

RESEARCH ARTICLE

Hydrogen storage capacity of $\text{Be}_2(\text{NLi})_2$ cluster with ultra-short beryllium–beryllium distanceKangkan Sarmah¹ | Amlan J. Kalita¹ | Dimpul Konwar² | Ankur K. Guha¹ ¹Advanced Computational Chemistry Centre, Cotton University, Guwahati, Assam, India²Department of Material Science and Engineering, Gachon University, Seongnam-si, Gyeonggi, Republic of Korea

Correspondence

Dimpul Konwar, Department of Material Science and Engineering, Gachon University, Bokjung-dong, Seongnam-si, Gyeonggi 1342, Republic of Korea.
Email: dkonwar@gachon.ac.krAnkur K. Guha, Advanced Computational Chemistry Centre, Cotton University, Panbazar, Guwahati, 781001 Assam, India.
Email: ankurkantiguha@gmail.com

Abstract

Quantum chemical calculations have been carried out to investigate the hydrogen storage capacity of $\text{Be}_2(\text{NLi})_2$ cluster. Calculations reveal that the cluster can take up to eight H_2 molecules reaching a maximum gravimetric density of 21.04 wt%. Six H_2 molecules bind at the Li atoms and two H_2 bind at the Be atoms with moderate binding energy which is required for reversible storage of H_2 . Symmetry-adapted perturbation analysis reveals the significant contribution of electrostatic and induction and very minor contribution of dispersion toward the total interaction energy. Molecular dynamics simulations reveal that the H_2 molecules are strongly bound at 77 K and get slowly released at elevated temperatures.

KEYWORDS

hydrogen storage, Li cluster, theoretical

1 | INTRODUCTION

The large use of traditional and fossil fuel increases the major greenhouse gas CO_2 in the atmosphere which severely threaten the human survival and development.¹ So, a clean, environmental friendly green fuel is very necessary for future generations. The use of green fuel for future is very challenging task for automobiles as well as industrial purposes. Hydrogen as a fuel satisfies this requirement very nicely as water is the only by product during its combustion and also a clean, reasonably safe, and renewable fuel.^{2–4} But the storage of hydrogen and its applicability is very challenging in energy economical field. Many obstacles come for better materials for H_2 storage such as its volumetric as well as gravimetric density, favorable enthalpies for both hydrogen adsorption and desorption, stability at different temperatures, and so on.⁵ The US Department of Energy (US DOE) set a target of ideal storage materials with 5.5 wt% gravimetric density by year 2025.⁶ Rosi et al.⁷ experimentally suggested a microporous metal organic framework (MOFs) for H_2 storage and find a good adsorption and desorption criteria. After this finding, a large number of materials such that clathrates hydride,⁸ carbon-based nanomaterials,⁹ fullerene clusters,¹⁰ aluminum nitride,¹¹ porous polymer,¹² alanates,¹³ zeolites,¹⁴ and magnesium cluster¹⁵ have been investigated as H_2 storage material.

Blomqvist et al.¹⁶ studied the hydrogen adsorption in Li doped MOF and showed that there is notable upgrade of hydrogen storage in Li-doped MOF-5 as compared to undoped one. Later Ghosh and coworkers¹⁷ investigated an alkali metal doped fullerenes and closo-boranes¹⁸ and diborene ($\text{B}_2\text{H}_4\text{Li}_2$) and diboryne ($\text{B}_2\text{H}_2\text{Li}_2$)¹⁹ systems as H_2 storage materials with maximum adsorption of three H_2 molecule which corresponds to a gravimetric density 24 wt%. Srinivasu et al. have performed a theoretical investigation in all metal aromatic cluster,²⁰ namely, Be_3M_2 , Mg_3M_2 , Al_4M_2 ($\text{M} = \text{Li}, \text{Na}, \text{K}$). In 2012, Giri et al. designed a star like C_6Li_6 cluster as 6–12 hydrogen storage material.^{21,22} Due to low molecular weight of Li atom, it is also used in some cluster for improving the uptake of H_2 with good desorption criteria.^{23–29} From these studies it is clear that Li can absorb molecular hydrogen more efficiently when it adsorbed or allowed to react with some chemical system. Chattaraj and coworker revealed that the incorporation of an electronegative element in Pyridine- Li^+ complex can give a good 1:1 ratio of the complex and hydrogen with a better gravimetric wt%.³⁰ Recently, a unique beryllium cluster, $\text{Be}_2(\text{NLi})_2$, has been proposed theoretically³¹ which contains the ultra-short Be–Be distance. Despite this interesting feature, the cluster contains Li atom. Therefore, it will be interesting to investigate the H_2 adsorption capacity of this cluster. Herein, we have undertaken a theoretical study to investigate

the H₂ adsorption/desorption capacity of this unique cluster. Our calculations reveal that the cluster can form up to 1:8 H₂ complex with the binding energy between chemisorption and physisorption. The calculated gravimetric density reaches up to 21.04%.

2 | COMPUTATIONAL DETAILS

Since the present study deals with weak non-covalent interactions, all the molecules were fully optimized at MP2³² and ω B97XD³³ levels in combination with def2-TZVP basis set. Harmonic frequency calculations were performed at the same level of theory to understand the nature of stationary points. All these structures were found to be at their local minima with real values of the Hessian matrix. All energies are zero point and thermal corrected. Natural bond orbital³⁴ calculations were also performed to understand the electronic structure of the systems. All these calculations were performed using the Gaussian 16 suite of program.³⁵

To evaluate the reversibility of H₂ storage, we calculated consecutive adsorption energy (E_r) also called binding energy as the energy obtained by successive additions of H₂ molecules using Equation (1) and for the adsorption capabilities, the average adsorption energy (E_{ads}) was measured for Be₂(NLi)₂ molecule using Equation (2).

$$\Delta E_r = \{E(\text{Be}_2(\text{NLi})_2 - n\text{H}_2)\} - \{E(\text{Be}_2(\text{NLi})_2 - (n-1))\text{H}_2 + \text{H}_2\}. \quad (1)$$

$$\Delta E_{\text{ads}} = [\{E(\text{Be}_2(\text{NLi})_2 - n\text{H}_2)\} - \{E(\text{Be}_2(\text{NLi})_2) + E(n\text{H}_2)\}]/n. \quad (2)$$

where $E(\text{Be}_2(\text{NLi})_2)$, $E(\text{Be}_2(\text{NLi})_2 - n\text{H}_2)$, $E(n\text{H}_2)$ are total the energy of Be₂(NLi)₂ cluster, H₂ containing Be₂(NLi)₂ cluster and H₂ molecule.

Gravimetric density (wt%) is calculated using the formula given below:

$$\text{wt}\% = \frac{M_{\text{H}_2}}{M_{\text{H}_2} + M_{\text{complex}}}.$$

Chemical hardness (η)³⁶ and electrophilicity (ω)³⁷ values were calculated using the following formula:

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta},$$

$$\chi = \frac{I+A}{2} \approx \frac{E_{\text{HOMO}} - E_{\text{LUMO}}}{2},$$

$$\eta = I - A \approx E_{\text{LUMO}} - E_{\text{HOMO}},$$

where χ is electronegativity, μ is electronic chemical potential, I and A represent the ionization potential, and electron affinity of the system, respectively. Here I is calculated as the negative value of HOMO energy and A as negative value of LUMO energy as this approximation is validated and used in various similar study.^{30,38–40}

Furthermore, the topology of electron density was analyzed within the realm of quantum theory of atoms in molecules (QTAIM)⁴¹ electron localization function (ELF)⁴² at MP2/def2-TZVP level using Multiwfn program code.⁴³ To decompose the binding energy into physically meaningful quantities such as electrostatic, exchange, induction, and dispersion interaction, we have also performed symmetry adapted perturbation theory truncated at second order, that is, SAPT (2)⁴⁴ using an aug-cc-pVTZ basis set in PSI4 suite of program.⁴⁵

Finally, the desorption phenomenon was investigated using Born–Oppenheimer molecular dynamics (BOMD) at 77, 300, and 400 K using ω B97XD/def2-TZVP level. The time step of 0.5 fs was used for the simulation for a time period of 2000 fs. The equilibrium geometry of the 1:8 complex was taken for BOMD simulation. BOMD calculations were also performed using Gaussian16 suite of program.

3 | RESULTS AND DISCUSSION

We first start with the structural and electronic description of the Be₂(NLi)₂ cluster. Figure 1A shows the optimized geometry of the cluster. From the values of the Wiberg bond indices and natural charges, it is clear that Li atoms are bonded to N atoms through electrostatic attraction. Two dimensional-plot of ELF (Figure 1B) clearly reveals that there is hardly any localized electron between N and Li atom, thus rendering electrostatic interaction. The calculated natural charge at the Li atom is 0.94 e while it is 1.65 e in Be. Thus, considering the natural charges, Be seems to be the most likely target of the H₂ molecules. However, the molecular electrostatic surface potential (MESP) plot (Figure 1C) reveals that the most electropositive zone is localized at the Li atom with V_{max} of 156.4 kcal/mol compared to V_{max} of 38.4 kcal/mol at Be. We feel that MESP region of maximum best describes the location of the incoming H₂ molecule. We therefore, started attaching H₂ molecules at the Li atoms. We found that six H₂ molecules first bind at the two Li atoms and two H₂ molecules then bind at the two Be atoms resulting in the total binding of eight H₂ molecules. Figure 2 shows the optimized geometries of 1: n H₂ adsorbed molecules ($n = 1-8$).

Figure 2 shows the optimized geometries of the H₂ adsorbed complexes. The Li–H distances range from 2.1 to 2.3 Å and the H–H distance elongates marginally from the normal H–H distance of 0.738 Å at MP2/def2-TZVP level. However, there is a decrease in H–H stretching frequency. The calculated H–H stretching frequencies at MP2/def2-TZVP and ω B97XD/def2-TZVP levels are 4543.72 and 4438.19 cm^{−1}, respectively. The decrease in H–H stretching frequency in the 1: n complexes reflects a substantial amount of charge transfer from H–H σ bond to Li center. Figure 3 shows the electron density shift plot of 1:1 complex as a representative case. The amount of charge transfer from H₂ to Li in 1: n complexes are summarized in Table S1. It should be noted that there is no

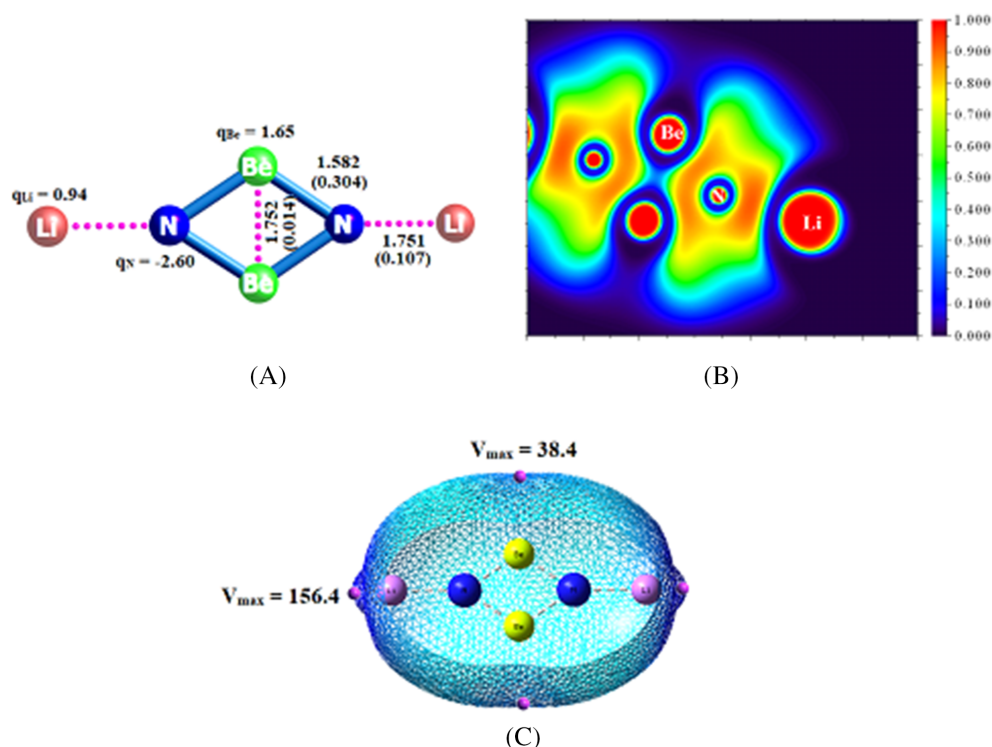


FIGURE 1 (A) MP2/def2-TZVP calculated optimized geometry of $\text{Be}_2(\text{NLi})_2$. Bond lengths are in Å and Wiberg bond indices are given within parenthesis. Natural charge, $q(e)$ for each atom is also shown. (B) 2D-plot of ELF in the molecular plane and (C) Molecular electrostatic surface potential isosurface of $\text{Be}_2(\text{NLi})_2$ showing the positions (pink dots) and values (kcal/mol) of the V_{max}

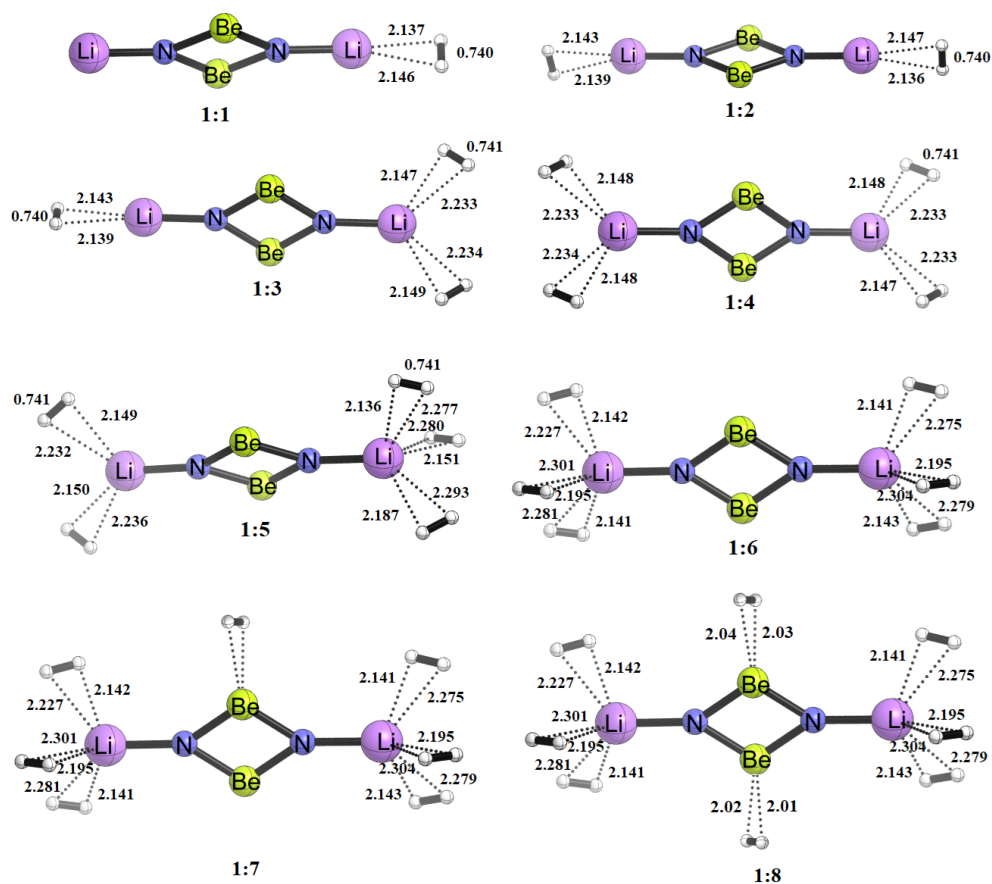


FIGURE 2 MP2/def2-TZVP calculated optimized geometries of the $1:n$ ($n = 1-8$) complexes. Bond lengths are in Å

significant change in Be–Be distance suggesting that the ultra-short nature of this bond remain intact after H_2 adsorption which may render stability to the cluster.

We then analyzed the topological feature of electron density at the H^-Li bond critical points (BCPs) of the $1:n$ complex mention in Figure 4 within the realm of QTAIM. Table 1 summarizes the

results. Positive values of the Laplacian, $\nabla^2\rho(r_c)$ and negative values of the local electronic energy density, $H(r_c)$ along with the negative ratio of $G(r_c)$ and $V(r_c)$ indicate the covalence character of $\text{Li}\cdots\text{H}$ interaction.⁴⁶ The molecular graph of all these 1: n complexes is shown in Figure 4.

The calculated H—H stretching frequency ($\nu_{\text{H-H}}$, un-scaled) values of the 1: n complexes are shown in Table 2. There is a decrease in $\nu_{\text{H-H}}$ values indicating adsorption of the H_2 molecule

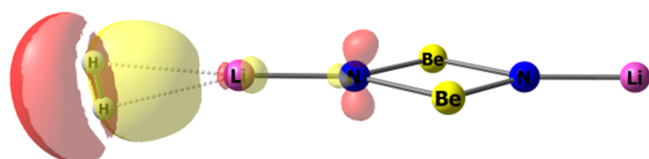


FIGURE 3 Electron density shift plot of 1:1 complex. The red and yellow isosurfaces correspond to +0.0003 and −0.0003 au, respectively

at the Li atom of the cluster. This adsorption may lead to a loss of stability of the system due to the increase in translational energy of the H_2 molecule. Electronic structural concepts such as maximum hardness (η) and lowest electrophilicity (ω) can be used to examine the stability of gas adsorption complexes.⁴⁷ The calculated chemical hardness (η), electrophilicity (ω), and electronegativity (χ) for respective complexes in Table 3 show that the hardness (η) value increases gradually with the addition of hydrogen. This indicates a potential rigidity of the complexes with the subsequent addition of H_2 molecule. Hence, the complex becomes stable with an increase of H_2 adsorption.

The calculated E_r values of these 1: n complexes are in the range of 0.15–0.31 eV which are between physisorption and chemisorption with good reversibility criteria^{48,49} with maximum gravimetric density of 21.04% which exceeds the target set by US DOE. The calculated ΔE_r and ΔE_{ads} values at different levels are also similar (Table S2) suggesting the reliability of the present level of calculations. Further, the binding energy has been transformed into physically meaningful components such as electrostatic, exchange, induction, and dispersion

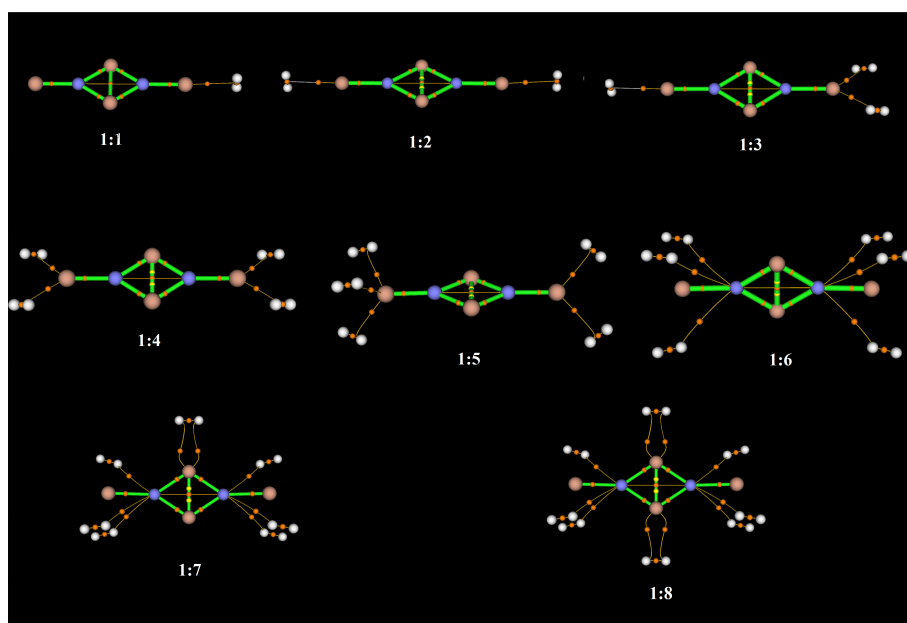


FIGURE 4 Molecular bond path of $\text{Be}_2(\text{NLi})_2\text{-}n\text{H}_2$ complex ($n = 1\text{--}8$). The orange ball indicates the bond critical point (BCP)

TABLE 1 Electron density descriptors (au) at the bond critical points of hydrogen and Li atom of $\text{Be}_2(\text{NLi})_2$ cluster calculated at MP2/def2-TZVP level

1: n	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$H(r_c)$	$G(r_c)$	$V(r_c)$	$-G(r_c)/V(r_c)$
1:1	0.008	0.047	0.0027	0.0089	−0.0061	1.45
1:2	0.008	0.048	0.0027	0.0092	−0.0065	1.41
1:3	0.006	0.04	0.0028	0.0081	−0.0055	1.47
1:4	0.006	0.04	0.0027	0.0053	−0.0046	1.15
1:5	0.009	0.03	0.0067	0.0049	−0.0040	1.22
1:6	0.006	0.04	0.0027	0.0082	−0.0053	1.54
1:7	0.007	0.03	0.0035	0.0061	−0.0049	1.24
1:8	0.006	0.05	0.0041	0.0075	−0.0062	1.20

TABLE 2 Calculated consecutive adsorption energy (E_r) also called binding energy in eV unit, average adsorption energy (E_{ads}) in eV unit, H–H stretching frequency (cm^{-1}), and gravimetric density (GD in wt%) in MP2 and ω B97xd level of theory with the combination of def2-TZVP basis set

1:n complex	MP2			ω B97XD			Gravimetric density (wt%)
	ΔE_r	ΔE_{ads}	$\nu_{\text{H-H}}^a$	ΔE_r	ΔE_{ads}	$\nu_{\text{H-H}}^b$	
1:1	0.15	0.15	4495.38	0.19	0.19	4210.41	3.2
1:2	0.15	0.14	4495.12	0.18	0.18	4208.81	6.3
1:3	0.22	0.17	4492.79	0.19	0.19	4232.76	9.1
1:4	0.22	0.18	4491.77	0.16	0.18	4244.41	11.8
1:5	0.24	0.19	4486.03	0.23	0.19	4258.74	14.2
1:6	0.29	0.21	4481.57	0.31	0.21	4271.33	16.6
1:7	0.2	0.24	4209.21	0.28	0.28	4300.08	18.89
1:8	0.24	0.23	4202.35	0.21	0.29	4292.03	21.04

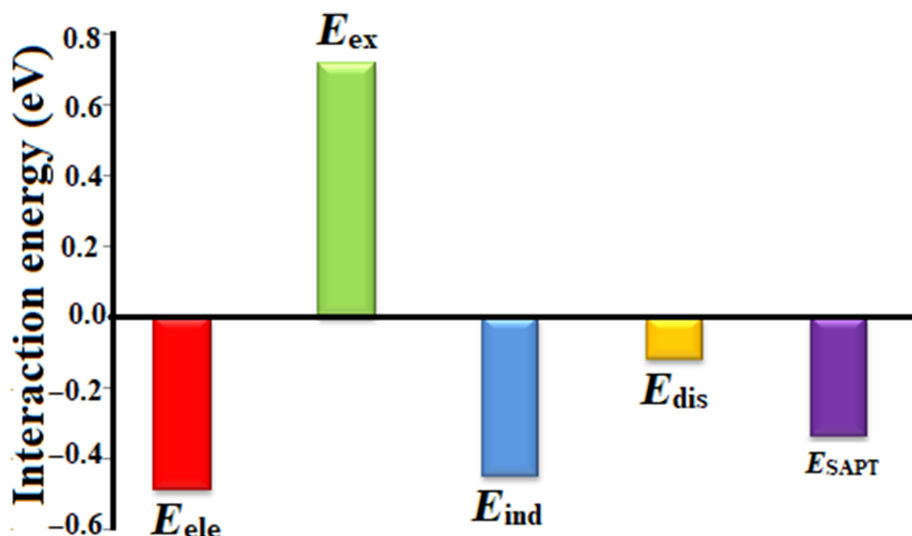
^a $\nu_{\text{H-H}}$ in free H_2 molecule at MP2/def2-TZVP level is 4543.72 cm^{-1} .^b $\nu_{\text{H-H}}$ in free H_2 molecule at ω B97XD/def2-TZVP level is 4438.19 cm^{-1} .**TABLE 3** Electronegativity χ (eV), hardness η (eV), and electrophilicity ω (eV) for $\text{Be}_2(\text{NLI})_2-n\text{H}_2$ complexes calculated at MP2/def2-TZVP level

Complex	χ	η	ω
1:1	2.41	6.16	0.46
1:2	2.12	6.73	0.31
1:3	2.01	6.81	0.29
1:4	1.95	6.92	0.27
1:5	1.93	6.94	0.26
1:6	1.92	6.96	0.26
1:7	1.87	7.01	0.23
1:8	1.86	7.23	0.24

interaction through symmetry adapted perturbation truncated at second order, that is, SAPT (2). Figure 5 shows the energy components of SAPT (2)/aug-cc-pVTZ level. It is evident from Figure 5 that exchange

in induction plays a vital role toward the total interaction energy of the 1:1 complex. The dispersion contribution is very less which justifies the large rotational barrier (14.2 kcal/mol) of the H_2 molecule around the symmetry axis.

Calculated BE values indicate that reversible binding of H_2 is feasible for this cluster. We therefore, carried out BOMD simulation at 77, 300, and 400 K for a time period of 2.0 ps. Figure 6 depicts the snapshots at different interval of time for the 1:8 complex. At 77 K, all the H_2 are adsorbed up to 2000 fs (Figure 6A). The distance of the H_2 molecules at 77 K within 2000 fs is within $3.00 \text{ \AA}$ indicating that they are adsorbed. At 300 K, two H_2 molecules start desorbing and reaches a distance of $\sim 7 \text{ \AA}$ at 1021 fs (Figure 6B). At 1920 fs, four H_2 molecules completely leave the electrostatic attraction field of the Li atoms (Figure 6B) and finally, when the temperature reaches 400 K, dissociation of all the adsorbed H_2 molecules takes place at 1392 fs. All the H_2 molecules are almost more than $7.0 \text{ \AA}$ away from the cluster. This BOMD simulation reveals that the cluster can strongly adsorb the H_2

**FIGURE 5** Energy components of SAPT (2) analysis of 1:1 complex

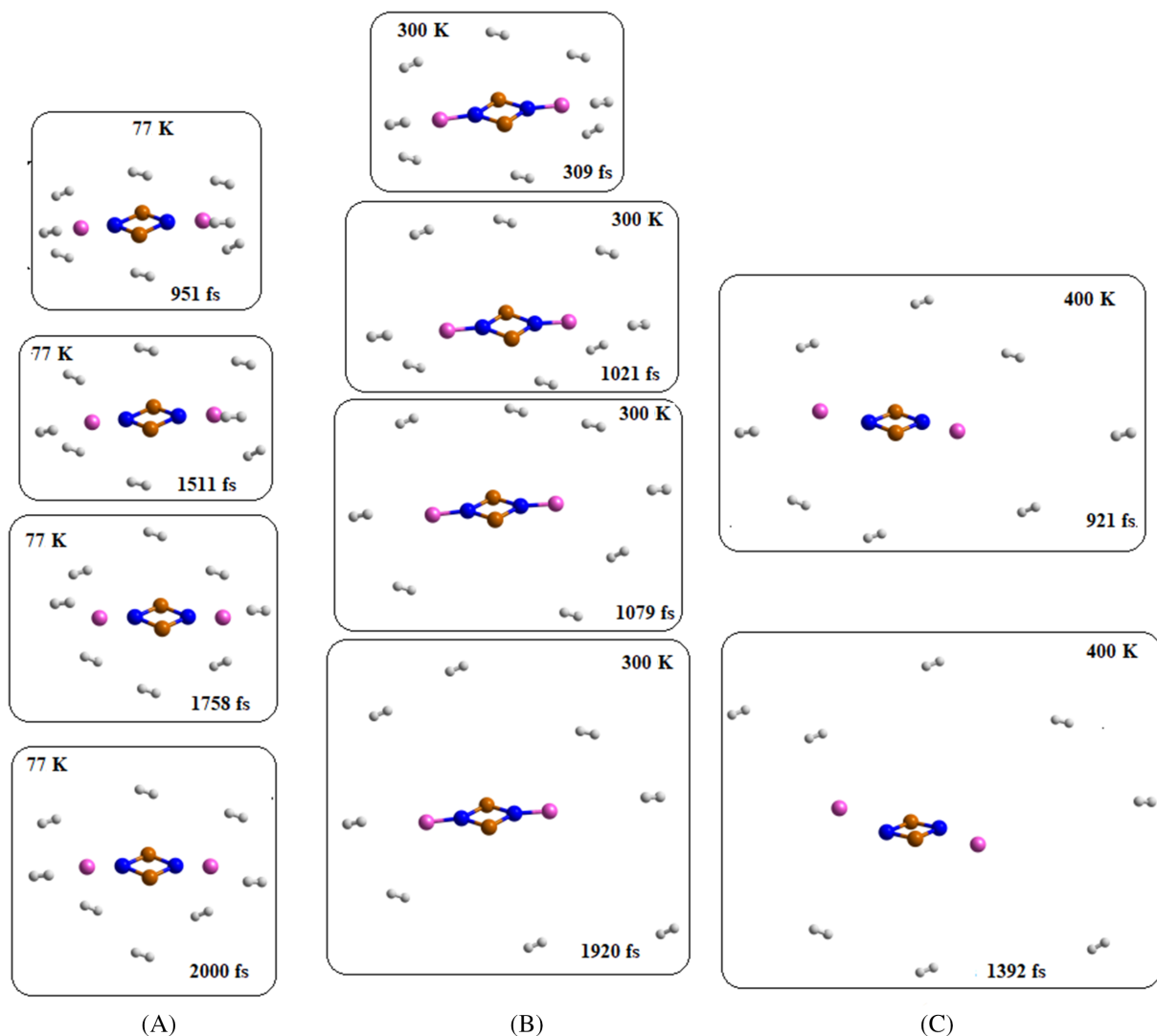


FIGURE 6 Snapshots of BOMD simulation at different time and temperatures for 1:8 complex

molecule at low temperature (77 K) which slowly releases the adsorbed H_2 molecules at room or at elevated temperature, thus, fulfilling the condition of reversibility.

4 | CONCLUSION

The search for reversible H_2 storage materials with high gravimetric density has continued for a long time. Herein, our computation reveals that $Be_2(NLi)_2$ neutral cluster is capable of showing reversible H_2 storage capacity. QTAIM analysis reveals that the interaction between the H and Li atoms has significant covalent contribution. The cluster can adsorb up to six H_2 molecules with binding energy which lies between the preferred range of physisorption and chemisorption. Decomposition of the binding energy into physically meaningful components using SAPT (2) calculations reveals that both exchange and induction plays a vital role toward the total interaction energy of the 1:1 complex. The minor contribution of dispersion is responsible for a high rotational

barrier of H_2 molecules along the symmetry axis. BOMD simulations reveal that all the H_2 molecules are strongly adsorbed at 77 K up to a time frame of 2000 fs. With an increase in temperature, the H_2 molecule starts desorbing from the cluster, and at 400 K, all the adsorbed H_2 molecules get desorbed within a time frame of 1392 fs. Our study provides a hint toward the applicability of the cluster toward reversible H_2 storage.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

All data related to this work can be found in the supporting information.

ORCID

Ankur K. Guha  <https://orcid.org/0000-0003-4370-8108>

REFERENCES

- [1] G. P. Peters, R. M. Andrew, J. G. Canadell, P. Friedlingstein, R. B. Jackson, J. I. Korsbakken, C. L. Quéré, A. Peregón, *Nat. Clim. Change* **2020**, 10, 3.
- [2] L. Schlapbach, *Nature* **2001**, 414, 353.
- [3] P. Moriarty, *Int. J. Hydrogen Energy* **2009**, 34, 31.
- [4] A. Züttel, A. Borgschulte, L. Schlapbach, *Environ. Eng. Manag. J.* **2008**, 7, 343.
- [5] Y. Zhao, Y. H. Kim, A. C. Dillon, M. J. Heben, S. B. Zhang, *Phys. Rev. Lett.* **2005**, 94, 155504.
- [6] DOE Technical Targets for Onboard Hydrogen Storage for Light Duty Vehicles, US Department of Energy, Washington, DC **2014**. <https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles>
- [7] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, 300, 1127.
- [8] H. Lee, J. W. Lee, D. Y. Kim, J. Park, Y. T. Seo, H. Zeng, I. L. Moudrakovski, C. I. Ratcliffe, J. A. Ripmeester, *Nature* **2005**, 434, 743.
- [9] W. C. Xu, K. Takahashi, Y. Y. H. Matsuo, M. Kumagai, S. Ishiyama, K. Kaneko, S. Iijima, *Int. J. Hydrogen Energy* **2007**, 32, 2504.
- [10] Q. Peng, G. Chen, H. Mizuseki, Y. Kawazoe, *J. Chem. Phys.* **2009**, 131, 214505.
- [11] Q. Wang, Q. Sun, P. Jena, Y. Kawazoe, *ACS Nano* **2009**, 3, 621.
- [12] N. B. McKeown, B. Gahnem, K. J. Msayib, P. M. Budd, C. E. Tattershall, K. Mahmood, S. Tan, D. Book, H. W. Langmi, A. Walton, *Angew. Chem. Int. Ed.* **2006**, 45, 1804.
- [13] C. P. Balde, B. P. C. Hereijgers, J. H. Bitter, K. P. de Jong, *Angew. Chem. Int. Ed.* **2006**, 45, 3501.
- [14] H. W. Langmi, A. Walton, M. M. AlMamouri, S. R. Johnson, D. Book, J. D. Speight, P. P. Edwards, I. Gameson, P. A. Anderson, I. R. Harris, *J. Alloys Compd.* **2003**, 356, 710.
- [15] R. W. P. Wagemans, J. H. van Lenthe, P. E. de Jongh, A. J. van Dillen, K. P. de Jong, *J. Am. Chem. Soc.* **2005**, 127, 16675.
- [16] A. Blomqvist, C. M. Araujo, P. Srepusharawoot, R. Ahuja, *Appl. Phys. Sci.* **2007**, 104, 20173.
- [17] Z. Xiong, G. Wu, J. Hu, Y. Liu, P. Chen, W. Luo, J. Wang, *Adv. Funct. Mater.* **2007**, 17, 1137.
- [18] A. Chakraborty, S. Mondal, R. Parida, S. Giri, P. K. Chattaraj, *A Conceptual DFT Approach Toward Analyzing Hydrogen Storage Potential*, Vol. 2, John Wiley & Sons, Inc., Germany **2022**.
- [19] Y. Zhang, X. Cheng, *Chem. Phys.* **2018**, 505, 26.
- [20] P. D. Wakchaure, B. Ganguly, *J. Comput. Chem.* **2020**, 41, 1271.
- [21] J. Du, X. Sun, L. Zhang, C. Zhang, G. Jiang, *Sci. Rep.* **2018**, 8, 1.
- [22] K. R. S. Chandrakumar, S. K. Ghosh, *Nano Lett.* **2008**, 8, 113.
- [23] K. Srinivasu, S. K. Ghosh, *J. Phys. Chem. C* **2011**, 115, 1450.
- [24] K. Srinivasu, S. K. Ghosh, *Int. J. Hydrogen Energy* **2011**, 36, 15681.
- [25] K. Srinivasu, S. K. Ghosh, R. Das, S. Giri, P. K. Chattaraj, *RSC Adv.* **2012**, 2, 2914.
- [26] S. Giri, L. Fernando, A. S. Nunez, A. T. Labbe, *J. Phys. Chem. C* **2013**, 117, 5544.
- [27] S. Giri, S. Bandaru, A. Chakraborty, P. K. Chattaraj, *Phys. Chem. Chem. Phys.* **2011**, 13, 20602.
- [28] S. Pan, S. Giri, P. K. Chattaraj, *J. Comput. Chem.* **2012**, 33, 425.
- [29] S. Pan, G. Merino, P. K. Chattaraj, *Phys. Chem. Chem. Phys.* **2012**, 14, 10345.
- [30] P. K. Chattaraj, K. Srinivasu, S. Mondal, S. K. Ghosh, *J. Phys. Chem. A* **2015**, 119, 3056.
- [31] C. Yuan, X. F. Zhao, Y. B. Wu, X. Wang, *Angew. Chem. Int. Ed.* **2016**, 55, 1.
- [32] C. Möller, M. S. Plesset, *Phys. Rev.* **1934**, 46, 618.
- [33] J. D. Chai, M. H. Gordon, *Phys. Chem. Chem. Phys.* **2008**, 10, 6615.
- [34] A. E. Reed, F. Weinhold, L. A. Curtiss, *Chem. Rev.* **1998**, 88, 899.
- [35] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16, Revision B.01*, Gaussian, Inc., Wallingford, CT **2016**.
- [36] R. G. Parr, R. G. Pearson, *J. Am. Chem. Soc.* **1983**, 105, 7512.
- [37] (a) R. G. Parr, L. V. Szentpaly, S. Liu, *J. Am. Chem. Soc.* **1999**, 121, 1922. (b) P. K. Chattaraj, U. Sarkar, D. R. Roy, *Chem. Rev.* **2006**, 106, 2065. (c) P. K. Chattaraj, D. R. Roy, *Chem. Rev.* **2007**, 107, PR46.
- [38] C. C. Zhan, J. A. Nichols, D. A. Dixon, *J. Phys. Chem. A* **2003**, 107, 4184.
- [39] S. Pan, R. Saha, A. Gupta, P. K. Chattaraj, *J. Chem. Sci.* **2017**, 129, 849.
- [40] S. Mondal, M. Ghara, P. K. Chattaraj, *Comput. Theor. Chem.* **2015**, 1071, 18.
- [41] R. W. F. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford **1990**.
- [42] (a) B. Silvi, A. Savin, *Nature* **1994**, 371, 683. (b) A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, 92, 5397.
- [43] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, 33, 580.
- [44] B. Jeziorski, R. Moszynski, K. Szalewicz, *Chem. Rev.* **1994**, 94, 1887.
- [45] J. M. Turney, A. C. Simmonett, R. M. Parrish, E. G. Hohenstein, F. A. Evangelista, J. T. Fermann, J. T. Mintz, L. A. Burns, J. J. Wilke, M. L. Abrams, N. J. Russ, M. L. Leininger, C. L. Janssen, E. T. Seidl, W. D. Allen, H. F. Schaefer, R. A. King, E. F. Valeev, C. D. Sherrill, T. D. Crawford, *WIREs Comput. Mol. Sci.* **2012**, 4, 556.
- [46] D. Cremer, E. Kraka, *Angew. Chem. Int. Ed.* **1984**, 23, 627.
- [47] M. Torrent Sucarrat, J. M. Luis, M. Duran, M. Solà, *J. Mol. Struct.: THEOCHEM* **2005**, 727, 139.
- [48] C. Guo, C. Wang, *Int. J. Hydrogen Energy* **2017**, 43, 1658.
- [49] Q. Lu, J. Meng, W. Song, J. Wan, *Int. J. Hydrogen Energy* **2013**, 38, 13328.

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