

Are HBO⁻ and BOH⁻ electronically stable?

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The binding of an excess electron to HBO and BOH was studied at the coupled cluster level of theory with single, double and non-iterative triple excitations and with extended basis sets to accommodate the loosely bound excess electron. The bent BOH molecule, with a dipole moment of 2.803 D, binds an electron by 39 cm⁻¹, whereas the linear HBO tautomer possesses a similar dipole moment (2.796 D) yet binds the electron by less than 1 cm⁻¹. It is therefore likely that HBO⁻ is not stable when rotational energies are included whereas BOH⁻ is for low rotational quantum numbers.

1. Introduction

1.1. HBO and BOH tautomers and their cations

1.1.1. Neutral species

The HBO and BOH isomers have been the target of intensive theoretical [1–5] and experimental [6–9] studies mostly because (i) solid boron and boron-based materials are among candidates for rocket fuels [10] and (ii) high energy density materials are of great immediate interest. The potential creation of HBO and BOH in reactions arising in the oxidation of such materials makes it important that they be characterized. One of the possible means of extracting energy from high energy substances is the conversion of metastable molecular configurations, which possess significant lifetimes to decay, to lower energy structures. It has been pointed out [4] that HYO compounds (and their YOH tautomers) are of special interest in this matter since usually they differ considerably in energy and possess a significant barrier to HYO \longleftrightarrow YOH interconversion. In particular, those HYO/YOH pairs are interesting whose barriers to rearrangement are substantial yet surmountable (e.g. through a photochemical route). Among the HYO compounds, those with boron as Y attract special attention since they fulfil the conditions formulated above and possess relatively simple and already well understood electronic structures.

Recently, the Schaefer group [2, 3] provided highly correlated *ab initio* results considering the HBO and

BOH molecules. In particular, they discussed the HBO \longleftrightarrow BOH conversion using an energy derivative analysis technique [2]. In a more recent contribution [3], they extended their studies and determined the geometries and physical properties for two equilibrium geometries and two transition state structures on the HBO/BOH potential energy surface examined at the CCSD(T) level with a variety of one-electron bases, among which the triple-zeta quality bases with double polarization function (TZ2P) supplemented with higher angular momentum functions (f and d symmetry) were the largest. They achieved very good agreement between their highest level results (i.e. CCSD(T)/TZ2P(f,d)) and the experimental geometrical parameters and vibrational frequencies. In particular, they found that linear HBO corresponds to the global minimum on the HBO/BOH potential energy surface of the neutral and lies 44.4 kcal mol⁻¹ below the bent BOH tautomer. In addition, the Schaefer group found that the kinetic barrier for the isomerization (tautomerization) HBO \longrightarrow BOH is 71.0 kcal mol⁻¹ while that for the reverse process is 26.6 kcal mol⁻¹ (again at the CCSD(T)/TZ2P(f,d) level). It was also concluded that HBO is more stable than BOH due to the triple bond character of the BO bond [3].

In contrast to well established experimental results available for the HBO tautomer, those for the BOH have not been published thus far, to our knowledge. This is certainly because of the thermodynamic instability of the latter and thus to the difficulties one faces in creating BOH samples. However, the theoretical results indicate [3] that BOH should be detectable if

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formed (e.g. the infrared intensities of the three harmonic vibrational frequencies for BOH are several times higher than those of HBO). Moreover, possible synthesis routes to produce the BOH tautomer were suggested recently by Gole and Michels [4]. It was proposed that at temperatures approaching 1000 °C, BOH and HBO may be produced (via *in situ* synthesis) by passing H₂O (D₂O) over boron in a flow system [4]. In addition, these authors pointed out it should be possible to form BOH through the reaction of an intense boron atom beam with water vapour or dilute hydrogen peroxide [4]. The third route suggested was based on the action of sodium hydroxide on boron at temperatures between 500 °C and 800 °C, although this route was described as most probably demanding a more deleterious environment [4]. Gole and Michels concluded that the BOH isomer should possess a significant lifetime facilitating its storage before isomeric transformation or oxidation. They also stated that BOH, once formed, will be a very floppy molecule whose effective geometry will be near linear at elevated temperatures [4].

1.1.2. HBO⁺ and BOH⁺

Although it is well established that the linear HBO isomer is the global minimum on the neutral HBO/BOH ground state potential energy surface and that the bent BOH isomer lies about 44 kcal mol⁻¹ higher in energy [3], relatively little was known about the corresponding cations (i.e. HBO⁺ and BOH⁺) until 1999 when Boldyrev and Simons reported their *ab initio* investigation results on that species [5]. They employed the QCISD(T) method with 6-311++G(2df,2pd) basis sets and showed that ionization inverts the relative stability of HBO and BOH. Hence, Boldyrev and Simons concluded that for the positively charged system, HBO⁺ is less stable (by 36.9 kcal mol⁻¹) than the BOH⁺ isomer [5]. This unusual finding was then explained in terms of the electronic structures of HBO, BOH, HBO⁺ and BOH⁺. Considering the neutral species, however, these two authors pointed out that, although the BO bond in HBO could indeed be considered as possessing double/triple bond character, the same BO bond in BOH probably exhibits single-bond character, since the extent of BO π bonding in B=O—H is very weak [5].

1.1.3. Anionic species supported by HBO and BOH

To the best of our knowledge there is neither theoretical nor experimental evidence of negatively charged HBO⁻ and BOH⁻ in the literature thus far. This was the first reason we decided to undertake our study whose main goal was to answer the question about the existence of electronically stable HBO⁻ and BOH⁻. The investigation of the existence of these anions was also stimulated by the Litherland experimental physics group

(University of Toronto), who expressed interest in knowing how tightly these anions bind their excess electron (assuming their existence). The Litherland group believe they may have created HBO⁻ or BOH⁻ (their mass spectrometric measurement does not allow determination of which) but suspect these anions could be destroyed in electric fields in their apparatus unless the binding energy exceeds ~ 120 cm⁻¹ [11].

Hence, in this contribution we present our *ab initio* study on the negatively charged species supported by HBO and BOH molecules.

1.2. Dipole-bound anions

The binding of electrons to polar molecules has been addressed in many theoretical studies [12–33]. It has been shown that, within the Born–Oppenheimer (BO) approximation, a dipole moment greater than 1.625 D possesses an infinite number of bound anionic states [14], although a more practical critical value to experimentally observe a dipole-bound anion was found to be ~ 2.5 D [15, 16].

Jordan and Luken demonstrated that the loosely bound electron in a dipole-bound state occupies a diffuse orbital localized mainly on the positive side of the dipole [17]. This finding was confirmed by many subsequent studies. The role of non-BO coupling has been studied by Garrett, who concluded that such couplings are negligible for dipole-bound states with electron binding energies D much larger than the molecular rotational constants [18].

The simplest theoretical approach to estimate D is based on Koopmans' theorem (KT) [34] for which the binding energy D^{KT} is the negative of the energy of the relevant unfilled orbital obtained from a Hartree–Fock self-consistent field (SCF) calculation on the neutral molecule. Orbital relaxation effects, which are neglected in the KT approximation, have been found to be quite small for most dipole-bound anionic states [19]. By contrast, the role of electron correlation has proved to be very significant. In fact, in many cases the electron binding energy of the dipole-bound anion is dominated by the contribution from electron correlation [19, 23, 24].

In the present paper we examine the dipole-bound anions that result from attaching an electron to the HBO and BOH molecules. We employ extended basis sets and a variety of treatments of electron correlation.

2. Methods

We first studied the ground state potential energy surface of the neutral systems at the QCISD (quadratic configuration interaction including single and double substitutions) [35] level of theory. The electron binding energies D were calculated at the QCISD optimized

geometries of the neutral species, since the electron binding in these cases is sufficiently weak that the geometry relaxation upon electron attachment is negligible. In particular, we verified that attaching an extra electron causes only minor geometrical changes in the BOH tautomer (i.e. the bond lengths change by less than 0.001 Å and the <BOH valence angle changes by only 0.5°). (These tests were performed at the MP2 level with the aug-cc-pVTZ+10s9p9d6f basis set to assure excess electron binding. The BOH tautomer was chosen to perform these tests since it binds an extra electron much more strongly than HBO, so the predicted geometrical changes are going to be larger in its case.)

We calculated the values of D by using a supermolecular approach (i.e. by subtracting the energies of the anion from those of the neutral). This approach requires the use of size-extensive methods, for which we have employed Møller–Plesset perturbation theory up to the fourth order and the coupled-cluster method with single, double and non-iterative triple excitations (CCSD(T)) [36, 37]. In addition, for both the HBO⁻ and BOH⁻ minimum energy structures, D was analysed within the perturbation framework designed by Gutowski and Skurski for dipole-bound anions and solvated electrons [22].

The polarization of the neutral N by the excess electron and the effect of back-polarization are taken into account when the SCF calculation is performed for the anion A , and the accompanying induction contribution to D is given by

$$\Delta D_{\text{ind}}^{\text{SCF}} = D^{\text{SCF}} - D^{\text{KT}}, \quad (1)$$

where

$$D^{\text{SCF}} = E_{\text{N}}^{\text{SCF}} - E_{\text{A}}^{\text{SCF}}, \quad (2)$$

and $E_{\text{N}}^{\text{SCF}}$ and $E_{\text{A}}^{\text{SCF}}$ stand for the SCF energies of the neutral and the anion, respectively.

The dispersion interaction between the loosely bound electron and N was extracted from the MP2 contribution to D . The dispersion term is a second-order correction with respect to the fluctuation-interaction operator and it is approximated here by $\Delta D_{\text{disp}}^{\text{MP2}}$, which takes into account proper permutational symmetry for all electrons in the anion

$$\epsilon_{\text{disp}}^{(02)} \approx \sum_{\text{a} \in \text{N}} \sum_{r < s} \frac{|\langle \phi_{\text{a}} \phi_{\text{lbe}} | \phi_r \phi_s \rangle|^2}{e_{\text{a}} + e_{\text{lbe}} - e_r - e_s} = -\Delta D_{\text{disp}}^{\text{MP2}}, \quad (3)$$

where ϕ_{a} and ϕ_{lbe} are spinorbitals occupied in the anion UHF wavefunction, ϕ_r and ϕ_s are unoccupied orbitals, and the e 's are the corresponding orbital energies. The subscript lbe denotes the loosely bound electron's spin orbital.

The total MP2 contribution to D defined as

$$\Delta D^{\text{MP2}} = D^{\text{MP2}} - D^{\text{SCF}} \quad (4)$$

is naturally split into dispersion and non-dispersion terms,

$$\Delta D^{\text{MP2}} = \Delta D_{\text{disp}}^{\text{MP2}} + \Delta D_{\text{no-disp}}^{\text{MP2}}, \quad (5)$$

with the latter dominated by the correlation correction to the static Coulomb interaction between the loosely bound electron and the charge distribution of N .

The higher order MP contributions to D are defined as

$$\Delta D^{\text{MP}n} = D^{\text{MP}n} - D^{\text{MP}(n-1)} \quad n = 3, 4. \quad (6)$$

The contributions beyond the fourth order are estimated by subtracting MP4 results from those obtained at the coupled-cluster SD level,

$$\Delta D^{\text{CCSD}} = D^{\text{CCSD}} - D^{\text{MP4}}, \quad (7)$$

while the contribution from non-iterative triple excitations are obtained as

$$\Delta D^{\text{CCSD(T)}} = D^{\text{CCSD(T)}} - D^{\text{CCSD}}. \quad (8)$$

The diffuse character of the orbital describing the loosely bound electron (figure 1) necessitates the use of extra diffuse basis functions having very low exponents [19]. In addition, the basis sets chosen to describe the

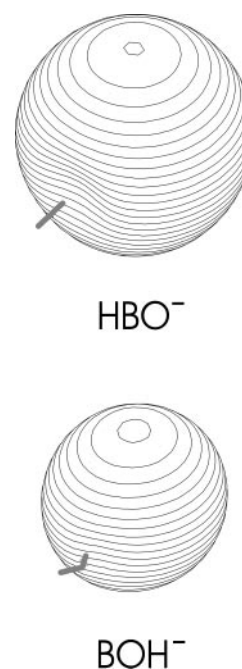


Figure 1. Singly occupied molecular orbital (SOMO) holding the excess electron in the ground electronic state of HBO⁻ (top) and BOH⁻ (bottom), plotted with 0.001 57 $a_0^{-3/2}$ contour spacing.

neutral molecular host should be flexible enough to (i) describe accurately the static charge distribution of the neutral and (ii) allow for polarization and dispersion stabilization of the anion upon electron attachment. The geometry optimizations and frequency calculations were carried out with the aug-cc-pVTZ basis sets [38] for the neutral species only (as explained earlier) while the electron binding energies were evaluated with the aug-cc-pVTZ basis set supplemented with a 10s9p9d6f set of diffuse functions centred on the hydrogen atom (since this is at or near the centroid of the positive end of the dipole). The aug-cc-pVTZ basis set was chosen since we earlier showed its usefulness in describing dipole-bound anions compared with other commonly used one-electron basis sets [39]. The extra diffuse functions do not share exponent values and we used even-tempered [40] ten-term s, nine-term p, nine-term d and six-term f basis sets. The geometric progression ratio was equal to 3.2 [41], and for each symmetry we started to build up the exponents of the extra diffuse functions from the lowest exponent of the same symmetry included in the aug-cc-pVTZ basis set designed for hydrogen. As a consequence, we achieved lowest exponents of $2.243\,538\,67 \times 10^{-7}$, $2.899\,014\,34 \times 10^{-6}$, $7.020\,162\,21 \times 10^{-6}$ and $2.300\,366\,7 \times 10^{-4}$ au, for the s, p, d and f symmetries, respectively. We examined the lowest eigenvalue of the atomic orbital overlap matrix to determine that near linear dependence was not a problem (the smallest eigenvalue of the overlap matrix was 4.369×10^{-5}).

All calculations were performed with the Gaussian98 program [42] on AMD Athlon 2000 + 1.6 GHz and Pentium IV 1.7 GHz computers, and on SGI Origin2000 and Compaq Sierra systems. The 3-dimensional plots of molecular orbitals were generated with the Molden program [43].

3. Results

3.1. Properties of HBO and BOH

We optimized the geometries and calculated harmonic vibrational frequencies of HBO and BOH at the QCISD level, and the resulting bond lengths and angles are collected in table 1. We then calculated the relative energies of both tautomers at the CCSD(T) level and corrected them with corresponding zero-point vibrational energies using QCISD vibrational frequencies. As described in [1–3], we found that HBO lies lower than BOH by $43.2 \text{ kcal mol}^{-1}$. We also verified that the HBO equilibrium geometry is linear while that of BOH is bent (figure 1, table 1). The BO bond order in HBO is between 2 and 3 while the order of the BO bond in BOH is closer to 1. This is consistent with the observation that the BO bond length in HBO is shorter (by 0.104 \AA) than in BOH (table 1).

Table 1. QCISD geometries and corresponding QCISD harmonic vibrational frequencies of the two minimum-energy tautomers HBO and BOH calculated with the aug-cc-pVTZ basis set (bond lengths r in \AA , valence angles α in deg, frequencies and rotational constants in cm^{-1}). The corresponding QCISD zero-point vibrational energies are given in kcal mol^{-1} .

Species and symmetry	Geometrical parameters	Vibrational frequencies	Rotational constants
HBO $C_{\infty v}$	$r(\text{BO}) = 1.207$	$\nu_{1,2}(\pi) = 768^a$	$B_1 = 27.6$
	$r(\text{HB}) = 1.170$	$\nu_3(\sigma) = 1834$	$B_2 = 1.4$
	$\alpha(\text{HBO}) = 180.00$	$\nu_4(\sigma) = 2889$	$B_3 = 1.3$
		$E_{0,\text{vib}} = 8.948$	
BOH C_s	$r(\text{BO}) = 1.311$	$\nu_1(\text{a}') = 641$	$B_{1,2} = 1.3$
	$r(\text{OH}) = 0.962$	$\nu_2(\text{a}') = 1392$	$B_3 = 0.0$
	$\alpha(\text{BOH}) = 120.82$	$\nu_3(\text{a}') = 3870$	
		$E_{0,\text{vib}} = 8.439$	

^aThese two frequencies are not degenerate due to the Renner–Teller effect but they differ by less than 0.5 cm^{-1} .

Table 2. Dipole moments (in D) of HBO (linear) and BOH (bent) calculated from the SCF, MP2, MP3, MP4(SDQ) and QCISD densities with the aug-cc-pVTZ basis set.

	SCF	MP2	MP3	MP4(SDQ)	QCISD
HBO ($C_{\infty v}$)	3.377	2.674	2.932	2.786	2.803
BOH (C_s)	2.895	2.935	2.823	2.836	2.796

The dipole moments μ for these two isomers (i.e. linear HBO and bent BOH) are very important since they indicate whether a stable dipole-bound anionic state can be formed at these geometries. We found SCF dipole moments of 3.38 D and 2.90 D, for HBO and BOH, respectively (table 2). Thus, one would expect a weakly bound anion formed by the latter and a more strongly bound anion supported by the former. However, as indicated by our calculations, the charge distribution reproduced by the SCF method is not highly accurate, especially for the HBO tautomer. In table 2 we also present the dipole moments of the neutral HBO (linear) and BOH (bent) calculated from the MP2, MP3, MP4(SDQ) and QCISD densities. We believe the values of μ for HBO and BOH obtained from the MP4 or QCISD densities are our best estimates, and they happen to be very close to each other (i.e. 2.803 D and 2.796 D for HBO and BOH, respectively). This might suggest that the excess electron binding that arises from the dipole potential should be similar for these two tautomers. However, as we show in this contribution, this is not the case.

3.2. HBO⁻ and BOH⁻

Neither HBO nor BOH forms a valence-bound anion. However, as pointed out above, the dipole moments calculated for these two conformers are larger than 2.5 D (table 2), which suggests the possibility of binding an extra electron by the dipole potential to form stable dipole-bound anionic states. In this section we present detailed results for the linear C_{∞v} symmetry structure of HBO and bent C_s symmetry structure of BOH that correspond to minima on the ground state potential energy surface. The relevant rotational energy level spacings for BOH⁻ (table 1) are much smaller than the calculated values of D . Hence, coupling between the electronic and rotational degrees of freedom is expected to be of secondary importance for this anion for low rotational levels, and is not considered in this study. However, since the electron binding energy calculated for HBO⁻ is very small (our best estimate is 0–1 cm⁻¹), and thus not in excess of the rotational level spacings for this species (table 1), we conclude that the HBO⁻ anion, even if formed, would eject the extra electron while rotating.

The electron binding energy was partitioned into incremental contributions calculated at ‘successive’ levels of theory (KT, SCF, MP n ($n = 2, 3, 4$), CCSD and CCSD(T)), and the results for the optimal (C_{∞v} for HBO and C_s for BOH) structures are presented in table 3. In the KT approximation, the electron binding energy results from the electrostatic and exchange interactions of the loosely bound electron with the SCF charge distribution of the neutral molecule (primarily characterized by the dipole moment, but interactions with higher permanent multipoles and penetration effects are also included). For both systems, the D^{KT}

Table 3. Electron binding energies (in cm⁻¹) of HBO⁻ and BOH⁻ dipole-bound anions calculated with aug-cc-pVTZ + 10s9p9d6f basis set

	HBO	BOH
D^{KT}	9	4
$\Delta D_{\text{ind}}^{\text{SCF}}$	0	0
$\Delta D_{\text{disp}}^{\text{MP2}}$	5	8
$\Delta D_{\text{no-disp}}^{\text{MP2}}$	-17	0
ΔD^{MP3}	6	-2
ΔD^{MP4}	-7	4
ΔD^{CCSD}	5	14
$\Delta D^{\text{CCSD(T)}}$	-2	11
ΔD^{total}	-1 (0) ^a	39

^aThe negative value of the electron binding energy is an artefact caused by the use of the limited (i.e. not complete) basis sets and has no physical meaning, but it indicates that the electron affinity of the neutral molecular parent is equal to zero.

values are very small: 9 cm⁻¹ for HBO and only 4 cm⁻¹ for BOH.

The SCF binding energies include orbital relaxation, and thus take into account static polarization of the neutral molecule by the extra electron and the secondary effect of back-polarization. In both cases, these contributions (which may be interpreted as orbital relaxation corrections to D^{KT} , denoted $\Delta D_{\text{ind}}^{\text{SCF}}$) are extremely small (not exceeding 0.2 cm⁻¹) and thus negligible. Although usually significant for valence-bound anions, orbital relaxation effects are usually negligible and rarely responsible for more than a few per cent of the total value of D for the majority of dipole-bound anions studied so far [19, 24].

The contribution denoted $\Delta D_{\text{disp}}^{\text{MP2}}$ results from dynamic correlation between the loosely bound electron and the electrons of the neutral molecule. This stabilization is caused by quantum mechanical charge fluctuations, and is twice as large as D^{KT} for BOH anion and comparable with D^{KT} for HBO⁻ (table 3). The finding that the dispersion contribution is substantial is consistent with our earlier results for other dipole-bound anions. The value of $\Delta D_{\text{disp}}^{\text{MP2}}$ increases from 5 cm⁻¹ at the optimal geometry of HBO to 8 cm⁻¹ at the optimal geometry of BOH.

In addition to the dispersion interaction, other electron correlation factors may also affect the charge distribution (and dipole moment) of the neutral molecule, and thus its electrostatic interaction with the extra electron. This effect first appears at the MP2 level and is denoted by $\Delta D_{\text{no-disp}}^{\text{MP2}}$. In the case of HBO, the MP2 electron correlation effects reduce the dipole moment of the neutral system by 0.7 D in comparison with the SCF value (table 2). This is a very large decrease and it causes the value of $\Delta D_{\text{no-disp}}^{\text{MP2}}$ to be destabilizing and the total MP2 contribution to D also to be destabilizing (-17 cm⁻¹). We observe a different situation in the case of the BOH tautomer, where $\Delta D_{\text{no-disp}}^{\text{MP2}}$ is destabilizing but negligible (-0.1 cm⁻¹). This causes the total MP2 contribution to D to be stabilizing due to the dominant role of the dispersion component, and equal to 8 cm⁻¹, which represents 21–29% of the total D (table 3).

The convergence of the MP series for the electron binding energy is satisfactory for neither HBO nor BOH (table 3). Therefore, we prefer to rely on the method that includes higher than fourth-order correlation effects, approximated here by ΔD^{CCSD} (the difference between CCSD and MP4 binding energies). The ΔD^{CCSD} terms are significant and stabilizing for both the systems studied. The subsequent inclusion of the non-iterative triple excitations at the coupled-cluster level (labelled $\Delta D^{\text{CCSD(T)}}$) produce our final predictions for the vertical electron attachment energies of 39 cm⁻¹ and -1 cm⁻¹ for BOH and HBO, respectively. Cer-

tainly, the negative value of the electron attachment energy has no quantitative meaning, and indicates only that this anion is electronically unstable, since its electron binding energy would be essentially zero if the complete basis set were used for calculations.

Since the accuracy of the non-iteratively calculated triple excitation at the CC level was brought into question by Peterson and Gutowski [44], we suggest interpreting our results on the basis of both CCSD and CCSD(T) binding energies; thus we consider our calculated vertical electron attachment energies as being 28–39 cm⁻¹ for the bent BOH and 0–1 cm⁻¹ for the linear HBO.

We note that electron correlation effects represent 86–90% of the electron binding energy for the BOH⁻ anion. This finding is consistent with recent results for other dipole-bound species, where the correlation contributions were always crucial and very often responsible for more than 50% of the total value of D . This contribution is comparable with that found for the isoelectronic HNC⁻ (for which the correlation effects represent ~90% of the electron binding energy) [44]. Although the correlation effects represent more than 80% of the electron binding energy for BOH⁻, it should be noted that this anionic bound state exists primarily due to the long range $\mu \cos \theta / r^2$ potential, which causes localization of the excess electron on the positive side of the molecular dipole (figure 1), as discussed in [12].

Since the higher than fourth-order contributions to D are very large in the case of BOH⁻ we decided to discuss them in further detail for this anion (we also present the analogous results for the HBO⁻ tautomer for comparison, table 4). The MP4 contribution from double and quadruple excitation $\Delta D^{\text{MP4(DQ)}}$ is smaller than 1 cm⁻¹ and thus negligible. The contributions from single excitations, given by the difference between $\Delta D^{\text{MP4(SDQ)}}$ and $\Delta D^{\text{MP4(DQ)}}$, is stabilizing and equal to 2 cm⁻¹. The

contribution from triple excitations, given by the difference between $\Delta D^{\text{MP4(SDTQ)}}$ and $\Delta D^{\text{MP4(SDQ)}}$, is also stabilizing and of similar importance (2 cm⁻¹). The final fourth-order contribution $\Delta D^{\text{MP4(SDTQ)}}$ amounts to 4 cm⁻¹.

The effect of single excitations is eight times more important when evaluated in the framework of coupled-cluster theory where its contribution, calculated as the difference between D^{CCSD} and D^{CCD} , amounts to 17 cm⁻¹. The contribution from non-iterative triple excitations, calculated as the difference between $D^{\text{CCSD(T)}}$ and D^{CCSD} , contains the fourth-order contribution with the CCSD amplitudes and a fifth-order term, which are labelled T4(CCSD) and T5(CCSD), respectively. The T4(CCSD) term is significant, stabilizing and amounts to 18 cm⁻¹, while the T5(CCSD) contribution is destabilizing and amounts to -7 cm⁻¹. Hence, the contribution from non-iterative triple excitations is stabilizing amounts to 11 cm⁻¹ and is dominated by the fourth-order contribution (with the CCSD amplitudes). However, as explained above, we are not confident that the inclusion of the non-iterative triples at the coupled-cluster level is highly accurate, so, in this case, we prefer to rely on the CCSD results.

Higher than fourth-order electron contributions to D may also be obtained by calculating the differences between the D^{CCD} and $D^{\text{MP4(DQ)}}$, and between the D^{CCSD} and $D^{\text{MP4(SDQ)}}$ electron binding energies. The difference between D^{CCD} and $D^{\text{MP4(DQ)}}$ is very small and amounts to -1 cm⁻¹. However, when single excitations are included, the situation is quite different. Indeed, the difference between D^{CCSD} and $D^{\text{MP4(SDQ)}}$ amounts to 16 cm⁻¹. The role of single excitations is extremely important, and may be related to the fact that the charge distribution of the extra electron is seriously altered when the neutral molecular core is modified by electron correlation effects.

4. Conclusion

On the basis of CCSD(T) calculations with the aug-cc-pVTZ + 10s9p9d6f basis sets we have drawn three conclusions. (i) The gas phase equilibrium bent BOH forms an electronically stable dipole-bound anion whose binding energy is 39 cm⁻¹. We expect this anion to exist for low rotational quantum numbers as explained in § 3.2. (ii) The linear HBO binds an extra electron by less than 1 cm⁻¹, and therefore we predict it to be extremely short-lived since we expect the extra electron to autodetach while the anion rotates. (iii) Unlike HBO⁺/BOH⁺, the gain of an electron by HBO/BOH has little effect on the relative stability of these species due to the very small excess electron binding energies.

Table 4. Contributions of various classes of excitation to D (in cm⁻¹) at the QCISD equilibrium geometries of HBO and BOH from table 1. Results obtained with the aug-cc-pVTZ + 10s9p9d6f basis set

Method	HBO ⁻		BOH ⁻	
	D	ΔD	D	ΔD
UMP4(DQ)	2	-1	10	0
UMP4(SDQ)	0	-3	12	2
UMP4(SDTQ)	-4	-7	14	4
CCD	2	0	9	-1
CCSD	1	1	28	16
CCSD(T)	-1	3	39	25
T4(CCSD)	...	-2	...	18
T5(CCSD)	...	0	...	-7

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