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Generation and characterization of ionic and neutral dihydroxy boron $B(OH)_2^{+/0}$ in the gas phase

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Abstract

The dicoordinated borinium ion, dihydroxyborinium, $B(OH)_2^+$ is generated from methyl boronic acid $CH_3B(OH)_2$ by dissociative electron ionization and its connectivity confirmed by collisional activation. Neutralization–reionization (NR) experiments on this ion indicate that the neutral $B(OH)_2$ radical is a viable species in the gas phase. Both vertical neutralization of $B(OH)_2^+$ and reionization of $B(OH)_2$ in the NR experiment are, however, associated with particularly unfavorable Franck-Condon factors. The differences in adiabatic and vertical electron transfer behavior can be traced back to a particular π stabilization of the cationic species compared to the sp^2-type neutral radical. Thermochemical data on several neutral and cationic boron compounds are presented based on calculations performed at the G2 level of theory. (Int J Mass Spectrom 197 (2000) 105–111) © 2000 Elsevier Science B.V.

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1. Introduction

In recent years, dicoordinated boron compounds have aroused considerable interest because of their importance in organoboron chemistry and the combustion of boron compounds in aerospace systems. Although the borinium ions have been proposed as transient intermediates in condensed phase reactions, many of the corresponding neutral analogs have so far escaped experimental detection. This has been mainly attributed to the high electrophilicity and thus reactivity of subvalent boron compounds owing to the presence of two empty *p* orbitals.

The structures and stabilities of oxygenated boron cations have long been of interest in mass spectrometry. Hettich et al. [1] reported the gas-phase ion chemistry of methyl and ethyl borates, which Attiná et al. [2] has extended to free boric acid. The chemical reactivity of various borinium ions toward different organic substrates has been thoroughly investigated by Kenttämaa and co-workers using ion-cyclotron resonance mass spectrometry [3–7]. Later, Brodbelt and co-workers [8–10] extended these studies and

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demonstrated that borinium ions can be used as reagents in the chemical ionization of drugs. Ma et al. [11] have studied the relative affinities of borinium cations toward pyridines by the kinetic method by using a multistage mass spectrometer and complementary ab initio methods. Nevertheless, as Smolanoff et al. [12] have pointed out, knowledge of the precise thermochemistry of boron oxides remains somewhat uncertain. More recently, Rablen and Hartwig [13] as well as Duan et al. [14] used computational chemistry at the G2 level of theory [15] to estimate the heats of formation of several boron species including boron oxides and hydroxides. The latter molecules are of paramount importance as transients in the combustion of boron in oxygen and fluorine containing environments. Neutralization–reionization (NR) [16] mass spectrometry is an established technique for probing such elusive transient intermediates. Here, we report on the characterization of cationic and neutral dihydroxy boron species in the gas phase by tandem mass spectrometric methods complemented by a theoretical study using the G2 approach.

2. Experimental and computational methods

The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration which has been described elsewhere [17,18]. The ions of interest were generated by electron ionization (EI, 70 eV) of methyl boronic acid. After acceleration to a kinetic energy of 8 keV, the ions were mass selected by using B(1) and E(1) at mass resolutions $m/\Delta m$ between 3000 and 5000 to achieve separation from isobaric interferences, except those due to overlaps of ^{10}B and ^{11}B compounds. For collisional activation (CA), oxygen was used as collision gas at 80% transmission (T) in the field-free region E(1) and B(2). In the NR experiments, the cations were collided with xenon (80% T) to afford neutralization. The remaining ions were deflected from the beam and the neutrals were subsequently reionized upon collision with oxygen (80% T). In both types of experiments, the cations formed were recorded by scanning B(2). All mass spectra were on-line processed and accumulated using the AMD/Intectra data system.

G2 calculations [15] were performed with the Gaussian series of programs [19,20]. This approach is expected to yield accurate energetics, within $\pm$ 2 kcal/mol, in all but a few notorious cases [15,21–23]. The energetics of vertical electron-transfer processes of interest (see Sec. 3) were obtained by using the optimized geometry of the species in question and subsequently performing the G2 series of single-point calculations on the neutralized or ionized species, respectively, incorporating the so-called higher level corrections of the G2 method, but no zero-point vibrational energies. In addition B3LYP/6-31G(*d*) calculations were performed (see Sec. 3) by using the standard routines implemented in GAUSSIAN 98 [20].

3. Results

The electron-ionization mass spectrum of methyl boronic acid $CH_3B(OH)_2$ displays an ion at $m/z = 45$ with the elemental composition [^{11}B, O_2, H_2]; interferences by the ^{10}B isotope are negligible (<1%). Considering the structure of the precursor compound, formation of the borinium ion $B(OH)_2^+$ is implied; this is further supported by the fact that the metastable molecular ion undergoes unimolecular loss of a methyl radical, i.e. $CH_3B(OH)_2^+ \rightarrow B(OH)_2^+ + CH_3^{\cdot}$.

The CA mass spectrum of the $[B, O_2, H_2]^+$ ion [Fig. 1(a)] is simple and its interpretation is straightforward. The spectrum exhibits abundant ions at $m/z = 44$ ($HOBO^+$) and $m/z = 28$ (BOH^+) corresponding to losses of $H^{\cdot}$ and $OH^{\cdot}$ radicals, respectively. Structurally indicative are (1) the signal at $m/z = 17$ (OH^+) together with the absence of $H_2O^{+\cdot}$ at $m/z = 18$ thus disfavoring a $OB(OH_2)^+$ structure, and (2) the significant $^{11}B^+$ signal. In contrast, the signals for BH^+ and BH_2^+ do not exceed the noise level, thereby excluding the presence of B–H bonds in the precursor ion. Let us therefore assume that the borinium ion $B(OH)_2^+$ is formed exclusively. Note however, that the peaks at $m/z = 29$ (BOH_2^+) and

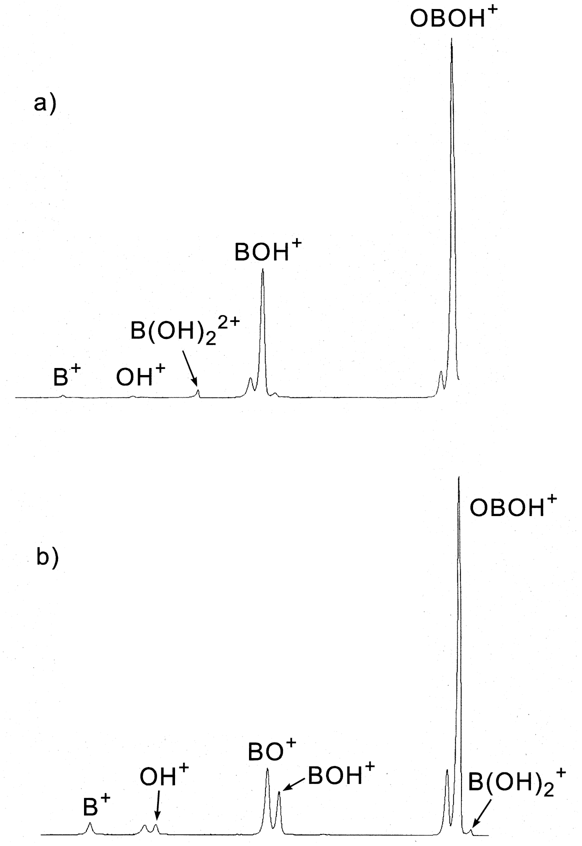

Fig. 1. (a) Collisional activation and (b) neutralization-reionization spectra of B(1)/E(1) mass-selected [B, O_2, H_2]$^+$ generated by dissociative electron ionization of methyl boronic acid.

$m/z = 27$ (BO^+) may indicate a possible contribution of some $OB(OH_2)^+$ cation (see the following). A charge stripping [24] signal at $m/z = 22.5$ corresponding to the doubly charged ion is also observed in Fig. 1(a), indicating the existence of $B(OH)_2^{2+}$ as a small, long-lived molecular dication [25].

The NR mass spectrum of [B, O_2, H_2]$^+$ shows a survivor signal of moderate intensity [Fig. 1(b)]. We also applied neutralization agents other than xenon like NO and $(CH_3)_3N$, but found no major increase in the intensity of the survivor ion signals. The fragmentation pattern of the NR spectrum is by and large that found in the CA spectrum indicating that the connectivity of the $B(OH)_2^+$ ion is maintained upon neutralization which implies that neutral $B(OH)_2^{\cdot}$ is a stable species in the gas phase. This is in line with recent theoretical calculations which predict trans–trans-$B(OH)_2^{\cdot}$ as the global minimum on the respective potential-energy surface [14]. However, the peaks at $m/z = 27$ (BO^+) and $m/z = 16$ (O^+) are significantly more intense in the NR spectrum suggesting some variation of the fragmentation behaviour at the neutral stage. The possible contribution to the recovery signal from ^{10}B isotopic [e.g. $^{10}BH(OH)_2$] and other isobaric impurities can be ruled out based on the absence of any spurious signals in the CA and NR spectra. For example, neither the CA nor the NR spectrum shows a detectable signal at $m/z = 10$, i.e. $^{10}B^+$. These experimental results are further supported by a study of the lower isotope analogue $^{10}B(OH)_2^+$. Both the CA and NR spectra are similar to those of $^{11}B(OH)_2^+$ except for a more intense NR survivor signal, which we attribute to the contribution from $^{11}B(O)OH^+$ to the mass-selected ions at $m/z = 44$. Considering that ^{10}B contributions to $m/z = 45$ are negligible, it can thus safely be concluded that the neutral [B, O_2, H_2]$^{\cdot}$ radical is a stable species in the gas phase.

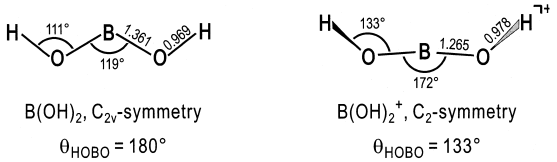

Fig. 2. Calculated G2 geometries of neutral $B(OH)_2$ radical and the $B(OH)_2^+$ cation; bond lengths in angstroms and angles in degree.

In our theoretical study, we took advantage of the recent G2 study by Duan et al. [14] and adopted this level of theory to enable a direct comparison. This also allowed us to restrict our computational search to the trans–trans conformers of $B(OH)_2^{+/0}$. Interestingly, the optimized structures of neutral and cationic forms differ substantially (Fig. 2). Neutral $B(OH)_2^{\cdot}$ radical exhibits a structure of C_{2v} symmetry with $\alpha_{OBO} = 119.4°$ and $r_{BO} = 1.36$ Å. These features are consistent with an sp^2-type hybridization of boron and two B–O single bonds; according to [14], typical B–O single bonds range from 1.34 to 1.37 Å. This description is further in line with the fact that the uncoupled spin in the $^2A_1$ ground state of neutral $B(OH)_2^{\cdot}$ is almost completely located on boron (0.98).

Table 1
Calculated G2 energies E_{tot} (Hartree) and relative energies E_{rel} (kcal/mol) of possible fragmentation channels of the [B, O_2, H_2]$^+$ cation at 0 K

	E_{tot} (G2)	E_{rel}
$B(OH)_2^+$	−176.042 143	0.0[a]
$HOBO^+$ + H	−175.816 154	141.8
BO_2^+ + H_2	−175.747 393[b]	185.0[b,c]
HBO^+ + OH	−175.654 562	243.2
BOH^+ + OH	−175.779 471	164.8
BO^+ + H_2	−175.744 171	187.0[c]

[a] The difference of the total energies yields $IE_a[B(OH)_2] = 6.76$ eV, and combined with $\Delta H_{f,0}[B(OH)_2] = -97.2$ kcal/mol (Table 2), $\Delta H_{f,0}[B(OH)_2^+] = 58.6$ kcal/mol is predicted.

[b] The computed structure of BO_2^+ has a small imaginary frequency (31 cm^{-1}), and can thus not be regarded as a true minimum at this level of theory.

[c] Combined with literature thermochemistry, these channels lead to $D(OB^+\text{–}O) = 116.2$ kcal/mol which agrees reasonably well with an experimental estimate of 119.9 kcal/mol [12].

Table 2
Calculated G2 energies E_{tot} (Hartree) and relative energies E_{rel} (kcal/mol) of possible fragmentation channels of the neutral [B, O_2, H_2] radical at 0 K

	E_{tot} (G2)	E_{rel}
$B(OH)_2$	−176.290 59	0.0[a,b]
HOBO + H	−176.260 51	18.9
BO_2 + H_2	−176.239 36	32.1
HOBO + OH	−176.210 29	50.4
BOH + OH	−176.138 79	95.3
BO + H_2O	−176.221 75	43.2

[a] The G2 atomization method [26] using experimental values for the heats of formation of the atoms predicts $\Delta H_{f,0}[B(OH)_2] = -97.2$ kcal/mol. $\Delta H_{f,298}[B(OH)_2] = -97.6$ kcal/mol is obtained using the calculated thermal corrections.

[b] Isomeric $OB(OH_2)$ is another minimum on the neutral surface with $E_{\mathrm{rel}} = 31.5$ kcal/mol.

Instead, in the $B(OH)_2^+$ cation the OBO unit is almost linear ($\alpha_{\mathrm{OBO}} = 172.3°$), and the contraction of r_{BO} to 1.26 Å indicates double bond character of the B–O units. These effects point toward a significant π-type stabilization in the cationic species, i.e. interaction of the occupied p_π orbitals of oxygen with the empty p_π on boron. Optimized overlap of the π orbitals is associated with a torque of the hydrogen atoms out-of-plane leading to a C_2 symmetrical structure. Note that a previous Møller-Plesset (MP) study at the MP3 level predicted a similar geometry except for a linear OBO unit [2]. All attempts to locate an $OB(OH_2)^+$ structure as a stationary point on the cation surface failed, thus lending confidence to our above mentioned assignment that $B(OH)_2^+$ is generated exclusively. In contrast, the neutral $OB(OH_2)^{\cdot}$ radical was found as a minimum albeit higher in energy than $B(OH)_2^{\cdot}$ ($^2A_1$), by 31.5 kcal/mol at this level of theory. By using atomization energies as references in the G2 scheme [26], the heat of formation of $B(OH)_2^{\cdot}$ ($^2A_1$) is predicted to be −97.2 kcal/mol. Using the calculated adiabatic ionization energy $IE_a[B(OH)_2^{\cdot}] = 6.76$ eV, the heat of formation of the $B(OH)_2^+$ (^1A) cation is estimated as 58.6 kcal/mol (Tables 1 and 2). The magnitude of the calculated ionization energy is surprisingly low for a small boron compound, but the value is consistent with the description of the neutral as a subvalent compound and a significant π stabilization of the cationic species. The latter aspect is further supported by the experimental observation that $B(OH)_2^+$ is the least reactive species among a series of small $B_lO_mH_n^+$ cations [12].

To a first approximation, electron transfers in NR experiments occur vertically [16,18] and thus, the vertical recombination energy (RE_v) of the cation and the vertical ionization energy (IE_v) of the neutral need to be considered as well. At the G2 level of theory, both vertical transitions have substantial energy offsets from the adiabatic data $RE_a = IE_a = 6.76$ eV. Thus, vertical ionization of the neutral ($IE_v = 8.56$ eV) requires almost 2 eV more than the adiabatic process, and likewise vertical neutralization of the cation's ground state ($RE_v = 4.77$ eV) is almost 2 eV lower than IE_a. Thus, vertical electron transfer between $B(OH)_2^{\cdot}$ and $B(OH)_2^+$ is associated with unfavorable Franck-Condon factors in both directions. These in turn restrict the NR efficiency and are likely to lead to a significant deposition of energy in the neutral species formed in the experiment (see the following). These effects are consistent with the notable geometry differences between the neutral and the cationic species described previously and also explain the very small survivor signal in the NR experiment [Fig. 1(b)].

The third aspect of the computational study concerns the most likely fragmentation channels of neutral and cationic $B(OH)_2^{+/0}$. For the cation (Table 1), all dissociation channels are rather high in energy. In agreement with the CA mass spectrum [Fig. 1(a)], the routes leading to $OBOH^+$ and $BOH^+ + OH^{\cdot}$ are computed to have the lowest energy demands. In marked contrast, several low-lying dissociation channels are calculated for the neutral species (Table 2), and qualitatively these predictions agree well with the most abundant $OBOH^+$, BOH^+, and BO^+ fragments observed in the NR spectrum [Fig. 1(b)]. Finally, our G2 calculations complement the extensive work reported in [14] by providing accurate thermochemical information about some cationic species. Combined with literature data [27], these values can be used to extract binding energies, ionization thresholds and proton affinities. The most notable aspect of these computations is the remarkable difference in stability between [B, O, H] ions and neutrals [12]. Thus, neutral HBO [15] is 44.9 kcal/mol more stable than its BOH isomer, whereas cationic $HBO^{+\cdot}$ is 78.4 kcal/mol less stable than $BOH^{+\cdot}$. These changes are consistent with a more significant π stabilization in the neutral HBO and the $BOH^{+\cdot}$ cation as compared to their respective counterparts $HBO^{+\cdot}$ and BOH. Accordingly, G2 theory predicts a difference of as much as about 5.3 eV for the adiabatic $IE_a(HBO) = 15.1$ eV and $IE_a(BOH) = 9.8$ eV of the two [B, O, H] isomers.

4. Discussion

The spectral features of the $[B, O_2, H_2]^+$ ion under study are consistent with formation of the borinium ion $B(OH)_2^+$ upon dissociative ionization of $CH_3B(OH)_2$. The theoretically predicted structure of the cation indicates a substantial π stabilization in the cationic species resulting in an almost linear arrangement of the OBO unit (Fig. 2). In contrast, neutral $B(OH)_2$ can be described in terms of a boron-centred radical where the unpaired electron resides in one of the sp^2 hybrids with typical bond lengths and angles. The relevant geometric parameters are α_{OBO}, α_{BOH}, θ_{HOBO}, and r_{BO} of which the two former decrease and the latter increase substantially in going from $B(OH)_2^+$ to $B(OH)_2$. These geometric differences result in large differences between adiabatic and vertical electron transfer for boron compounds as pointed out previously [12]. To sort out the various contributions to the difference between vertical and adiabatic electron transfer energies, we performed a brief additional computational study by using the more cost-effective B3LYP/6-31G(d) approach. At this level of theory, RE_v and RE_a of the cation are calculated as 3.79 and 6.58 eV, respectively. Stepwise variation of the relevant parameters reveals that α_{OBO} imposes the major effect on the electron transfer energies and is thus the major contributor to the reaction coordinate λ in Fig. 3. Thus, keeping all other parameters fixed, lowering α_{OBO} from 172° as in the cation to $\alpha_{OBO} = 119°$ as calculated for the neutral, leads to an increase of RE by about 1.8 (Fig. 4).

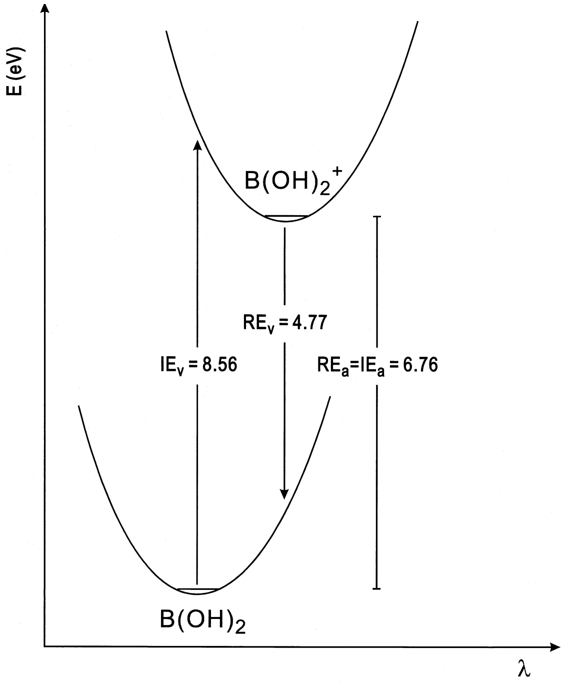

Fig. 3. Schematic G2 potential-energy surfaces for the sequential electron transfer during the NR sequence $B(OH)_2^+ \rightarrow B(OH)_2 \rightarrow B(OH)_2^+$.

With respect to the NR process, these results suggest a schematic potential-energy diagram where both cation and neutral reside in reasonably deep

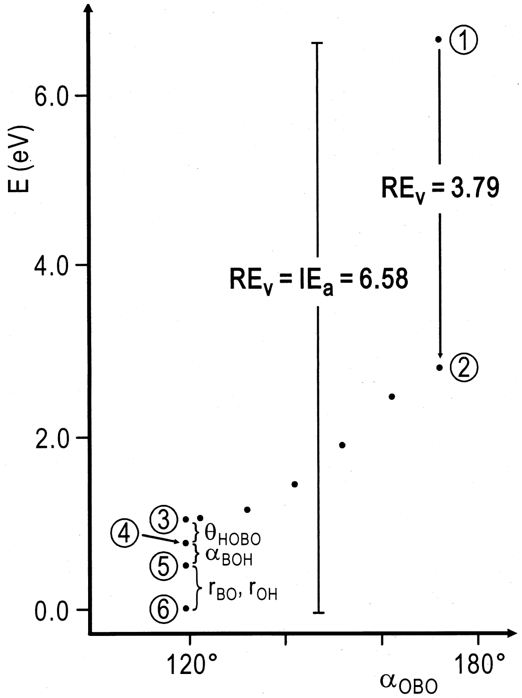

Fig. 4. B3LYP/6-31G(*d*) study (without inclusion of ZPVE) of the neutralization of $B(OH_2)^+$ as a function of geometry. Starting from fully optimized $B(OH)_2^+$ cation ①, RE_v to the corresponding neutral species ① → ② is calculated as 3.79 eV at this level of theory. Keeping all other parameters fixed, progression from $\alpha_{OBO} = 172°$ at ② to $\alpha_{OBO} = 119°$ at ③ lowers the relative energy by 1.78 eV. Subsequent changes of θ_{HOBO} from 133° to 180° ③ → ④, of α_{BOH} from 133° to 111° ④ → ⑤, and of r_{BO} from 1.265 to 1.361 Å ⑤ → ⑥ lower the energy of neutral $B(OH)_2$ further by 0.26, 0.25, and 0.50 eV, respectively, reaching the optimized structure of the neutral (changes in r_{OH} are negligible). At this level of theory, the energy demand of the adiabatic electron transfer ⑥ → ① is computed as 6.58 eV.

wells, but with a significant offset of both curves (Fig. 3). This stems from the notion that addition of an extra electron to the cation structure works precisely opposite the π stabilization in the cation which leads to the geometry differences, i.e. at the cation's geometry the incoming electron is associated with significant antibonding interactions. As a consequence, vertical electron transfer to $B(OH)_2^+$ deposits about 2 eV (46 kcal/mol) excess internal energy in the neutral counterpart. Considering the data given in Table 2, this amount of energy is roughly sufficient to cause fragmentation of the neutral radical via the low-lying routes leading to $OBOH + H^·$, $BO_2 + H_2$, $HBO + OH^·$, and $BO^· + H_2O$, i.e. precisely those fragments that are most abundant in the NR spectrum [Fig. 1(b)]. Moreover, the changes in the fragmentation channels leading to $BO^· + H_2O$ and [B, O, H] + $OH^·$ account for the significant changes in the $BO^+/BOH^{+·}$ ratios in Fig. 1(a) and b.

5. Conclusions

In summary, the $B(OH)_2^+$ cation exhibits a stable neutral counterpart whereas forward and backward electron transfer in terms of an NR experiment is hampered by very unfavorable Franck-Condon factors. Thus, the low recovery-ion yield in the NR experiment is not indicative of a particularly low stability of the neutral species—in fact, the calculated well-depth of 18.9 kcal/mol for loss of a H atom is significant—but results from the combination of unfavorable Franck-Condon factors with the availability of competing dissociation channels. This scenario also accounts for the fact that neutralization agents other than xenon fail to increase the recovery-ion yields because unfavorable Franck-Condon factors are inherent to the system and are not affected by the nature of the collision gas. One prominent example is the acetyl cation, which almost fails to yield a NR recovery ion due to unfavorable Franck-Condon factors whereas the ionization of neutral acetyl radical produced independently is quite facile [28]. In a more general sense, the large reorganization energies upon electron transfer [29] suggest that low-valent boron compounds [12] are attractive candidates for probing systems having inner-sphere electron-transfer transition structures [30].

Acknowledgements

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