Estimation of Reduced Partition Function Ratios of Lithium-Graphite Intercalation Compounds by Density Functional Theory

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The reduced partition function ratio (RPFR) of lithium in lithium-graphite intercalation compounds (Li-GICs) was evaluated at the UB3LYP/6-311G(d) level of theory. The partition functions were written in the usual rigid-rotor harmonic oscillator approximation. With a $C_{24}H_{12}$ coronene molecule as the model of graphene, lithium-coronene sandwich, and club sandwich compounds were considered as models of Li-GICs. The estimated value of the ^{6}Li-to-^{7}Li RPFR was 1.0402 at 25 °C, which yielded 1.034 as the value of the equilibrium constant, K, of the lithium isotope exchange reaction between a lithium ion in an ethylene carbonate/ethylmethyl carbonate mixed solvent and a lithium atom in interlayer space of graphite. The estimated value of K was larger than the experimental value of 1.025. The unsatisfactory agreement between the estimated and experimental K values suggested that larger molecules should be used as models of graphene and that the vibrational anharmonicity should also be taken into consideration.

Key words: Lithium Graphite Intercalation Compounds (Li-GICs), Lithium Isotopes, Reduced Partition Function Ratio (RPFR), Density Functional Theory, Lithium Isotope Exchange Reaction.

1. Introduction

Lithium ion secondary batteries (LISBs), the basic conformation of which is a cathode, an anode, and an electrolyte solution, are one of today's key energy devices. Lithium-graphite intercalation compounds (Li-GICs) with a maximum lithium content corresponding to the chemical formula of LiC_6 are used as the anode of most LISBs [1 – 3].

We have observed lithium isotope effects in experiments in which the reduction of lithium was made to occur in an apparatus mimicking LISBs [4]; lithium ions in an organic electrolyte solution, a 1 : 2 v/v mixture of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) containing 1 M lithium perchlorate (EC/EMC/$LiClO_4$), were inserted into graphite as lithium atoms, and the lithium isotope effects accompanying the insertion were observed. The magnitude of the observed isotope effects can be evaluated as the degree of the deviation of the equilibrium constant, K, of the lithium isotope exchange reaction from unity:

$$^6\mathrm{Li(electrolyte)} + {}^7\mathrm{Li(graphite)} \rightleftarrows {}^7\mathrm{Li(electrolyte)} + {}^6\mathrm{Li(graphite)}\,. \tag{1}$$

In (1), ^{n}Li(electrolyte) and ^{n}Li(graphite) denote the lithium isotope with the mass number n (= 6 or 7) in the electrolyte solution and graphite phases, respectively. The formal charge of lithium is +1 in the former (lithium ion) and 0 in the latter (lithium atom). Experimentally, the value of K was obtained from the mass-spectrometric measurements of the ^{7}Li/^{6}Li isotopic ratios of the two phases, and was found to be larger than unity with the maximum value of 1.025 at 25 °C [4]. This meant that the lighter isotope of lithium was preferentially fractionated into the graphite phase, and indicated that charge–discharge reactions of LISBs could be utilized for lithium isotope separation [4, 5].

Theoretically, the value of K can be evaluated by knowing all the frequencies of the chemical species involved in (1). Based on the Bigeleisen–Mayer theory of equilibrium isotope effects [6], K of (1) is given as the ratio of the ^{6}Li-to-^{7}Li reduced partition function ratios (RPFRs) of lithium in the two phases,

$$K = \mathrm{RPFR}_{\mathrm{electrolyte}}/\mathrm{RPFR}_{\mathrm{graphite}}\,, \tag{2}$$

where $\mathrm{RPFR}_{\mathrm{electrolyte}}$ and $\mathrm{RPFR}_{\mathrm{graphite}}$ denote the RPFRs in the electrolyte solution and the graphite

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phases, respectively. The general expression for the RPFR, under the Born–Oppenheimer and harmonic oscillator approximations and the approximation that the rotations are classical (i.e., that the ratio of their partition functions is unity), is given as

$$(s/s')f = \prod_{i=1}^{p} \frac{u_i \exp(-u_i/2)/\{1-\exp(-u_i)\}}{u'_i \exp(-u'_i/2)/\{1-\exp(-u'_i)\}}, \qquad (3)$$

where $u_i = hc\omega_i/(kT)$ and $u'_i = hc\omega'_i/(kT)$; p is the degree of freedom of molecular vibration, h Planck's constant, and c the velocity of light; ω_i and ω'_i are the wave numbers of the ith molecular vibration of the heavier and the lighter isotopic species, respectively; k is the Boltzmann constant and T the absolute temperature [6]. It is quite often difficult to observe all the isotopic vibrational frequencies of a chemical species even with state-of-the-art spectrometers. Molecular orbital (MO) calculations can be a powerful alternative to obtain all the frequencies, if the chemical species of interest are adequately modelled.

In our previous paper [7], we reported the theoretical results on the solvation state of the lithium ion in the EC/EMC mixed solvent and its RPFR based on MO calculations. The solvation number of the lithium ion in the mixture is four in the primary solvation sphere and an EC molecule is a better ligand of the lithium ion than an EMC molecule, which means that $Li^+(EC)_4$ is the most appropriate expression of the solvated lithium ion in the EC/EMC/$LiClO_4$. The value of the RPFR of $Li^+(EC)_4$ was estimated to be 1.0812 at 25 °C at the UB3LYP/6-311G(d) level of density functional theory (DFT) without frequency correction [5, 7].

Although several MO studies on Li-GICs and related compounds have been reported [8 – 12], none referred to their RPFRs except for ours [13]. In this previous paper [13], we considered a lithium atom interacting with a graphene sheet, a mono-layer of graphite, as model of a lithium atom in Li-GICs, and we considered aromatic hydrocarbons with condensed benzene rings, the largest being a coronene molecule, $C_{24}H_{12}$, as models of graphene. We obtained a value for the RPFR of lithium in Li-GICs of 1.0457 at 25 °C at the UB3LYP/6-311G(d) level of theory without frequency correction [13].

With these models of lithium in the EC/EMC/$LiClO_4$ and in graphite, we obtained a K value of 1.034 at 25 °C [5], which should be compared with the experimental value of 1.025. Our DFT calculations thus yielded a lithium isotope effect of the same order as the experimental one, but the quantitative agreement is not satisfactory. With frequency correction, the estimated value of K will become slightly smaller and be closer to the experimental one.

In the theoretical elucidation of the lithium isotope effects accompanying the electrochemical insertion from the EC/EMC/$LiClO_4$ into graphite, a lithium atom interacting with a mono-layer of graphite is evidently a poor model of the lithium atom in Li-GICs. In the present study, we considered lithium atoms sandwiched by two graphene sheets and those club-sandwiched by three graphene sheets to better represent lithium atoms in Li-GICs. Multiple lithium atoms are included in each model species instead of just one in the previous calculations [13]. As a model of a graphene sheet, we considered a coronene molecule. We calculated the RPFRs of those models, and using the present and previous results on RPFRs of the lithium species involved in (1), we estimated the value of K of (1). In this paper, we report such calculations on RPFRs and K.

2. Calculations

All the MO calculations were made at the computer facility at Sophia University or with our unix and personal computers using the Gaussian 98, 03, and 09 program packages (Gaussian Inc.) [14]; Gauss View (Gaussian Inc.) and Free Wheel (Butch Software Studio) were used for the graphics.

A coronene molecule, $C_{24}H_{12}$, was used as the model of a graphene sheet. As models of Li-GICs, we considered tri-lithium-on-the-graphene-sheet compounds, $Li_3 \cdot (C_{24}H_{12})$, $Li_3 \cdot (C_{24}H_{12})_2$, and $Li_6 \cdot (C_{24}H_{12})_3$. Their optimized structures are shown in Figure 1. The $Li_3 \cdot (C_{24}H_{12})$ compound is a mono-layer model. For the Gaussian input for $Li_3 \cdot (C_{24}H_{12})$, we located each of the three lithium atoms above the center of every other benzene ring so that the three lithium atoms were symmetrically arranged as well as possible and no two lithium atoms came above the two benzene rings adjacent to each other. The 'every other packing' of lithium atom on benzene rings is the one experimentally observed [15]. The $Li_3 \cdot (C_{24}H_{12})_2$ compound, a lithium-coronene sandwich

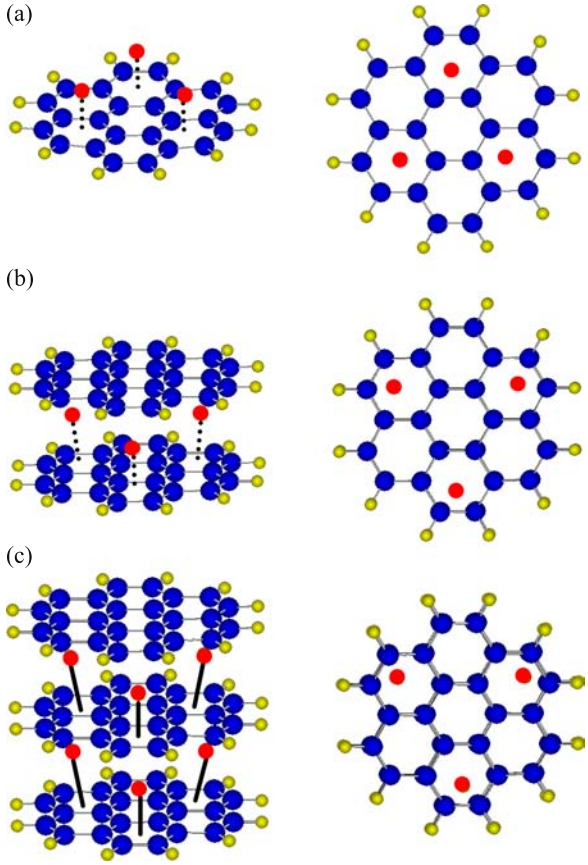

Fig. 1 (colour online). Optimized structures of (a) $Li_3 \cdot (C_{24}H_{12})$, (b) $Li_3 \cdot (C_{24}H_{12})_2$, and (c) $Li_6 \cdot (C_{24}H_{12})_3$. The red, blue, and yellow spheres represent lithium, carbon, and hydrogen atoms, respectively. No significance is attached to the relative sizes of those spheres.

compound, is a double-layer model. For the Gaussian input for $Li_3 \cdot (C_{24}H_{12})_2$, the two coronene molecules were parallelized and three lithium atoms were placed between them so that the relative positions of three lithium atoms and a coronene molecule was the same as in $Li_3 \cdot (C_{24}H_{12})$. The $Li_6 \cdot (C_{24}H_{12})_3$ compound was a club-sandwich typed lithium-coronene compound with three lithium atoms in each interlayer space, and was considered to be the 'best' model of lithium atoms in Li-GICs among the three model compounds. For the Gaussian input for $Li_6 \cdot (C_{24}H_{12})_2$, the three coronene molecules were stacked with an interplane distance of 4.2 Å and six lithium atoms were placed, three each, between the two adjacent coronene molecules. We also considered the mono-lithium counterparts, $Li \cdot (C_{24}H_{12})$, $Li \cdot (C_{24}H_{12})_2$, and $Li_2 \cdot (C_{24}H_{12})_3$. In these compounds, the lithium atom was placed above the central benzene ring of the coronene molecule.

The theoretical level and the basis set chosen was DFT UB3LYP/6-311G(d) so that the present MO calculations are consistent with the previous ones [5, 13]. The total charge of each of the compounds considered was set to zero. The possible spin multiplicities (SMs) were 2 for $Li \cdot (C_{24}H_{12})$ and $Li \cdot (C_{24}H_{12})_2$, 2 or 4 for $Li_3 \cdot (C_{24}H_{12})$ and $Li_3 \cdot (C_{24}H_{12})_2$, and 1 or 3 for $Li_2 \cdot (C_{24}H_{12})_3$, for this compound calculations were made only for an SM of 1, SM = 1, 3, 5 or 7 for $Li_6 \cdot (C_{24}H_{12})_3$, here calculations were made only for those with the SM = 1 or 3. Hereafter, the compounds are designated by the symbol, Gl(m,n), where l, m, and n represent the number of coronene molecules (graphene sheets), the number of lithium atoms, and the SM of the compound, respectively. For instance, G2(3,2) represents the $Li_3 \cdot (C_{24}H_{12})_2$ compound with the SM of 2.

All the geometry optimizations were conducted without symmetry constraints. For each of the structures considered, the bond lengths, bond angles, and dihedral angles were varied independently to achieve the minimum energy geometry, at which the vibrational analysis was carried out. The ^{6}Li-to-^{7}Li RPFR was then calculated by using the frequencies scaled by 0.966 [16]. Only the mono-isotope substitutions were considered with the ^{1}H and ^{12}C basis.

3. Results and Discussion

3.1. Optimized Structures

As examples of the optimized structures, those of G1(3,4), G2(3,2), and G3(6,1) are depicted in Figure 1. No imaginary frequency was observed in the vibrational analyses of the compounds that were used for the RPFR estimation. Every optimized structure was thus at the global or local minimum of the potential energy surface. In all optimized structures, the coronene molecules are nearly (i.e., within the accuracy of the method) planar. The calculated average Mulliken charges on the lithium atoms, average lithium–benzene ring distances, and average lithium–lithium distances are summarized in Table 1. Although the possible spin multiplicity of $Li_3 \cdot (C_{24}H_{12})$ is 2 or 4, the optimization converged only for the one with SM 4 (G1(3,4))

Table 1. Computational conditions and results.

Symbol	Spin multiplicity	Molecular formula	Mulliken charge on Li	Li–benzene ring distance (Å)	Li–Li distance (Å)	RPFR at 25 °C	K
G1(1,2)	2	$Li \cdot (C_{24}H_{12})$	0.619	1.719		1.0428	1.032
G1(3,2)[a]	2	$Li_3 \cdot (C_{24}H_{12})$	–	–		–	–
G1(3,4)	4		0.334	1.807	4.020	1.0308	1.044
G2(1,2)	2	$Li \cdot (C_{24}H_{12})_2$	1.088	2.049		1.0202	1.055
G2(3,2)	2	$Li_3 \cdot (C_{24}H_{12})_2$	0.838	1.961	4.930	1.0402	1.034
G2(3,4)	4		0.841	2.005	4.950	1.0323	1.042
G3(2,1)	1	$Li_2 \cdot (C_{24}H_{12})_3$	1.142	2.015		1.0236	1.051
G3(6,1)	1	$Li_6 \cdot (C_{24}H_{12})_3$	0.892	1.961	5.087	1.0402	1.034
G3(6,3)[a]	3		–	–		–	–

[a] The optimized structure was not obtained.

(Fig. 1a). Similarly, for the $Li_6 \cdot (C_{24}H_{12})_3$ molecule, a minimum energy structure was obtained only for SM 1 (Fig. 1c). For the $Li_3 \cdot (C_{24}H_{12})_2$ molecule, the structure optimization converged for both SM 2 and 4. The former (Fig. 1b) is lower than the later in its electronic energy by 17 kJ/mol, which may be reflected in the difference in the average lithium–benzene ring distance. In each of the optimized structures of G2(3,2), G2(3,4), and G3(6,1), no lithium atom is located above the center of the benzene ring; it is found slightly outside of the center of the coronene molecule. This may be due to the repulsive forces between the lithium atoms. The situation may be different, if we use as a model of graphene poly-benzenes larger than coronene and a larger number of lithium atoms. In every optimized structure of the mono-lithium models, the lithium atom was located above the center of the central benzene ring.

The average Mulliken charge on a lithium atom is always positive and tends to increase with increasing number of coronene molecules for each series of compounds, i.e., G3(6,1) > G2(3,2); G2(3,4) > G1(3,4) and G3(2,1) > G2(1,2) > G1(1,2). This tendency is probably due to the fact that charge redistribution occurs more effectively in a larger molecule. It is also seen in Table 1 that the average Mulliken charge on a lithium atom tends to increase with decreasing number of lithium atoms for compounds with the same number of coronene molecules, i.e., G1(1,2) > G1(3,4); G2(1,2) > G2(3,2), G2(3,4), and G3(2,1) > G3(6,1). This is simply because a small number of lithium atoms means there are a relatively larger number of carbon atoms that can accommodate the negative charge. The average Mulliken charge on lithium atoms in the interlayer space is never less than 0.84, which indicates that, although the formal charge of lithium atoms is zero in graphite, they are actually positively charged; they may be regarded as cations rather than atoms.

The lithium–benzene ring distance varied from 1.72 to 2.05 Å. There is a tendency that the distance is shorter for the mono-layer models than for the multi-layer models; G1(1,2), G1(3,4) < G2(1,2), G2(3,2), G2(3,4), G3(2,1), G3(6,1). This is because, while the attractive force acts on the lithium atom from one side in the former models, the lithium atom is pulled by two coronene molecules on the opposite side. The interlayer distance, which is twice the lithium–benzene ring distance, was 3.9 Å (G2(3,2) and G3(6,1)) and was slightly longer than the experimental value of 3.7 Å obtained for LiC_6 [3]. The difference may be in part due to the small degree of lamination of graphene layers in the present calculations (up to only three layers) compared to the actual graphite used for electrodes, and in part due to the repulsion between hydrogen atoms of different coronene molecules, which do not exist in graphite. The average lithium–lithium distance was 4.02 to 5.09 Å and has a tendency to increase with increasing number of coronene molecules. The experimental value is 4.2 Å.

3.2. Reduced Partition Function Ratios and Equilibrium Constants of Lithium Isotope Exchange Reactions

The value of RPFR obtained ranged from 1.0202 to 1.0428 at 25 °C, as summarized in Table 1. For multi-lithium compounds, the value of RPFR shown is the one averaged over the number of possible mono-isotope substitutions. It is interesting to compare the RPFRs of tri-lithium-on-the-graphene-sheet compounds with the corresponding mono-lithium compounds. That is, G1(3,4) vs. G1(1,2), G2(3,2) and G2(3,4) vs. G2(1,2), and G3(6,1) vs. G3(2,1). While the mono-lithium compound has a larger RPFR than the corresponding tri-lithium compound in the case of the mono-layer compounds, the reverse is the case with the sandwich and club-sandwich compounds, meaning that in the latter compounds, interactions among lithium atoms enhance the RPFRs. It is also noted in Table 1 that the lithium–benzene ring distance is inversely correlated with the value of RPFR in each series of compounds; a longer distance results in a smaller value of RPFR. This indicates that the vibrational motion perpendicular to the molecular plane of coronene is a major contributor to the RPFR. In fact, for instance, this motion is the largest contributor to the RPFR of G2(1,2) and accounts for 39% of the logarithm of the RPFR.

The equilibrium constant K of (1) is also listed for each compound in Table 1. The model lithium species in the electrolyte solution adopted here was $Li^+(EC)_4$ as determined in our previous paper [13], and the value of its RPFR was 1.07603 at 25 °C calculated here at the UB3LYP/6-311G(d) level of theory with scaling by a factor of 0.966 [16]. The optimized structure of $Li^+(EC)_4$ is depicted in Figure 2. The calculated value of K ranged from 1.032 to 1.055 at 25 °C, which should be compared with the experimental value of 1.025 [4]. All the present model compounds overestimate the value of K. Of the lithium-coronene compounds considered, the one that best mimics Li-GICs is expected to be G3(6,1), which gives a K value of $1.0760/1.0402 = 1.034$. Ironically enough, G1(1,2), the 'worst' model, gives a K value of 1.032, closest to the experimental one.

The present calculations overestimate the K value of (1). In other words, the calculations underestimate the RPFR of Li-GICs, provided that the lithium ions in the EC/EMC mixture are more accurately described than the lithium atoms in graphite and that consequently the RPFR of the former is more reliable.

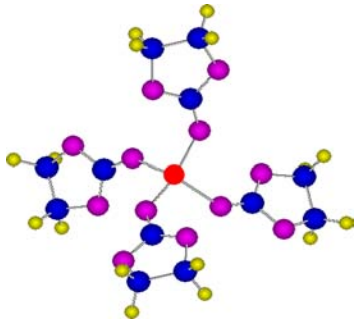

Fig. 2 (colour online). Optimized structure of $Li^+(EC)_4$. The red, purple, blue, and yellow spheres represent a lithium ion and oxygen, carbon and hydrogen atoms, respectively. No significance is attached to the relative sizes of those spheres.

Four plausible reasons for this unsatisfactory agreement between the calculations and the experiments concerning the lithium isotope effects accompanying the electrochemical insertion of lithium from the $EC/EMC/LiClO_4$ into graphite can be pointed out.

The first possibility is related to the experimental K value. Experimentally, K is obtained by measuring the $^7Li/^6Li$ isotopic ratios of the electrolyte solution and graphite phases by mass spectrometry. For the measurement of the isotopic ratio of the graphite phase, the lithium-inserted graphite electrode was washed thoroughly with dehydrated hexane to remove the electrolyte solution adhering to the surface of the electrode. If this hexane washing is incomplete, a small portion of lithium ions in the electrolyte solution is included in the lithium in the graphite. This makes the $^7Li/^6Li$ isotopic ratio of the graphite slightly larger since the $^7Li/^6Li$ isotopic ratio of the electrolyte is larger than that of the graphite, which leads to a smaller value of K.

The second one is also related to the experimental aspect, i.e., the formation of a solid electrolyte interface (SEI) [15, 17]. It is generally accepted that stable surface films, the reaction products of lithium and electrolyte solution, are formed on graphite edge surfaces of graphite electrodes in EC based electrolyte solutions upon the first charging, and thereby the carbon surface is passivated. This film, called SEI, has lithium-ion conductivity but does not show electronic conductivity. Once formed, it suppressed further solvent decomposition, but even through it lithium ions can be inserted in graphite. Although the chemical composi-

tion of the film is not yet well understood, its property is expected to be closer to the electrolyte solution than to graphite. This is because the film is formed from lithium ions and EC molecules. This means that the RPFR of lithium in the film is expected to be closer to that of the electrolyte solution than to that of the graphite. The film is not peeled off by hexane washing, which means that the lithium in the film can be considered as being inserted in the graphite. This also enhances the RPFR of graphite and leads to a decrease in the experimentally obtained K value.

The third one is again concerned with the experimental aspect, i.e. the possibility that the local temperature at the electrode/electrolyte solution interface may be higher than 25 °C. The electrolysis (lithium insertion) was carried out in the constant current–constant voltage mode to avoid the possible deposit of lithium on the graphite electrode and possible overheat at the electrode/electrolyte solution interface, and the temperature of the electrolyte solution was kept constant at 25 °C by circulating thermostatted water around the electrolytic cell during the electrolysis. However, the local temperature at the interface may have been higher because the lithium insertion is exothermic. In general, equilibrium isotope effects are smaller at higher temperatures. The value of K calculated using the RPFRs of G3(6,1) and $Li^{+}(EC)_4$ is 1.031 and 1.030 at 40 and 50 °C, respectively. Thus, even if we assume an experimental temperature higher than 25 °C, the present calculations still overestimate the K value of (1).

The above three possibilities are related to experiments and should be clarified experimentally, for instances, by improving the method of hexane washing, by measuring the amount of SEI, and by measuring the local temperature at the electrode/electrolyte solution interface.

The forth possibility is a theoretical one and is concerned with the models of the lithium atoms in graphene sheets. The largest compound treated in the present study was $Li_6 \cdot (C_{24}H_{12})_3$, while a graphite particle of the electrode has the size of several dozens of μm. The size gap between the actual Li-GICs and their models adopted here is still very large. Martínez et al. [11] stated that the interaction of a lithium atom and the $C_{24}H_{12}$ coronene is very different from the interaction between lithium and graphene and that this is a typical size effect; $C_{24}H_{12}$ and graphene have very different electronic structures in the energy region around the Fermi level, and consequently the interaction of these two systems with atoms can be very different. More specifically, according to Martínez et al. [11], the interaction of lithium with coronene is weak owing to the large HOMO–LUMO gap of the coronene, while, in contrast, graphene has zero gap, which allows for a strong interaction between lithium and graphene. Their conclusion suggests a larger value of the RPFR of the lithium in Li-GICs and consequently a smaller value of theoretical K with bigger poly-benzene molecules. We thus certainly need bigger compounds to better mimic the properties of graphene and to calculate the RPFR of Li-GICs.

The present calculations of RPFRs are based on and within the frame work of the Bigeleisen–Mayer theory [6], which assumes that molecular vibrations are harmonic. That is, the vibrational anharmonicity is totally ignored in the present calculations. It is said that the contribution of the anharmonic vibration correction to the isotope fractionation factor is small [18, 19] especially for molecules with high frequencies. The correction is of the order of 1% for D/H exchange reactions [19, 20]. However, the vibrational anharmonicity may be relatively important for the compounds dealt with here, since vibrational frequencies that significantly contribute to the RPFRs are not so high. For instance, the largest contributor to the RPFR of G1(1,2), which accounts for 47.2% of the logarithm of the RPFR, is the reciprocating motion of the lithium atom perpendicular to the molecular plane with the vibrational frequency of 456.444 and 430.135 cm^{-1} for the ^6Li and ^7Li isotopic species, respectively. The second largest one is a reciprocating motion of the lithium atom parallel to the molecular plane, which constitutes 12.4% of ln(RPFR) with the ^6Li frequency of 229.623 cm^{-1}. Although it is beyond the scope of the present study, the consideration to the vibrational anharmonicity may be an important issue in future works.

4. Conclusion

To summarize the present study, we make the following statements.

With the $Li_3 \cdot (C_{24}H_{12})_2$ and $Li_6 \cdot (C_{24}H_{12})_3$ compounds as models of Li-GICs, the interlayer distance was calculated to be 3.92 Å at the UB3LYP/6-311G(d) level of theory, which is slightly larger than the experimental value of 3.7 Å. The Mulliken charge

on a lithium atom in those compounds was more than $0.84|e|$, which suggested that the interaction of a lithium atom with graphene is essentially of ionic character in Li-GICs.

The RPFR of the 'best' model compound of Li-GICs among the models considered was calculated to be 1.0402 at 25 °C, which gave 1.034 as the value of equilibrium constant, K, of the isotope exchange reaction between the lithium ion in the EC/EMC mixed solvent medium and the lithium atom in Li-GICs. The agreement of the calculation (1.034) and experiment (1.025) is not satisfactory. The necessity of the use of a larger molecule than coronene as a model of graphene is suggested.

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