

# A highly accurate first principles determination of the electron affinity of $\text{BO}(\text{X}^2\Sigma^+)$ and binding energy of $\text{BO}^-(\text{X}^1\Sigma^+)$

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## Abstract

Highly accurate values of the adiabatic electron affinity (EA) of the ground state ( $\text{X}^2\Sigma^+$ ) of the BO molecule, and the dissociation energy ( $D_0$ ) of the anion  $\text{BO}^-(\text{X}^1\Sigma^+)$ , have been determined using the CCSD(T) approach in conjunction with a series of doubly augmented correlation consistent basis sets, d-aug-cc-pVnZ,  $n = 3-6$ . In addition, the full potential energy curve of  $\text{BO}^-(\text{X}^1\Sigma^+)$  has been constructed at the multireference configuration interaction,  $n = 5$  level. Our final values are,  $\text{EA}(\text{BO}) = 2.50$  eV and  $D_0(\text{BO}^-) = 215.7$  kcal/mol, in excellent agreement with experimental results. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Electron affinities (EA) belong to a class of atomic or molecular properties that are not so easily computed, the reason being the totally different electronic structures of the two species involved in the calculation, for instance, X and  $\text{X}^-$ . As a reminder we can define adiabatic electron affinities, adiabatic electron affinities corrected with respect to the zero point energy (ZPE), and vertical electron affinities,  $\text{EA}(\text{ad})$ ,  $\text{EA}(\text{ZPE})$ , and  $\text{EA}(\text{vrt})$ , respectively, according to the following relations:

$$\begin{aligned}\text{EA}(\text{ad}) &= E(\text{optimized X}) \\ &\quad - E(\text{optimized X}^-) \\ \text{EA}(\text{ZPE}) &= E(\text{ZPE-corrected X}) \\ &\quad - E(\text{ZPE-corrected X}^-)\end{aligned}$$

$$\begin{aligned}\text{EA}(\text{vrt}) &= E(\text{optimized X}) \\ &\quad - E(\text{X}^- \text{ at X optimum geometry}).\end{aligned}$$

Obviously for bound species  $\text{X}^-$ , electron affinities are positive quantities with  $\text{EA}(\text{ad}) \geq \text{EA}(\text{vrt})$ .

The purpose of the present study is the accurate determination of the ground  $\text{X}^2\Sigma^+$  state EA of BO, and the bond dissociation energy and structural characteristics of the corresponding anion,  $\text{BO}^-$ .

To the best of our knowledge, three experimental values of the BO EA exist in the literature. The oldest by Jensen [1] assigned a lower limit EA value of 2.48 eV. In 1971 Srivastava et al. [2] reported an EA value of  $3.12 \pm 0.1$  eV. Finally, the most recent EA value of BO, determined via the 351 nm photoelectron spectrum of  $\text{BO}^-$ , is  $2.508 \pm 0.008$  eV [3].

Theoretically, a variety of electron affinity values for BO have been reported, as discussed in the work by Rienstra and Schaefer [4], with the best values in the range 2.17–2.79 eV. Rienstra and Schaefer, employing the CCSD(T) approach cou-

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pled with an augmented correlation consistent basis of quadruple-zeta quality (aug-cc-pVQZ), obtained the adiabatic EA of BO as  $2.57 \pm 0.05$  eV. Calculated EA values of BO are also reported by Wenthold et al. [3] using a variety of methods: while some of their results are in good agreement with their experimental findings, the small basis set used (6-311+G(d)) casts some doubt regarding the validity of their theoretical values. Finally, from the very recent work by Jursic [5] on the EA of BO, no useful conclusions can be drawn.

Determined to obtain a definitive value of the EA of BO, as well as accurate structural parameters of the ground  $X^1\Sigma^+BO^-$  state, we have performed high level ab initio CCSD(T) and MRCI calculations in conjunction with very large basis sets. Some of our results on the  $BO^-$  anion are reported for the first time in the literature.

## 2. Methods

The sequence of doubly augmented basis sets [6–8], d-aug-cc-pVnZ,  $n = 3–6$  has been employed in all our calculations. Although the double augmentation (two sets of diffuse functions for every angular momentum of the plain sets) could be considered as redundant at least for the neutral BO system, we do not feel so for the anion. Therefore, for reasons of uniformity the d-aug sets were used for both species: BO and  $BO^-$ . Our largest ( $n = 6$ ) basis set (18s12p7d6f5g4h2i)<sub>B,O</sub> generally contracted to [9s8p7d6f5g4h2i]<sub>B,O</sub>, contains 450 spherical Gaussian functions.

Electron affinities of  $BO(X^2\Sigma^+)$  and bond distances ( $r_e$ ), dissociation energies ( $D_0 = D_e - \omega_e/2$ ), and harmonic frequencies ( $\omega_e$ ) of BO and  $BO^-$  were obtained by the coupled-cluster RCCSD(T) method (single + double excitations with a perturbative estimate of the connected triple excitations from a restricted Hartree–Fock reference wave function [9,10]). It is reminded that the CCSD(T) approach is size-extensive but non-variational. Only the valence electrons were allowed to correlate, the  $1s^2$  B and O (or  $O^-$ ) electrons were always constrained to be doubly occupied.

In order to obtain the full potential energy curve of the  $BO^-(X^1\Sigma^+)$ , the complete active

space (CASSCF) + single + double excitations (CASSCF + 1 + 2 = MRCI) method in conjunction with the d-aug-cc-pV5Z basis set were employed. The selected reference orbital space consists of eight orbital functions, correlating asymptotically to the ‘valence’ occupied species of  $B(^2P; 2s + 2p_{x,y,z})$  and  $O(^2P; 2s + 2p_{x,y,z})$ . The reference space (CAS), created by distributing the 10 valence (active) electrons of  $BO^-$  to the eight orbitals, is composed of 328 configuration functions (CF). This gives rise to  $\sim 50 \times 10^6$  CFs at the MRCI level, reduced to about  $10^6$  CFs using the internally contracted technique [11–13]. At this level of theory size non-extensivity errors amount to 10 mE<sub>h</sub>. To ameliorate the non-extensivity problem, MRCI+Q (MRCI+Davidson correction [14,15]) and MR-ACPF (multi reference averaged coupled pair functional [16]) potential energy curves were constructed with size-extensivity errors of 3 and 0.4 mE<sub>h</sub>, respectively.

All calculations were performed with the MOLPRO 2000.1 suite of codes [17].

## 3. Results and discussion

The bonding in the  $X^2\Sigma^+ \sim 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 1\pi_y^2$  state of BO consists of a genuine triple bond, two  $\pi$  and one  $\sigma$ , with the symmetry carrying electron localized on the B atom, and the in situ B atom in its first excited  $^4P$  state [18]. Obviously, the addition of an electron to the BO molecule leads to the closed-shell  $X^1\Sigma^+$  triple bonded  $BO^-$  anion, isoelectronic andisodesmic to the CO and N<sub>2</sub> molecules.

Table 1 lists total energies, equilibrium bond distances  $r_e$ , ZPE-corrected binding energies  $D_0$ , and harmonic frequencies  $\omega_e$  for both BO and  $BO^-$  systems, as well as EA(ad) values of BO at the RCCSD(T)/d-aug-cc-pVnZ,  $n = 3, 4, 5$ , and 6 levels. Note the monotonic convergence of all numbers as a function of the basis set cardinal number  $n$ , and the excellent agreement of all listed quantities with experiment at the  $n = 5$  and 6 levels. The  $\Delta r_e = 0.003$  Å difference between theory and experiment of BO is due mainly to the core-correlation effects; it is well known by now that inclusion of core-correlation decreases bond

Table 1

Total energies  $E$  ( $E_h$ ), bond distances  $r_e$  (Å), dissociation energies  $D_0$  (kcal/mol), and harmonic frequencies  $\omega_e$  ( $\text{cm}^{-1}$ ) of  $\text{BO}(\text{X}^2\Sigma^+)$  and  $\text{BO}^-(\text{X}^1\Sigma^+)$ , and electron affinities EA (eV) of BO at the CCSD(T)/d-aug-cc-pVnZ,  $n = 3(\text{T}), 4(\text{Q}), 5, 6$  and CBS<sup>a</sup> levels of theory

Property	Basis set ( $n$ ) <sup>b</sup>	<sup>11</sup> B <sup>16</sup> O	<sup>11</sup> B <sup>16</sup> O <sup>-</sup>
$E$	3	-99.87653	-99.96813
	4	-99.90170	-99.99364
	5	-99.90951	-100.00161
	6	-99.91213	-100.00432
	CBS	-99.9132 ± 0.0001	-100.0055 ± 0.0001
	$r_e$	3	1.2157
4		1.2096	1.2418
5		1.2083	1.2406
6		1.2079	1.2401
CBS		1.2079	1.2401 ± 0.0002
Experiment		1.2049 <sup>c</sup>	1.236 ± 0.01 <sup>d</sup>
$D_0^e$	3	185.1	211.7
	4	189.2	214.6
	5	190.3	215.4
	6	190.7	215.7
	CBS	190.8 ± 0.1	215.8 ± 0.05
	Experiment	192.3 ± 3.5 <sup>c</sup> 190.9 <sup>f</sup>	216.5 ± 3.5 <sup>c</sup>
$\omega_e$	3	1886.1	1710.2
	4	1866.6	1688.0
	5	1862.8	1684.8
	6	1862.2	1683.8
	CBS	1862.0 ± 0.001	1683.9 ± 0.03
	Experiment	1875 ± 30 <sup>d</sup> 1885.7 <sup>f</sup>	1665 ± 30 <sup>d</sup>
EA(ad) <sup>g</sup>	3	2.48	–
	4	2.49	–
	5	2.50	–
	6	2.50	–
	Experiment	2.508 ± 0.008 <sup>d</sup>	–

<sup>a</sup> Complete basis set limit, see text.

<sup>b</sup>  $n$ , basis set cardinality number.

<sup>c</sup> Taken from [24].

<sup>d</sup> Taken from [3].

<sup>e</sup>  $D_0 = D_e - \omega_e/2$  with respect to  $\text{B}({}^2\text{P}) + \text{O}^-({}^2\text{P})$ .

<sup>f</sup> Taken from [25].

<sup>g</sup> Zero point energy corrected adiabatic electron affinities.

distances by a few thousandths of an Ångström depending on the system [19–22]. Complete basis set (CBS) extrapolated values of  $r_e$ ,  $D_0$  and  $\omega_e$  using a simple exponential formula  $P_n = P_\infty + Ae^{-Bn}$ , where  $n$  is the basis set cardinality and A and B fitting constants [23], prove the complete convergence of our numbers (Table 1). Note in particular the complete agreement between the theory and experiment [3] of the EA(ad), ZPE

corrected with respect to the  $\omega_e$ 's as listed in Table 1. Thus, we can claim with certainty that the EA of  $\text{BO}(\text{X}^2\Sigma^+)$  is 2.50 eV, putting an end to all previous controversies (vide supra).

Fig. 1 shows the PECs of the  $\text{X}^1\Sigma^+\text{BO}^-$  state at the MRCI, MRCI+Q and MR-ACPF/d-aug-cc-pV5Z levels of theory while Table 2 presents corresponding spectroscopic constants. The latter were extracted from the  $G(v) + F_v(J)$  energy levels

Table 2

Total energies  $E$  ( $E_h$ ), bond distances  $r_e$  (Å), dissociation energies  $D_0$  (kcal/mol), and harmonic frequencies  $\omega_e$  ( $\text{cm}^{-1}$ ), first and second anharmonicity corrections  $\omega_e x_e$ ,  $\omega_e y_e$  ( $\text{cm}^{-1}$ ), rotational–vibrational coupling constants  $\alpha_e$  ( $\text{cm}^{-1}$ ), and centrifugal distortion constants  $\bar{D}_e$  ( $\text{cm}^{-1}$ ) of the  $\text{BO}^-(X^1\Sigma^+)$  molecule at the MRCI, MRCI+Q and MR-ACPF/d-aug-cc-pV5Z levels of theory

	MRCI	MRCI+Q <sup>a</sup>	MR-ACPF <sup>b</sup>
$E$	-99.97888	-99.9959	-99.9939
$r_e$	1.2415	1.243	1.243
$D_0$	219.7	215.7	215.2
$\omega_e$	1710.6	1699	1699
$\omega_e x_e$	13.94	13.90	14.00
$\omega_e y_e$	0.979	0.970	1.00
$\alpha_e$	$1.70 \times 10^{-2}$	$1.73 \times 10^{-2}$	$1.73 \times 10^{-2}$
$\bar{D}_e$	$6.56 \times 10^{-6}$	$6.43 \times 10^{-6}$	$6.44 \times 10^{-6}$

<sup>a</sup> MRCI + multireference Davidson correction for unlinked quadruples.

<sup>b</sup> Multireference averaged coupled pair functional.

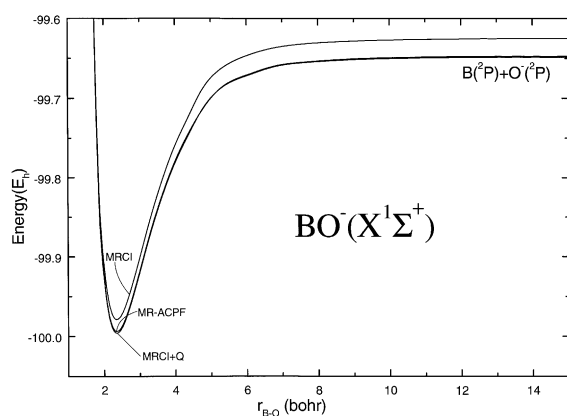


Fig. 1. Potential energy curves of the  $\text{BO}^-(X^1\Sigma^+)$  state at the MRCI, MRCI+Q and MR-ACPF levels of theory.

of the  $\text{BO}^-(X^1\Sigma^+)$  potential well, after solving numerically the one-dimensional rovibrational Schrödinger equation. We observe excellent agreement among the MRCI+Q, MR-ACPF and CCSD(T)/d-aug-cc-pV5Z results of Table 1, and of course with the corresponding experimental values. However, the MRCI  $D_0$  value is higher by  $\sim 4$  kcal/mol than the MRCI+Q, MR-ACPF and CCSD(T) values, and possibly the experimental  $D_0$  value. This discrepancy can be traced to the rather large size non-extensivity error ( $\sim 10 \text{ mE}_h$ ) of the MRCI method for the 10 (active) electron  $\text{BO}^-$  system. Finally, it should be mentioned that EAs of  $\text{BO}(X^2\Sigma^+)$  calculated by the MRCI, MRCI+Q or MR-ACPF/d-aug-cc-pV5Z techniques fail. For instance, at the MRCI level we calculate  $\text{EA}(\text{BO}) = 2.18 \text{ eV}$ . This large error is due to the

inability of the MRCI method to describe adequately the process  $\text{O}(^3\text{P}) + e^- \rightarrow \text{O}^-(^2\text{P})$ :  $\text{EA}(\text{O})/\text{MRCI}(\text{d-aug-cc-pV5Z}) = 1.096 \text{ eV}$ , while  $\text{EA}(\text{O})/\text{RCCSD}(\text{T})(\text{d-aug-cc-pV5Z}) = 1.430 \text{ eV}$  ( $1.440 \text{ eV}$  at the d-aug-cc-pV6Z level) as contrasted to the experimental value of  $1.461 \text{ eV}$  [26].

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## References

- [1] D.E. Jensen, J. Chem. Phys. 52 (1970) 3305.
- [2] R.D. Srivastava, O.M. Uy, M. Farber, Trans. Faraday Soc. 67 (1971) 2941.
- [3] P.G. Wenthold, J.B. Kim, K.-L. Jones, W.C. Lineberger, J. Phys. Chem. A 101 (1997) 4472.
- [4] J.C. Rienstra, H.F. Schaefer III, J. Chem. Phys. 106 (1997) 4472.
- [5] B.S. Jursic, J. Mol. Struct. (Theochem) 467 (1999) 1.
- [6] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
- [7] A.K. Wilson, T.V. Mourik, T.H. Dunning Jr., J. Mol. Struct. (Theochem) 388 (1997) 339.
- [8] D.E. Woon, T.H. Dunning Jr., J. Chem. Phys. 100 (1994) 2975.
- [9] K. Ragavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.
- [10] R.J. Bartlett, J.D. Watts, S.A. Kucharski, J. Noga, Chem. Phys. Lett. 165 & 167 (1990) 513, 609E.
- [11] H.-J. Werner, P.J. Knowles, J. Chem. Phys. 89 (1988) 5203.
- [12] P.J. Knowles, H.-J. Werner, E.-A. Reinsch, J. Chem. Phys. 76 (1982) 3144.

- [13] H.-J. Werner, *Adv. Chem. Phys.* LXIX (1987) 1.
- [14] S.R. Langhoff, E.R. Davidson, *Int. J. Quantum Chem.* 8 (1974) 61.
- [15] M.R.A. Blomberg, P.E.M. Siegbahn, *J. Chem. Phys.* 78 (1983) 5682.
- [16] R.J. Gdanitz, R. Ahlrichs, *Chem. Phys. Lett.* 143 (1988) 413.
- [17] MOLPRO is a package of ab initio programs written by H.-J. Werner, P.J. Knowles with contributions from J. Almlöf et al.
- [18] A. Papakondylis, A. Mavridis, *J. Phys. Chem. A* 103 (1999) 9363.
- [19] K.A. Peterson, T.H. Dunning Jr., *J. Chem. Phys.* 106 (1997) 419.
- [20] J.M.L. Martin, *Chem. Phys. Lett.* 273 (1997) 273.
- [21] I.S.K. Kerkines, A. Mavridis, *J. Phys. Chem. A* 104 (2000) 408.
- [22] D. Tzeli, A. Mavridis, *J. Phys. Chem. A* 105 (2001) 1175.
- [23] K.A. Peterson, T.H. Dunning Jr., *J. Mol. Struct. (Theorchem)* 400 (1997) 93, and references therein.
- [24] M. Tanimoto, S. Saito, E. Hirota, *J. Chem. Phys.* 84 (1986) 1210.
- [25] K.P. Huber, G.H. Herzberg, *Molecular Spectra and Molecular Structure*, vol. IV Constants of Diatomic Molecules, Van Nostrand Reinhold, New York, 1979.
- [26] D.M. Neumark, K.R. Lykke, T. Andersen, W.C. Lineberger, *Phys. Rev. A* 32 (1985) 1890.