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NiB₁₀, NiB₁₁⁻, NiB₁₂, and NiB₁₃⁺: Half-Sandwich Complexes with the Universal Coordination Bonding Pattern of σ Plus π Double Delocalization

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Abstract

Transition-metal-doped boron clusters have received considerable attention in recent years. The experimentally observed planar or quasi-planar C_{2h} B₁₀(**I**), $C_{2\nu}$ B₁₁⁻(**II**), $C_{3\nu}$ B₁₂(**III**), and $C_{2\nu}$ B₁₃⁺(**IV**) are known to be boron analogs of benzene. Extensive global minimum searches and first-principles theory investigations performed herein indicate that doping these aromatic boron clusters with a nickel atom generates the closed-shell half-sandwich complexes $C_{2\nu}$ NiB₁₀(**1**, ¹A₁), C_s NiB₁₁⁻(**2**, ¹A'), $C_{3\nu}$ NiB₁₂(**3**, ¹A₁), and C_s NiB₁₃⁺(**4**, ¹A') which are all well-defined global minima of the systems with the coordination numbers of CN = 10, 11, 12, and 13, respectively. Detailed bonding analyses indicate that these Ni-doped boron complexes are effectively stabilized by coordination interactions between the Ni center and aromatic B_n^{-/0/+} ligands (n = 10–13) and follow the universal coordination bonding pattern of σ plus π double delocalization. Molecular dynamics simulations show that, among these complex clusters, NiB₁₁⁻(**2**) behaves like a Wankel motor at room temperature with the B₃ inner wheel rotating almost freely inside the quasi-rotating B₈ outer bearing in a concerted mechanism, revealing typical bonding fluctuations/fluxionalities in a molecular motor due to thermal vibrations. The IR, Raman and electronic spectra of the concerned species are computationally simulated to facilitate their experimental characterizations.

Keywords Half-sandwich complexes · Wankel motor · First-principles theory · Structurers · Bonding fluctuations

Introduction

As prototypical electron deficient element in the periodic table, boron has a vast variety of geometrical and electronic structures in both bulk allotropes and polyhedron molecules due to its strong propensity to form multicenter-twoelectron (mc-2e) bonds. Persistent joint photoelectron spectroscopy (PES) and first-principles theory (FPT)

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investigations in the past decade have shown that $B_n^$ monoanions possess planar or quasi-planar (2D) structures in an unexpectedly wide range of cluster sizes (n = 3-30, 33-38, and 40), [1-19] while B_n neutrals favor 2D geometries with n up to at least 20 [20] and B_n⁺ moncations remain planar with n < 15, [21] unveiling a flat world of boron in close analogy with polycyclic aromatic hydrocarbons. Flat boron clusters are governed by localized twocenter-two-electron (2c-2e) σ -bonds on the periphery and delocalized multicenter mc-2e σ and π bonds over the molecular moieties involving both the inner and peripheral atoms. 2D aromatic boron clusters prototyped with B12 (n = 1) and B_{16}^{2-} (n = 2) conform to the 4n + 2 Hückel rule and are expected to be effective inorganic ligands to various transition metal centers. Furthermore, 2D $C_{2\nu} B_{11}^{-}$, $C_{2\nu} B_{13}^{+}$, $C_s B_{15}^{+}$, $C_s B_{18}^{2-}$, and $C_{2\nu} B_{19}^{-}$ have been proposed to be molecular Wankel motors with the inner wheels rotating almost barrierlessly inside the pseudo-rotating outer bearings [5, 22–27].

Inspired by the observation of the boron-centered 2D aromatic $B @B_7^{2-}$ and $B @B_8^{-}$ clusters, a series of

transition-metal-centered 2D boron wheels $M \otimes B_n^-$ (M = Co, Rh, Ir, Ru, Ta, and Nb, n = 8-10) [28-30] have been characterized in PES experiments in combination with extensive FPT calculations. It has been concluded that the wheel-like NbB_{10}^{-} and TaB_{10}^{-} possess the highest possible coordination number of CN = 10 in planar environments in chemistry. Two larger metal-doped boron clusters, CoB_{12}^{-} and RhB_{12}^{-} [31] were late found to adapt half-sandwich structures. Interestingly, half-sandwich IrB_{12}^{-} was found to be a molecular Wankel motor [32] with the energy barrier effectively decreased by doping an Ir atom into B_{12}^{-} . A tubular molecular rotor B_2 -Ta@ B_{18}^{-} was observed via a joint PES and FPT investigation with an energy barrier of 1.13 kcal mol^{-1} . [33] Very recently, Chen and co-workers found that $TaB_n^{0/-}$ (n = 11–15) clusters adapted half-sandwich geometries. [34] Small halfsandwich $MnB_n^{-/0/+}$ (n = 10–13) [35] in high spin states and MoB₁₀ and MoB₁₂ [36] in singlet states are also found to be the most stable isomers of the systems. Different and even controversial bonding analyses have been presented in literature for these half-sandwich species [31, 32, 34, 35] which require further investigations and clarifications. PES experiments in combination with FPT theory calculations also show that PrB₇⁻ takes a half-sandwich structure with C_{6v} symmetry. [37] In a recent communication, our group presented a systematical FPT investigation on a series of endohedral cage-like complexes $Ta@B_n^q$ (n = 23 ~ 28, $q = -1 \sim +3$) which possess the highest coordination number of $CN_{max} = 28$ in spherical environments known in chemistry. [38].

Using the experimentally confirmed aromatic C_{2h} B₁₀(I), $C_{2\nu} B_{11}^{-}$ (II), $C_{3\nu} B_{12}$ (III), and $C_{2\nu} B_{13}^{+}$ (IV) as effective ligands and a Ni atom (Ni[Ar] $4s^23d^8$) as dopant, extensive global minimum (GM) searches and FPT calculations performed in this work indicate that the closed-shell halfsandwich $C_{2\nu}$ NiB₁₀(**1**, ¹A₁), C_s NiB₁₁^{-(**2**, ¹A'), $C_{3\nu}$ NiB₁₂(**3**,} ${}^{1}A_{1}$), and $C_{s} \operatorname{NiB}_{13}^{+}(4, {}^{1}A')$ are well-defined GMs of the systems with the coordination numbers of CN = 10, 11, 12,and 13, respectively. Detailed bonding analyses show that these Ni-doped boron complexes conform to the universal coordination bonding pattern of σ plus π double delocalization between the Ni center and $B_n^{-/0/+}$ ligands. Molecular dynamics simulations show that the half-sandwich $NiB_{11}^{-}(2)$ behaves like a Wankel motor at room temperature in a concerted mechanism, revealing the bonding fluctuation nature of structural fluxionality in a molecular motor.

Computational Methods

Extensive GM searches were performed on NiB_{10} , NiB_{11}^{-} , NiB_{12} , and NiB_{13}^{+} using both the Coalescence Kick (CK) [39] and TGmin [40, 41] algorithms, in combination with

manual structural constructions based on low-lying isomers of the previously reported B_{10} , B_{11}^{-} , B_{12} , and B_{13}^{+} [22, 23, 25]. Approximately 5000 trial structures were generated for each species in both singlet and triplet spin states. The low-lying isomers were then fully re-optimized at both PBE0/6-311 + G* [42, 43] and TPSSH/6- $311 + G^{*}$ [44] levels [45] using Gaussian 09 package [46] with vibrational frequencies checked. Single-point energies of the first twenty low-lying structures were further refined using the more accurate CCSD(T)/def2-TZVP//PBE0/6- $311 + G^*$ method [47–49] at PBE0 geometries. TS and OST2 calculations was performed to search the transition state (TS) of NiB₁₁⁻ which turned out to have a C_s symmetry. Intrinsic reaction coordinate (IRC) [50] calculation was carried out to confirm that the obtained structure is a true TS. Born-Oppenheimer molecular dynamics (BOMD) simulations were performed on $NiB_{11}^{-}(2)$ for 30 ps at PBE level using the CP2 K software package [51] with the time step of 10 fs. Bonding analyses were performed using the adaptive natural density partitioning (AdNDP) method [52] at PBE0/6-31G* level. The visualization of the AdNDP results was realized using the Molekel 5.4.0.8 program. [53].

Results and Discussion

Structures and Stabilities

Extensive GM searches and FPT calculations indicate that, with a nickel dopant, NiB₁₀, NiB₁₁⁻, NiB₁₂, and NiB₁₃⁺ possess closed-shell half-sandwich GM structures of $C_{2\nu}$ NiB₁₀(1), C_s NiB₁₁⁻(2), $C_{3\nu}$ NiB₁₂(3), and C_s NiB₁₃⁺(4) (see Fig. 1) which have the coordination numbers of CN = 10, 11, 12, and 13, and HOMO–LUMO energy gaps of $\Delta E_{gap} = 2.11$, 3.20, 3.89, and 2.88 eV at PBE0 level,



Fig. 1 Global minimum structures of NiB₁₀(1), NiB₁₁⁻(2), NiB₁₂(3), and NiB₁₃⁺(4) (*I*-4) optimized at PBE0/6-311 + G(d) level, with the experimentally confirmed bare B₁₀(I), B₁₁⁻(II), B₁₂(III), and B₁₃⁺(IV) depicted for comparisons

respectively. More alternative low-lying isomers are collectively depicted in Fig. S1-Fig. S4. The bare $B_{10}(I)$, $B_{11}^{-}(II)$, $B_{12}(III)$, and $B_{13}^{+}(IV)$ with a B_2 , B_2 , B_3 , or B_3 unit inside a B₈, B₉, B₉, or B₁₀ outer bearing possess the structural patterns of (2+8) (2+9), (3+9), and (3 + 10), respectively. Addition of a Ni dopant into the system induces remarkable intramolecular rearrangements in both NiB₁₁⁻⁽²⁾ and NiB₁₃⁺⁽⁴⁾ in which the B₁₁⁻ and B_{13}^{+} ligands have been rearranged from $B_{11}^{-}(II)$ (2 + 9) and $B_{13}^{+}(IV)$ (3 + 10) to $NiB_{11}^{-}(2)$ (3 + 8) and $\text{NiB}_{13}^+(4)$ (4 + 9), respectively. The B₂ bar in B₁₁⁻(II) has been changed into a B_3 triangle in NiB₁₁⁻(2) and the B_3 triangle in $B_{13}^+(IV)$ transferred to a B_4 rhombus in $NiB_{13}^{+}(4)$ (Fig. 1). Such structural rearrangements effectively improve the metal-ligand coordination interactions in both 2 and 4, as evidenced by the increase of the total Ni Wiberg bond order from $WBI_{Ni} = 1.46$ in the fourth isomer of $C_s \text{ NiB}_{11}(2 + 9)$ (Fig. S2) to $\text{WBI}_{\text{Ni}} = 1.76$ in C_s $NiB_{11}^{-}(2)$ (3 + 8) and from $WBI_{Ni} = 1.51$ in the seventh isomer $C_s \text{ NiB}_{13}^+$ (3 + 10) (Fig. S4) to WBI_{Ni} = 1.85 in C_s NiB₁₃⁺ (4) (4 + 9). The structural patterns of C_{2h} $B_{10}(I)$ (2 + 8) and C_{3v} $B_{12}(III)$ (3 + 9) are basically maintained in both $C_{2\nu}$ NiB₁₀(1) (2 + 8) and $C_{3\nu}$ NiB₁₂(3) (3 + 9), with more severe buckling in the complexes than in bare ligands. We notice that $C_{2\nu}$ NiB₁₀(1) possesses an imaginary vibrational frequency of 142i cm⁻¹ at PBE0 which leads to the second lowest-lying isomer of $C_s \text{ NiB}_{10}$ (Fig. S1) when fully relaxed. However, the two isomers are practically iso-energetic, with the former being 0.01 eV more stable than the latter at CCSD(T). $C_{2\nu}$ NiB₁₀(1) is therefore the vibrationally averaged GM of the system possible to exist in experiments. The open-shell triplet $C_{2\nu}$ NiB_{10} (³A₂) (Fig. S1) as the third isomer of the system appears to be 0.18 eV less stable than the $C_{2\nu}$ GM at CCSD(T) (Fig. S1). As shown in Fig. S2-S4, similar to NiB₁₀(1), half-sandwich NiB₁₁⁻(2), NiB₁₂(3), and C_s $NiB_{13}^{+}(4)$ are all well-defined GMs of the systems lying at least 0.17 eV lower than their alternative low-lying counterparts at CCSD(T). Triplet C_s NiB₁₁⁻ (³A') and C_s NiB_{13}^+ (³A') are found to lie much higher in energy (by + 1.25 eV and + 1.17 eV) than their singlet GMs at CCSD(T).

Bonding Analyses

To interpret the high thermodynamic stabilities of 1-4, we performed detailed structural and natural bonding orbital (NBO) [54] analyses on them. As shown in Table 1, the Ni–B distances between $r_{Ni-B} = 2.01-2.51$ Å and averaged Ni–B distances between $r_{Ni-B(av)} = 2.17-2.34$ Å in 1–4 belong to typical transition-metal-boron coordination bond lengths [38]. NBO analyses indicate that 1-4 possess the average Ni–B Wiberg bond orders of $WBI_{Ni-B(av)} =$ 0.14-0.16, showing that all the Ni-B coordination interactions in these complexes contribute almost equally to the overall Ni-B_n coordination interaction and all the boron atoms in the complexes should be treated as effective ligands to the Ni center. The calculated total Wiberg bond orders of Ni lie between $WBI_{Ni} = 1.62-1.85$ in 1-4, suggesting that the Ni centers in these half-sandwich complexes possess approximately an overall covalent valence of two. Molecular orbital analyses further show that the Ni ([Ar] $3d^84s^2$) atoms in **1–4** possess the electronic configurations of $[Ar]3d^{9.21}4s^{0.12}4p^{0.02}$, $[Ar]3d^{9.16}4s^{0.14}4p^{0.02}$, $[Ar]3d^{9.20}4s^{0.11}4p^{0.03}$, and $[Ar]3d^{9.09}4s^{0.14}4p^{0.03}$ and carry the positive net atomic charges of + 0.63, + 0.65, + 0.64, and + 0.71 lel, respectively. These results show that a Ni atom in 1–4 donates its $4s^2$ electrons almost completely to the bowl-shaped B_n ligands, while, in return, accepts approximately 1.0 \sim 1.3 electrons in its partially occupied $3d^8$ orbitals from the half-sandwich $B_n^{+/0/-}$ ligands via effective $p \rightarrow d$ back donations. Ni 4p orbitals with the low occupation numbers of 0.02-0.03 make negligible contribution to Ni– $B_n^{+/0/-}$ coordination interactions.

Detailed AdNDP analyses recover both the localized and delocalized bonding elements in these complexes. As depicted in Fig. 2, the chemical bonding elements in 1–4 can be divided into four categories: the localized and delocalized σ -bonds on the $B_n^{+/0/-}$ ligands in the first row, lone pairs on Ni in the second row, partially delocalized multicenter π - or σ -coordination bonds between Ni and B_n ligands in the third row, and the totally delocalized π -coordination bonds over the whole complexes in the fourth row. In specific, $C_{2\nu}$ NiB₁₀ (1) possesses 8 localized 2c-2e

Table 1 Calculated Ni–B distances (r_{Ni-B}) , average Ni–B distances (r_{Ni-B}) , average Ni–B Wiberg bond orders $(WBI_{Ni-B(av)})$, and total Wiberg bond orders (WBI_{Ni}) , natural atomic charges (q_{Ni}) , and

electronic configurations of the Ni centers in NiB₁₀(1), NiB₁₁⁻(2), NiB₁₂(3), and NiB₁₃⁺(4) at PBE0/6-311 + G(d) level

	$r_{Ni-B}/Å$	r _{Ni-B(av} /Å	WBI _{Ni-B(av)}	WBI _{Ni}	q _{Ni} /lel	Electronic-configuration	
NiB ₁₀ (1)	2.04-2.41	2.22	0.16	1.62	+ 0.63	Ni[Ar] $3d^{9.21}4s^{0.12}4p^{0.02}$	
$NiB_{11}^{-}(2)$	2.01-2.30	2.17	0.16	1.76	+ 0.65	Ni[Ar] $3d^{9.16}4s^{0.14}4p^{0.02}$	
NiB ₁₂ (3)	2.03-2.51	2.34	0.14	1.64	+ 0.64	NI[Ar] $3d^{9.20}4s^{0.11}4p^{0.03}$	
$NiB_{13}^{+}(4)$	2.01-2.39	2.27	0.14	1.85	+ 0.71	Ni[Ar] $3d^{9.09}4s^{0.14}4p^{0.03}$	



Fig. 2 AdNDP bonding patterns of $NiB_{10}(1)$ (a), $NiB_{11}^{-}(2)$ (b), $NiB_{12}(3)$ (c), and $NiB_{13}^{+}(4)$ (d), with the occupation numbers ON indicated

peripheral σ -bonds, 2 delocalized 3c-2e and 2 delocalized 4c-2e σ -bonds on the $C_{2\nu}$ B₁₀ ligand, 2 1c-2e long pairs $(3d_{xz} and 3d_{yz})$ on the Ni center, 1 3c-2e π coordination bond between Ni $(3d_{z2})$ and the B₂ unit directly under it at the center of the $C_{2\nu}$ B₁₀ ligand and 2 4c-2e σ -bonds between Ni $(3d_{x2-y2} \text{ and } 3d_{xy})$ and the two long edges of the B_{10} ligand, and three totally delocalized 11c-2e π -coordination bonds over the whole half-sandwich complex, in an overall symmetry of $C_{2\nu}$ (Fig. 2a). As shown in Fig. 2b–d, similar $\sigma + \pi$ double delocalization coordination covalent bonding interactions exist in $NiB_{11}^{-}(2)$, $NiB_{12}(3)$, and $NiB_{13}^{+}(4)$. In particular, $NiB_{11}^{-}(2)$ possesses 1 delocalized $3c-2e \sigma$ bond on the central B₃ triangle, 5 delocalized 3c-2e σ bonds between the B₃ inner ring and B₈ outer bearing, and 3 totally delocalized 12c-2e π bonds over the whole molecule (Fig. 2b). $NiB_{11}^{-}(2)$ is therefore triply aromatic according to the 4n + 2 Hückel rule, including one σ aromatic system with 2 electrons (n = 0) on the central B_3 triangle, one σ -aromatic system with 10 electrons (n = 2) between the inner B_3 ring and the B_8 outer bearing, and one π -aromatic system with 6 electrons (n = 1) over the whole half-sandwich complex. For $C_{3\nu}$ B₁₂(**3**), we define 3 equivalent 4c-2e σ bonds between Ni and the three edges of the $C_{3\nu}$ B₁₂ ligand in Fig. 2c, based on the fact that the three B atoms on each edge have almost the same Ni–B bond orders with WBI_{Ni–B} = 0.14, 0.16 and 0.14, respectively. Our σ bonding pattern is different from that of $C_{3\nu}$ RhB₁₂⁻ which was reported to contain 3 localized 2c-2e σ bonds between Rh center and three B atoms at the center of each edge of the $C_{3\nu}$ B₁₂ ligand [31]. Thus, **1–4** complexes follow the universal coordination bonding pattern of $\sigma + \pi$ double delocalization which renders high stability to their half-sandwich structures.

Intramolecular Pseudorotations and Bonding Fluctuations

Extensive molecular dynamics (MD) simulations show that, among these half-sandwich complexes, $C_s \operatorname{NiB}_{11}^{-}(2)$ behaves like a molecular Wankel motor at room temperature, with the B₃ inner triangle rotating almost freely inside the quasi-rotating B₈ outer bearing. Both the GM and transition state (TS) of NiB_{11}^{-} possess C_s symmetry (Fig. 3). The GM possesses the smallest vibrational frequency of 71.3 cm^{-1} at PBE0 which corresponds to a soft mode of intramolecular rotation of the peripheral B₈ ring with respect to the inner B₃ triangle. Following this mode, the TS structure is reached straightforward with an imaginary frequency of 55.1i cm⁻¹ which, interestingly, corresponds to a pseudorotation of the peripheral ring against the B_3 inner ring leading to a neighboring GM. The energy barrier between the GM and TS of NiB₁₁⁻ turns out to be 0.08, 0.13, and 0.06 kcal mol^{-1} at PBE0, TPSSH, and CCSD(T) levels, respectively. Such an energy barrier is much lower than the corresponding value of 0.35 kcal/mol



Fig. 3 Two views of the half-sandwich global minimum C_s NiB₁₁⁻(**2**) and the corresponding transition state (TS) C_s NiB₁₁⁻ at PBE0/6-311 + G(d) level. Arrows indicate the lowest-frequency (for GM) and the imaginary-frequency (for TS) normal vibrational modes

in the experimentally observed bare Wankel motor $B_{11}^{-}(II)$ [25] due to the existence of the Ni dopant in the complex.

Lipscomb proposed a general mechanism for the framework rearrangement in boranes and carboranes in 1966 [55]. Such a process involves the cooperative stretching of a diamond-shaped group of atoms into a square and back into a diamond shape. This diamondsquare-diamond mechanism requires relatively little atomic motion. Merino et al. [56] found that the dynamical behavior of boron clusters also follows this mechanism. Both the soft mode of 71.3 cm^{-1} in the GM and the imaginary frequency of 55.1i cm⁻¹ in its TS are closely associated with a square-to-rhombic conversion of the B2B3B8B10 four-membered unit (Fig. 3). The motion in the GM may start with a shrink of the B2-B8 distance, which turns the square into a rhombus corresponding to the bottom rhombic hole in the TS. During this motion, the B5–B7 distance expands which helps generate a new rhombic B10B5B9B7 hole at the top in the TS. Thus the soft rotational mode easily initiates the transition from the GM to TS at room temperature.

How such rotation of the inner triangle is possible within the B_8 outer bearing? This question can be answered by detailed AdNDP bonding analyses in the rotational process which unveils a consistent bonding pattern evolution between the GM (see Fig. 2b) and TS (see Fig S5). The 8 localized 2c-2e σ bands on the B₈ outer bearing, 1 delocalized 3c-2e σ band on the central B₃ triangle, and 3 totally 12c-2e π bonds over the whole molecule remain basically unchanged during the structural fluctuation. The main change in chemical bonding upon rotation occurs in the delocalized σ -framework between the inner B₃ triangle and peripheral B8 ring. Fig 2b and Fig S5 show that both the GM and TS of NiB₁₁⁻ possess 5 3c-2e σ bonds between the inner B₃ triangle and peripheral B₈ ring. However, the positions of these 3c-2e σ -bonds exhibit delicate differences between them. While the electron density migrates from one 3c-2e σ -bond to its neighboring 3c-2e σ -bond (for instance, from B5B7B10 in GM₁ to B7B1B10 in TS_{1-2} in Fig. 4), the other pairs of delocalized σ -electrons occupying 3c-2e σ -bonds remain almost unchanged in their positions. The next step involves a similar σ -electron density migration from B1B8B10 in TS_{1-2} to B8B2B10 in GM₂ (Fig. 4). There exist 24 equivalent GMs and 24 equivalent TSs in a full circle, with 15° in each step (Fig. 4).

In the MD process, each rhombic B_4 unit as a "defect site" in the GM and TS is flexible (like a flexible rhombus in a "foldable door"). It is the fluxional bonds that provide the driving force for the intramolecular rotation and adjust the spatial distribution of the island 3c-2e σ clouds. Take the B5B7B10 triangle as an example. At the initial GM₁,



Fig. 4 σ bonding fluctuations in NiB₁₁⁻(2) (3c-2e σ -bonds shaded in gray) during intramolecular rotation in 45° (with 15° in each step)

the σ cloud is islanded on this triangle. It leans to the B7B1B10 triangle in TS₁₋₂, where a σ cloud migrates spontaneously from B1B8B10 to B8B2B10 in GM₂ in a concerted mechanism. From GM₂ to TS₂₋₃, the σ cloud migrates from B2B11B5 to B5B11B6, initiating the second rotational step. Upon rotation of the peripheral ring in a full circle, the σ clouds accomplish a full period of electron density migration via continuous and synergetic breakages and formations of a series of closely related 3c-2e σ bonds, revealing typical bonding fluctuations due to thermal vibrations in a molecular Wankel motor with a low energy barrier. An extracted short movie illustrating the intramolecular rearrangements of NiB₁₁⁻(**2**) during the MD simulation at 300 K for 20 ps is provided in the ESI.

Simulated IR, Raman and PES Spectra of NiB₁₁⁻

Infrared photodissociation (IR-PD) spectroscopy in combination with first-principles calculations has proven to be a powerful approach in the characterizations of novel cluster monocations [57, 58]. We calculate the vibrational frequencies and simulate the IR and Raman spectra of $NiB_{11}^{-}(2)$ in Fig. 5 and that of $NiB_{10}(1)$, $NiB_{12}(3)$, and $NiB_{13}^{+}(4)$ in Fig S6 to facilitate their spectroscopic characterizations. The major IR bands $NiB_{11}^{-}(2)$ appear at 550 cm^{-1} (a"), 637 cm^{-1} (a"), 693 cm^{-1} (a"), 922 cm^{-1} (a'), 1089 cm⁻¹ (a"), 1144 cm⁻¹ (a'), and 1209 cm⁻¹ (a'). Its major Raman features occur at 550 cm^{-1} (a"), 785 cm^{-1} (a'), 1085 cm^{-1} (a'), and 1240 cm^{-1} (a'). As mentioned above, the energy barrier between the GM and TS is extremely low for $NiB_{11}^{-}(2)$ (0.06 kcal/mol at CCSD(T)). It is expected that the TS may coexist with the GM in IR and Raman measurements, similar to the situation in B_{13}^+ which has the GM-TS energy barrier of about 0.4 kcal/mol [58].

Finally, we simulate the PES spectrum of $C_s \operatorname{NiB}_{11}^{-}(2)$ using the TD-DFT approach [59] at PBE0 (Fig. 5c). It features six sharp peaks at X (3.69 eV), A (3.94 eV), B



Fig. 5 Simulated IR, Raman and PES spectra of $\rm NiB_{11}^{-}(2)$ at the PBE0/6-311 + G*level

(4.29–4.38 eV), C (4.98 eV), D (5.32–5.39 eV), and E (6.17 eV), respectively. The vertical detachment energies (VDEs) of the corresponding excitations are summarized in Table S1 (ESI†). The first peak X represents the vertical detachment transition from the ground state of the anion to

that of the neutral, while the other PES features originate from vertical detachment transitions to the excited states of C_s NiB₁₁. PES spectroscopy has served as the major experimental approach to characterize boron-based monoanions in gas phase in the past decade [1–19].

Conclusions

We have presented herein a systematic FPT investigation on half-sandwich $NiB_{10}(1)$, $NiB_{11}(2)$, $NiB_{12}(3)$, and NiB_{13}^{+} (4, ¹A') which all turn out to be well-defined global minima of the systems with a universal coordination bonding pattern of σ plus π double delocalization. Perfectly planar Ni∈B₁₈ and cage-like heteroborospherenes $Ni_n \in B_{40}$ (n = 1-4) have been predicted for bigger Nidoped boron clusters in theory. [60] MD simulations show that NiB_{11} (2) behaves like a Wankel motor at room temperature in a concerted mechanism, reflecting the bonding fluctuation nature of structural fluxionality in molecular motors. Fluxional bonds may play an important role in molecular dynamics and catalysis processes with low energy barriers and deserves further theoretical and experimental investigations. The metal-doped half-sandwich complexes predicted in this work invite experimental syntheses and characterizations to form novel transitionmetal borides and boron nanomaterials.

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