energy one. As shown in Fig. 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-})

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

			Theor.		Expt. X		X′	
Cluster	Isomer	ΔE	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				

bond *via* Li–O(H_2O) interaction and an OH···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 isomers **1c** and **1d** are calculated to be 1.22 and 0.77 eV, respectively. They may also contribute to peak X as 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 the water molecule interacts with Li and one H atom of the water molecule interacts with one O atom of the SO_4^{2-} moiety that connects to another Li atom forming an OH···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 the $Li_2SO_4(H_2O)^-$ 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 parallel to one Li–O bond, forming an OH···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···O hydrogen bond interactions.

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 structures. 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···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 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 clusters shown in Fig. 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···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···O(SO_4^{2-}) and one OH···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···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 clusters 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 structures. The most stable structure of $Li_2SO_4(H_2O)_3$ neutral clusters has a similar configuration as isomer **3c** but with one more OH···O(SO_4^{2-}) hydrogen bond.

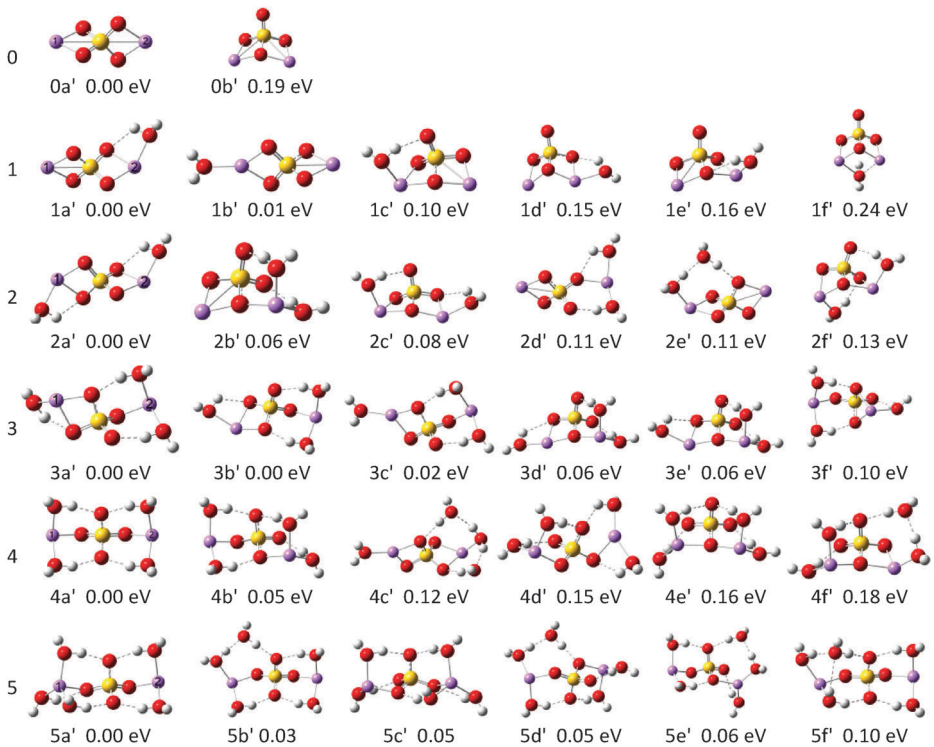

Fig. 3 Structures and the relative stability of the typical low-lying isomers of $Li_2SO_4(H_2O)_n$, (n = 0–5) calculated at the LC-ωPBE/6-311++G(d,p) level.

The structures of isomers **3b′** and **3c′** are similar to isomer **3a′**, but with the dangling water molecule pointing to a 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 a 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, which 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 cluster, 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 (Fig. S2, ESI†). 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 Fig. 2 are almost degenerate in energy. Isomers **5a**, **5b**, **5c**, and **5e** are turtle-shaped structures, while isomers **5d** and **5f** belong to propeller-shaped structures. Isomer **5a** is evolved from isomer **4a** or **4d**, with the fifth water molecule directly contacting 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** is 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 the neutral $Li_2SO_4(H_2O)_5$ cluster 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 molecule connected to SO_4^{2-} and one water molecule through OH···O hydrogen bonds.

Discussion

Both bare $Li_2SO_4^-$ and its neutral cluster 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 neutral clusters 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 neutral clusters, 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 molecules increases and likely reaches the onset of peak X and may be because the intensity of feature X′ is really weak and thereby is difficult to recognize. As shown in Fig. 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 neutral clusters tend to display similar structures as the number of water molecules increases.

The analysis of natural bond orbital (NBO) charge distributions (Table 2 and Fig. S2, ESI†) 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 +1.40 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 an 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 molecules) 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 +1.52 e whereas the charge carried by the 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.

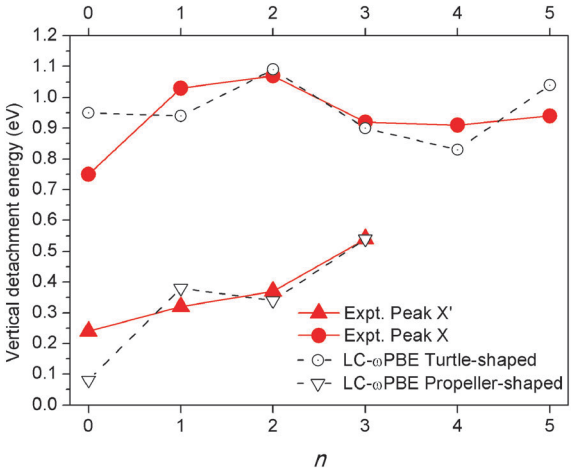

Fig. 4 Experimental VDEs of $Li_2SO_4(H_2O)_n^-$ (n = 0–5) clusters compared to those of the most stable isomers of turtle-shaped and propeller-shaped structures obtained using the LC-ωPBE method.

Table 3 shows the Li–S distance variation of the most stable isomers of $Li_2SO_4(H_2O)_n^-$ clusters and the corresponding neutral clusters. The Li–S distances in the $Li_2SO_4(H_2O)_n$ neutral cluster 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.

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			
		Turtle-shaped		Propeller-shaped				Turtle-shaped		Propeller-shaped	
Isomers	ΔE/eV	Li1	Li2	Li1	Li2	Isomers	ΔE/eV	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	—	—

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 neutral clusters

	Anion		Neutral	
Cluster	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

At n = 3, one Li–S bond distance increases significantly to 2.82 Å upon 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 compared to that of $Li_2SO_4(H_2O)_2^-$. Addition of the fourth and fifth water molecules increases the 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 the nth and (n+1)th water molecules interact with different Li atoms respectively. The modification of the two Li–S distances by the water molecules shows the 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 elongating the 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 the 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 the OH···O(SO_4^{2-}) hydrogen bond and the water···water hydrogen bond. The highest coordination number of the Li atom in the $Li_2SO_4(H_2O)_n$ anion and the neutral cluster is 4 (the number of Li–O contacts), consistent with the teracoordination of Li^+ in bulk water.[60] The current study also confirms that the structure of the 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 process 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 neutral clusters. 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 coexisting low-lying isomers, which are named 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···O(SO_4^{2-}) hydrogen bonds with the SO_4^{2-} moiety rather than with other water molecules, revealing that the Li–O and OH···O(SO_4^{2-}) interactions are stronger than the water–water interactions. For the most stable structures of $Li_2SO_4(H_2O)_n$ (n = 1–5) neutral clusters, 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 the SSIP.

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