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The  $P_4\cdots Li^+$  Ion in the Gas Phase: A Planetary SystemJ.-L. M. Abboud,<sup>\*,†</sup> I. Alkorta,<sup>\*,‡</sup> J. Z. Dávalos,<sup>†</sup> J.-F. Gal,<sup>\*,§</sup> M. Herreros,<sup>§</sup> P.-C. Maria,<sup>\*,§</sup> O. Mó,<sup>||</sup> M. T. Molina,<sup>‡</sup> R. Notario,<sup>\*,†</sup> and M. Yáñez<sup>\*,||</sup>

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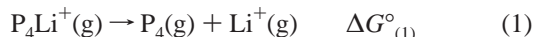
**Abstract:** Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT ICR) has revealed the existence of the  $P_4Li^+$  ion as a stable species in the gas phase. High-level ab initio calculations show that  $P_4Li^+$  appears as a "planetary system" wherein the lithium cation can easily move around the  $P_4$  moiety along paths (or "orbits") connecting the points above the middle points of the P–P edges with points above the center of the PPP faces, the movement toward the corners of the tetrahedron being the less favored. Due to symmetry, this orbiting is 4-fold degenerate.

Protonation of gaseous tetraphosphorus,  $P_4(g)$ , leads to a new chemical bond, the essentially covalent two-electrons-three-centers bond,  $P\cdots H\cdots P$ .<sup>1</sup> This has prompted us to investigate the interaction between  $P_4(g)$  and  $Li^+(g)$ . The latter is a cation known to lead to very strong, mostly electrostatic interactions with neutral species in the gas phase.<sup>2–5</sup> To this end, we have explored experimentally and computationally the existence, thermodynamic stability, and properties of the seemingly unknown ion  $P_4Li^+$  in the gas phase.

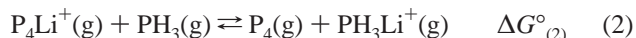
Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT ICR)<sup>6–8</sup> was used to establish the existence and to estimate the thermodynamic stability of  $P_4Li^+(g)$ . Gaseous lithium ions were generated by laser-ablation of lithium benzoate targets<sup>9</sup> and used as the adduct with propene,  $C_3H_6Li^+(g)$ .<sup>2</sup> It

was experimentally observed that this ion cleanly transfers  $Li^+(g)$  to  $P_4(g)$  and leads to the formation of  $P_4Li^+(g)$ .

The standard Gibbs energy of dissociation of this ion,  $\Delta G^\circ_{(1)}$ , defined through reaction 1 and also known as the lithium cation basicity (LCB) of  $P_4$ , was determined by experimental and computational methods.



The results were as follows: (1) Bracketting experiments show that  $P_4Li^+(g)$  irreversibly transfers  $Li^+(g)$  to dichloromethane, for which the experimental LCB amounts to  $22.2 \pm 2.0$  kcal mol<sup>−1</sup><sup>10</sup> (the G2-computed value is 21.1 kcal mol<sup>−1</sup><sup>11</sup>). In turn, propene, having an experimental LCB =  $16.5 \pm 2.0$  kcal mol<sup>−1</sup><sup>10</sup> (the G2-computed value is 16.3 kcal mol<sup>−1</sup><sup>12</sup>), irreversibly transfers  $Li^+(g)$  to  $P_4(g)$ . From these results, we estimate LCB( $P_4$ ) at  $19.4 \pm 4.8$  kcal mol<sup>−1</sup>. (2) Ab initio calculations at the G2 level (see below) lead to a value of LCB( $P_4$ ) of 17.5 kcal mol<sup>−1</sup>. (3) Double resonance experiments cleanly showed the reversibility of reaction 2<sup>13</sup>



From this fact it can be inferred that LCB( $P_4$ ) and LCB( $PH_3$ ) do not differ by more than about  $\pm 1.5$  kcal mol<sup>−1</sup>. The G2-calculated LCB for  $PH_3$  amounts to 17.1 kcal mol<sup>−1</sup>.<sup>14</sup>

The computational LCB( $P_4$ ) values are thus seen to be well within the uncertainty limits of the bracketing experiments.

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(10) Value obtained from the experimental LCA value taken from ref 2a, and the theoretical entropy value calculated at HF/6-31G(d) level.

(11) Determined in this work:  $G_{298}(CH_2Cl_2) = -958.72506$ ;  $G_{298}(CH_2Cl_2Li^+) = -966.00727$ ;  $G_{298}(Li^+) = -7.24859$ . All values in hartrees.

(12) Determined in this work:  $G_{298}(C_3H_6) = -117.67016$ ;  $G_{298}(C_3H_6Li^+) = -124.94475$ . All values in hartrees.

(13) Traces of water (a "strong" lithium cation acceptor) precluded the accurate determination of  $\Delta G^\circ_{(2)}$  by direct equilibration.

(14) Value obtained in this study (at the G2 level):  $G_{298}(PH_3) = -342.69899$ ;  $G_{298}(PH_3Li^+) = -349.97480$ . All values in hartrees (1 hartree = 2625.5 kJ mol<sup>−1</sup>).

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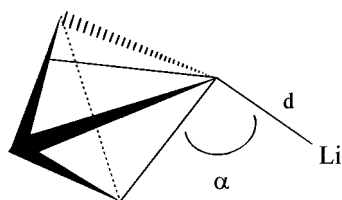
(5) For recent experimental and theoretical studies on the gas-phase reactivity of  $Li^+$ , see, e.g.: (a) Rodgers, M. T.; Armentrout, P. B. *J. Mass Spectrom.* **1999**, *187*, 359–380. (b) Rodgers, M. T.; Armentrout, P. B. *J. Chem. Phys.* **1998**, *109*, 1787–1800. (c) Rodgers, M. T.; Armentrout, P. B. *J. Phys. Chem. A* **1997**, *101*, 1238–1249. (d) Burk, P.; Koppel, I. A.; Koppel, I.; Kurg, R.; Gal, J.-F.; Maria, P.-C.; Herreros, M.; Notario, R.; Abboud, J.-L. M.; Anvia, F.; Taft, R. W. *J. Phys. Chem. A* **2000**, *104*, 2824–2833.

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Chart 1



Quantum-mechanical treatment of the problem fully confirms the experimental results and further uncovers some unsuspected features of the  $P_4Li^+(g)$  ion.

Initially, geometry optimizations were carried out at the MP2(full)/6-31G(d), MP2(full)/6-311G(d), and MP2(full)/6-31+G(d) levels. Harmonic vibrational frequencies were evaluated at the MP2(full)/6-31G(d) and MP2(full)/6-31+G(d) levels to identify the stationary points found as local minima or saddle points of the corresponding potential energy surface (PES). The final energies of all the stationary points were obtained using the G2 theory of Pople and co-workers,<sup>15</sup> which was shown to accurately reproduce the interaction between  $P_4$  and  $H^+$ . While the geometries of the stationary points in the original G2 method are determined at the MP2(full)/6-31G(d) level, here, as in ref 1, we went one step further and used the MP2(full)/6-31+G(d) level. This treatment is called here "G2+."<sup>16</sup> In the case of the minima, geometries were also optimized at the MP2(full)/6-311G(d) level. The energetics obtained at the G2 level based on these structures ("G2++" level)<sup>17</sup> are essentially identical with those obtained at the G2+ and G2 levels.

The bonding characteristics of the different species have been investigated by using the atoms in molecules (AIM) theory of Bader.<sup>18</sup> For this purpose, we have located the bond critical points, i.e., points where the electron density function,  $\rho(\mathbf{r})$ , is minimum along the bond path and maximum in the other two directions. We have also calculated the energy density,  $H(\mathbf{r})$ , at each bond critical point. In general, negative values of  $H(\mathbf{r})$  denote the existence of stabilizing charge concentrations within the bonding region, which are associated with covalent interactions. In contrast, ionic bonds, hydrogen bonds, or van der Waals interactions are characterized by positive values of the energy density. The AIM analysis was performed using the AIMPAC series of programs.<sup>19</sup>

This study of the isomerization barriers reveals the existence of four groups of stationary points in the PES of  $P_4Li^+$ . Three of them, corresponding respectively to the attachment of the  $Li^+$  cation to a corner or apex (1), an edge (2), and a face (3) of the tetrahedron were found to be local minima on the PES. Structures 1 and 3 are 4-fold degenerate and structure 2 is 6-fold degenerate. The fourth structure, in which  $Li^+$  occupies the center of the tetrahedron, was found to be a saddle point of the fifth order (five imaginary frequencies).

In what follows, the positions of the various stationary points are defined by means of the distance  $d$  between  $Li^+$  and the nearest P atom and the angle  $\alpha$  relative to a P–P bond involving this atom (Chart 1).

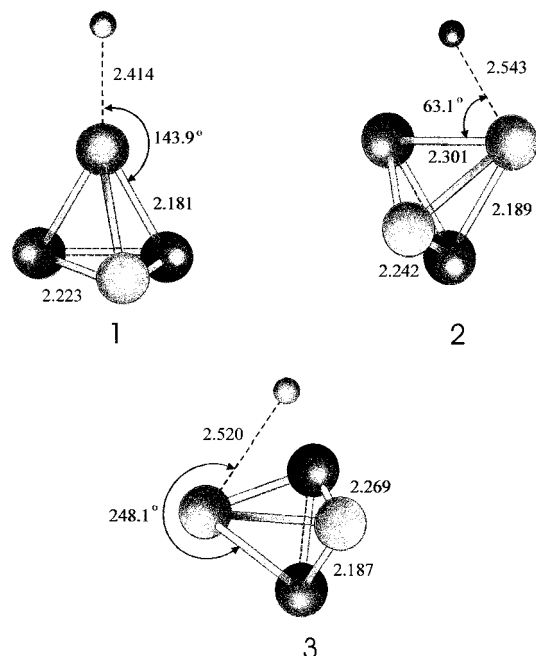
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(16) Energies obtained at the G2 level based on structures optimized at the MP2(full)/6-31+G(d) level, with frequencies evaluated at the same level and scaled by the factor 0.9641.

(17) Energies obtained at the G2 level based on structures optimized at the MP2(full)/6-311G(d) level, with frequencies evaluated at the HF/6-31G(d) level and scaled by the factor 0.8929.

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(19) The AIMPAC program was kindly provided by J. Cheeseman and R. F. W. Bader.



**Figure 1.** Structures of the three minima on the PES of  $P_4Li^+$ . Angles in deg and distances in Å.

Structures 1, 2, and 3 optimized at the MP2/6-311G(d) level are given in Figure 1. Also reported are the values of  $\alpha$  and  $d$ , as well as the various P–P distances. As it can be seen, the overall tetrahedral arrangement of the  $P_4$  moiety is preserved, with small distortions of the P–P distances ( $\pm 0.1$  Å) and PPP bond angles ( $\pm 2.5^\circ$ ). These distortions are reflected by a lowering of the symmetry of the  $P_4$  moiety, from  $T_d$  in isolated tetraphosphorus (the computed P–P distances being 2.202 Å) to  $C_{3v}$  in structures 1 and 3 and  $C_{2v}$  in structure 2. The computational results for the relevant species, as obtained at various levels, are given in Table 1. The thermodynamics for reactions  $1 \rightleftharpoons 2$ ,  $1 \rightleftharpoons 3$ , and  $3 \rightleftharpoons 2$  are summarized in Table 2.

The G2+ thermodynamic magnitudes for the transition states pertaining to reactions  $1 \rightleftharpoons 2$ ,  $1 \rightleftharpoons 3$ , and  $3 \rightleftharpoons 2$ , relative to the lowest minimum (structure 2), are given in Table 2. For the three TSs, the corresponding  $\alpha$  and  $d$  values are summarized in Table 3.

At all the computational levels the global minimum (in terms of energy) corresponds to structure 2, the least stable structure being 1. In the case of protonation the situation is different. Edge-protonation is also significantly favored over apical protonation. On the other hand, the face-protonated structure is not a minimum on the PES, but rather a second-order saddle point. This situation reflects the fundamental differences between the natures of the interactions of  $P_4$  with  $H^+$  and  $Li^+$ . In the first case, the P–H bonds formed are covalent, while the interactions with  $Li^+$  are essentially electrostatic. Indeed, a quantitative study of the energy density, as measured by  $H(\mathbf{r})$ ,<sup>20</sup> reveals that, for all the local minima,  $H(\mathbf{r})$  is negative within the P–P internuclear regions, indicating the existence of a stabilizing charge concentration typical of covalent bonds. At variance with this,  $H(\mathbf{r})$  is always positive in the P–Li internuclear regions, this showing that this sort of interaction is essentially electrostatic.

Polarization effects<sup>21</sup> are crucial to understand the relative stabilities of the three minima. Inspection of the electrostatic

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**Table 1.** Thermodynamic Data (energies at 0 K, zero-point vibrational energies, thermal correction to enthalpies and entropies) for Selected Species Examined in This Study As Computed at Various ab Initio Levels

species	$E_0^a$			ZPE <sup>a,c</sup>	TCE <sup>a,c</sup>	$S^\circ$ <sup>c,d</sup>
	G2 <sup>b</sup>	G2+ <sup>b</sup>	G2++ <sup>b</sup>			
P <sub>4</sub>	-1363.71963	-1363.71982	-1363.71979	0.00631	0.01166	66.75
Li <sup>+</sup>	-7.23584	-7.23584	-7.23584	0.00000	0.00236	31.80
<b>1</b>	-1370.98473	-1370.98501	-1370.98468	0.00721	0.01469	85.22
<b>2</b>	-1370.99088	-1370.99082	-1370.99052	0.00757	0.01471	82.53
<b>3</b>	-1370.98895	-1370.98846	-1370.98794	0.00751	0.01465	80.37
TS(1 $\rightleftharpoons$ 2)		-1370.984034		0.006996	0.012770	74.16
TS(1 $\rightleftharpoons$ 3)		-1370.984946		0.007165	0.013742	78.63
TS(2 $\rightleftharpoons$ 3)		-1370.987839		0.007368	0.013728	76.20

<sup>a</sup> Values in hartrees. <sup>b</sup> Defined in the text. <sup>c</sup> Computed at the MP2(full)/6-31+G(d) level. <sup>d</sup> Values in cal mol<sup>-1</sup> K<sup>-1</sup>.

**Table 2.** Standard Enthalpy and Gibbs Energy Changes (at 298.15 K) for Reactions **1**  $\rightarrow$  **2**, **1**  $\rightarrow$  **3** and **3**  $\rightarrow$  **2**, **2**  $\rightarrow$  TS(1 $\rightleftharpoons$ 2), **2**  $\rightarrow$  TS(1 $\rightleftharpoons$ 3), and **2**  $\rightarrow$  TS(2 $\rightleftharpoons$ 3) at the G2+ Level

process	$\Delta H^\circ$ /kcal mol <sup>-1</sup>	$\Delta G^\circ$ /kcal mol <sup>-1</sup>
<b>1</b> $\rightleftharpoons$ <b>2</b>	-3.9	-3.1
<b>1</b> $\rightleftharpoons$ <b>3</b>	-2.4	-0.9
<b>3</b> $\rightleftharpoons$ <b>2</b>	-1.5	-2.2
<b>2</b> $\rightarrow$ TS(1 $\rightleftharpoons$ 2)	4.0	6.5
<b>2</b> $\rightarrow$ TS(1 $\rightleftharpoons$ 3)	3.9	5.1
<b>2</b> $\rightarrow$ TS(2 $\rightleftharpoons$ 3)	2.0	3.9

**Table 3.** Geometrical Parameters  $\alpha^a$  and  $d^b$  for the Transition States TS(1 $\rightleftharpoons$ 2), TS(1 $\rightleftharpoons$ 3), and TS(2 $\rightleftharpoons$ 3)

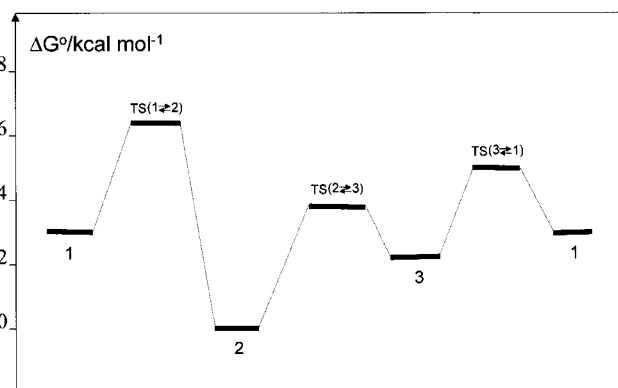
transition state	$d$	$\alpha$
<b>1</b> $\rightleftharpoons$ <b>2</b>	2.488	125.0
<b>1</b> $\rightleftharpoons$ <b>3</b>	2.465	191.1
<b>2</b> $\rightleftharpoons$ <b>3</b>	2.545	260.8

<sup>a</sup> In deg. <sup>b</sup> In Å.

potential around an isolated P<sub>4</sub> molecule shows that the strongest electrostatic attraction between P<sub>4</sub> and Li<sup>+</sup> should correspond to structure **1**, while the interaction would be much weaker in the case of **2** and would become eventually mildly repulsive in the case of **3**. The actual ranking of enthalpies of formation, **1** < **3** < **2**, follows, in addition, from two important factors: (i) Li<sup>+</sup> is not a point charge and its 1s<sup>2</sup> core leads to distances between the ion and the basic centers of the P<sub>4</sub> moiety being longer than in the case of a point charge.<sup>22</sup> (ii) Polarization effects are extremely efficient at enhancing the stabilities of species **2** and **3** relative to **1**. Actually, as illustrated in Figure 1 for structures **1**, **2**, and **3**, the distance between the metal cation and the nearest phosphorus atoms differs very little. Hence, while in the case of **2** and **3** these effects are substantial (because two and three lone pairs are simultaneously polarized), they are minimal in the case of **1** (only one lone pair).

Consideration of the standard Gibbs energy and enthalpy changes associated with the transformations **1**  $\rightleftharpoons$  **2**, **1**  $\rightleftharpoons$  **3**, and **3**  $\rightleftharpoons$  **2**, namely  $\Delta G^\circ(1,2)$ ,  $\Delta G^\circ(1,3)$ , and  $\Delta G^\circ(3,2)$  (given in Table 2), as well as of the relevant isomerization barriers reveals some remarkable properties of P<sub>4</sub>Li<sup>+</sup>.

In terms of Gibbs energies, the relative stabilities of the three isomeric forms are close, although structure **1** appears again as moderately less stable than structures **2** and **3**. It is significant that the computed values of LCB(P<sub>4</sub>) at all levels, 17.7, 17.6, and 17.5 kcal mol<sup>-1</sup> (G2, G2+, and G2++, respectively), are quite consistent and in nice agreement with the FT ICR data. Under equilibrium conditions at 298.15 K, the species "P<sub>4</sub>Li<sup>+</sup>"

**Figure 2.** Energetic diagram showing the stable structures **1**, **2**, and **3** for P<sub>4</sub>Li<sup>+</sup> as well as the transition states pertaining to the intramolecular interconversion of these structures.

is seen to be a mixture of **2** (96.9%), **3** (2.6%), and **1** (0.53%). At 600 K, a standard temperature in High-Pressure Mass Spectrometry (HPMS) studies, "P<sub>4</sub>Li<sup>+</sup>" is predicted to be a 0.12:0.80:0.08 mixture of **1**, **2**, and **3** (based on the data given in Table 2). Notice that at this temperature, **1** appears as slightly more stable than **3**.

The most important finding of this exploration is the fact that, while the isomerization barriers (in terms of Gibbs energy changes) between **1** and **2** or **3** are very small (3.1 and 0.9 kcal mol<sup>-1</sup> respectively at the G2+ level), the activation barrier between **3** and **2** is also small (1.7 kcal mol<sup>-1</sup> above structure **3**). The fact that the intramolecular process **3**  $\rightleftharpoons$  **2** has such a low barrier implies that P<sub>4</sub>Li<sup>+</sup> in the gas phase provides a nice example of a "planetary system" wherein the lithium cation can easily move around the P<sub>4</sub> moiety along paths (or "orbits") connecting the points above the middle points of the P-P edges with points above the center of the PPP faces, the movement toward the corners of the tetrahedron being the less favored (as deduced from Figure 2).

To summarize, we call P<sub>4</sub>Li<sup>+</sup> a "planetary system" in the sense that there are closed, thermally accessible paths or orbits of the metal cation around the P<sub>4</sub> moiety. It is clear that because of the symmetry of this moiety, this orbiting is 4-fold degenerate. Obviously, the motion of Li<sup>+</sup> will be favored by increasing the temperature of the system, and consideration of the various Gibbs energies of activation suggests that this orbiting will likely take place in a nanosecond time scale at room temperature. Using the data of Table 2 it appears that P<sub>4</sub>Li<sup>+</sup> should behave as a "planetary system" at temperatures of ca. 300 K or higher but that at very low temperatures its behavior would be that of a mixture of rigid systems. It is also important to mention that other fluxional, "planetary systems" involving lithium cation,<sup>3</sup> transition metal cations,<sup>23</sup> or hydrogen-bonded species<sup>24</sup> have already been described in the literature. In the systems involving

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a metal cation, the latter is bound to neutral molecules<sup>25–26</sup> [highly significant examples being  $\text{CH}_4\text{Li}^+$ ,<sup>25a</sup>  $\text{CCl}_4\text{Li}^+$ ,<sup>25b</sup> and  $\text{CH}_4\text{M}^+$  ( $\text{M}^+$  = transition metal cation)] or to formally anionic species, as in  $\text{SiLi}_4$ <sup>27</sup> or in the  $\text{LiSiH}_3/\text{SiH}_3\text{Li}$ <sup>28</sup> and  $\text{LiCN}/\text{LiNC}$ <sup>29</sup>

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systems. The most relevant feature of  $\text{P}_4\text{Li}^+$ , however, is the fact that all three symmetrical positions of the metal cation around the  $\text{P}_4$  moiety are local minima on the potential energy surface of the system.

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