

# Diatomics AB (A = Be, Mg; B = O, S) and oligomers thereof: A theoretical study

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## Abstract

A quantum chemical study of title systems and some related species (CaO, SrO, BaO and BaPo) was performed by B3LYP, H.F., MP2, TD DFT, and SAC-CI procedures. Structural features of isomers, vibrational frequencies, population analysis, ionization potential and in particular, electronic spectra. Electronic spectra of several monomers exhibit in accordance with experiments, the first electronic transitions in the near IR region (SAC-CI and TD DFT techniques). The passage to oligomers is accompanied by a very significant hypsochromic shift of the longest wavelength bands, increase of ionization potential and decrease of electron affinity.

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## 1. Introduction

Diatomic molecules formed by all combinations of atoms of IIa elements (Be, Mg, Ca, Sr, Ba) with atoms of VIa elements (O, S, Se, Te, Po) form an unsymmetrical matrix. Its lightest element is represented by BeO and the heaviest by BaPo. Except for a few species, primarily MgO and BeO, only minor theoretical attention has been paid to these potentially useful systems and their oligomers.

Attention has been paid to experimental and theoretical studies [1–12] of MgO and related systems. A small number of electrons in BeO makes this system attractive for theoretical treatment [13–15]; however, its toxicity makes this oxide mostly unattractive for experimentalists. Special attention was paid to the ground state electronic structure of MgO [5,6] and for years the electronic spectra of it have been investigated [10], while less attention was paid to infrared spectra [7] (only references of

crucial relevance are cited here, especially those which appropriately quote previous works). Open-shell systems derived from MgO, cations [8] and anions [2–4] were studied both theoretically and experimentally. Electron spectroscopy of radical anions is a valuable source of information not only about these species but also the parent molecules. Some effort was devoted to structural and electronic properties of bulk BeS [16]. The reversible storage of H<sub>2</sub> by BeS was studied theoretically [17].

It is appropriate to also consider studies concerning IIb–VIa binary systems and their clusters [18–23]. A lot of work was associated with ZnO [19,23], ZnS [20,23] and CdS [18,20–22]. Various characteristics of semiconductor nanocrystals as a function of size were reviewed [22].

## 2. Computational details

All calculations were done using the GAUSSIAN 03 [24] and MOLPRO 02 [25] program packages. To optimize the geometries, we used the DFT method with the B3LYP

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exchange-correlation functional and three different levels of the MO theory: the Hartree–Fock method (H.F.), the Møller–Plesset 2nd order perturbation theory (MP2), and the coupled cluster method with single and double excitations including non-iterative triple excitations (CCSD[T]). Electronic excitations were studied by means of the following three levels of theory: the time-dependent DFT (TD-B3LYP) theory, the symmetry-adapted cluster configuration interaction (SAC-CI) and the internally contracted multi-reference configuration interaction (icMRCI). The two latter methods were combined with single and double excitations. Comparison of the TD with the more robust MR procedure can help to evaluate the reliability of the single-reference TD approach regarding the calculation of molecules with a biradical character like MgO [6].

We employed the Dunning correlation consistent basis sets (cc-pVXZ) which are suitable for obtaining physical characteristics (e.g., heat of formation, excitation energies, ionization potentials) for a complete basis set (CBS). For screening through the sets of species in groups (e.g., from BeO to BaO) we used the Stuttgart/Dresden (SDD) basis sets involving effective core potentials which replace the explicit inner electrons and incorporate the scalar relativistic corrections.

Unless otherwise mentioned, the ionization potentials and electron affinities were computed as adiabatic with zero-point vibrational energy correction. The calculation of TD DFT and SAC-CI electronic excitations were carried out for vertical transition from the electronic ground states of the DFT and SAC-CI optimized molecular geometries. The oscillator strength  $f$  was defined as  $(8\pi^2/3)(m_e v / h e^2) | - e \int \Psi_i^* r \Psi_f d\tau |^2$ , where the symbols had their traditional meaning, and it was directly related to the intensity of the corresponding transition,  $\Psi_i \rightarrow \Psi_f^*$ .

### 3. Results and discussion

#### 3.1. Electronic spectra

In contrast to solid state oxides of the second group elements, the corresponding parent diatomics and small oligomers assume remarkable features. All of them have absorption bands in visible, near infrared, or even infrared regions (Tables 1 and 2). For the MgO there is a remarkably small gap between the adiabatic electronic  $X^1\Sigma^+ \rightarrow A^1\Pi$  transition ( $3563 \text{ cm}^{-1}$  [30]) and the vibrational mode (about  $1500 \text{ cm}^{-1}$ ). This fact could evoke a question about the trustworthiness of the Born–Oppenheimer approximation which is used in nearly all methods. The position of the first band in the visible region (at about  $13000\text{--}26000 \text{ cm}^{-1}$ ) is color-determining. The following colors of the oxides are expected: red (BeO and MgO), green (CaO and SrO), and blue (BaO). Being especially interested in clusters of diatomics under study, we have to pay attention to the TD DFT procedure, which is significantly less demanding than the more sophisticated techniques. A comparison of these procedures is made in Table 1 for the two lightest oxides (BeO, MgO) and sulphides (BeS, MgS). When passing from DZ to TZ basis set, the calculated bond lengths tend toward the experimental values. This is also true for the BeO and MgO longest wavelength transitions calculated with the SAC and MR methods. A broader comparison between vertical calculated and observed spectra is shown in Fig. 1; the overall comparison is satisfactory. In this figure calculated spectra for all four respective dimers are also depicted. Passing from monomers to dimers involves a remarkably large hypsochromic shift which amounts to  $10000\text{--}20000 \text{ cm}^{-1}$ ; the BeO and BeS dimers are even expected to be colorless. This transition is also

Table 1  
Optimized bond lengths  $R$  (Å) and wavenumbers ( $\text{cm}^{-1}$ ) of the vertical longest wavelength  $X^1\Sigma^+ \rightarrow A^1\Pi$  transitions,  $\Delta E^1$ , of BeO, MgO, BeS, and MgS

| Method and basis set  |   | BeO    |                    | MgO    |              | BeS    |              | MgS    |              |
|-----------------------|---|--------|--------------------|--------|--------------|--------|--------------|--------|--------------|
|                       |   | $R$    | $\Delta E^1$       | $R$    | $\Delta E^1$ | $R$    | $\Delta E^1$ | $R$    | $\Delta E^1$ |
| TD-B3LYP <sup>a</sup> | D | 1.3381 | 11197              | 1.7493 | 4242         | 1.7540 | 8781         | 2.1620 | 4614         |
|                       | T | 1.3233 | 11724              | 1.7430 | 4639         | 1.7414 | 9388         | 2.1514 | 5080         |
| SAC-CI(SD)            | D | 1.3487 | 9625               | 1.7892 | 4171         | 1.7628 | 9108         | 2.1807 | 5211         |
|                       | T | 1.3309 | 10375              | 1.7556 | 3915         | 1.7498 | 9942         | 2.1558 | 6030         |
| icMRCI <sup>b</sup>   | D | 1.3683 | 8893               | 1.7859 | 2796         | 1.7777 | 7897         | 2.1877 | 3911         |
|                       | T | 1.3431 | 10461              | 1.7716 | 3054         | 1.7614 | 9039         | 2.1711 | 4682         |
| Exp. <sup>c</sup>     |   | 1.3309 | 10951 <sup>d</sup> | 1.7490 | 3563         | 1.7415 | 7960         | 2.1425 | –            |

Calculations were carried out at TD DFT, SAC-CI, MR-CI levels for cc-pVXZ basis set ( $X = \text{D, T}$ ).

<sup>a</sup> TD calculations were carried out for B3LYP geometries.

<sup>b</sup> The following active spaces were used: BeO (7, 2, 2), MgO (9, 4, 4), BeS (9, 4, 4), MgS (12, 5, 5).

<sup>c</sup> Experimental  $T_e$  values taken from [29].

<sup>d</sup>  $T_v$  value taken from [15].

Table 2

Electronic spectral transitions of oxides of the second group metals:  $X^1\Sigma^+ \rightarrow A^1\Pi(\Delta E^1)$ ,  $X^1\Sigma^+ \rightarrow B^1\Sigma^+$  ( $\Delta E^2$ ),  $X^1\Sigma^+ \rightarrow B^1\Pi(\Delta E^3)$ ,  $X^1\Sigma^+ \rightarrow C^1\Sigma^+$  ( $\Delta E^4$ )<sup>a</sup>

| Oxid |   | $\Delta E^1$ | $\Delta E^2$ | $\Delta E^3$ | $\Delta E^4$ |
|------|---|--------------|--------------|--------------|--------------|
| BeO  | A | 11 197       | 21 702       | 56 541       | 72 511       |
|      | B | 16 904       | 25 900       | 61 811       | 83 987       |
|      | C | 9 406        | 21 254       | –            | –            |
| MgO  | A | 4 242        | 23 239       | 42 835       | 52 503       |
|      | B | 3 794        | 22 717       | 44 374       | 54 802       |
|      | C | 3 563        | 19 998       | 37 922       | 37 722       |
| CaO  | A | 13 443       | 14 334       | 26 221       | 28 590       |
|      | B | 13 286       | 14 434       | 26 744       | 29 525       |
|      | C | 8 433        | 11 555       | 25 991       | 28 858       |
| SrO  | A | –            | –            | –            | –            |
|      | B | 13 848       | 12 848       | 25 096       | 27 834       |
|      | C | 9 400        | 10 887       | 24 701       | 28 633       |
| BaO  | A | –            | –            | –            | –            |
|      | B | 20 309       | 16 154       | 33 071       | 31 673       |
|      | C | 17 691       | 16 807       | 32 866       | –            |

TD-B3LYP calculations were carried out with cc-pVDZ (A) and with SDD (B) basis set. Experimental values  $T_c$  [29] are collected in line C;  $\text{cm}^{-1}$  units are used throughout.

<sup>a</sup> Symmetries of transitions are considered and therefore in a few instances higher wavenumbers precede the lower ones.

related to an increase of ionization potential and a decrease of electron affinity. All these shifts embody the opposite of what we are familiar with from organic chemistry. It is possible to rationalize all these shifts by examining the correlation diagram of  $(\text{BeO})_2$  as it is formed from two subunits (Fig. 2). For the sake of completeness, the correlation diagram of BeO formation is also included.

In Table 2 wavenumbers of the first four transitions of the oxides under study (BeO through BaO) are presented. Time-dependent DFT calculations were combined with the cc-pVDZ basis set as well as with relativistic pseudopotential basis set, SDD. Wherever possible, we tried to use standard bases with systems consisting of elements belonging to the 2nd through the 4th row of the periodic system and pseudopotentials for heavier elements (the 4th through the 6th row). This meant we always sought to have an overlap of the results for the standard and pseudopotential basis sets. The  $X^1\Sigma^+ \rightarrow A^1\Pi$  transition is the longest wavelength with BeO, MgO, CaO, while with BaO  $X^1\Sigma^+ \rightarrow B^1\Sigma^+$  is the longest wavelength transition; for SrO these two transitions are close to each other. The overall agreement is better than semiquantitative. Let us add for the sake of completeness data for the first transition of barium polonide (B3LYP/SDD; BaPo:  $X^1\Sigma \rightarrow A^1\Sigma^+$ ,  $9416 \text{ cm}^{-1}$ ,  $f = 0.0034$ ;  $(\text{BaPo})_2$ :  $^1A_{1g} \rightarrow ^1B_{3u}$ ,  $17267 \text{ cm}^{-1}$ ,  $f = 0.032$ ). Regarding our intention to treat oligomers of the oxides, passing to more extensive bases is of limited sense. It can be affirmed, however, that the

transition to larger bases improves the SAC and MR data but makes TD excitation energies of poorer quality. When plotting excitation energies against  $1/n$  (where  $n$  means the total number of basis functions), we can obtain by extrapolation ( $1/n \rightarrow 0$ ) CBS estimates of the longest wavelength transition in the framework of the MR, SAC, TD and compare them with the Bauschlicher result of  $10951 \text{ cm}^{-1}$  [15] (he used FCI/Be[4s2p]; O[4s2p] with a diffuse 2p function and further augmented by either a 1d or 2d set). Our extrapolated values for the TD, SAC, MR procedures amount to 12225, 10830,  $11994 \text{ cm}^{-1}$ , respectively. The TD method offers the best result for a rather poor DZ basis set which one could consider as an intrinsic feature of the method. In the case of the next electronic transition ( $X^1\Sigma^+ \rightarrow B^1\Sigma^+$ ), the TD values converge to the CBS limit  $21483 \text{ cm}^{-1}$  ( $21444 \text{ cm}^{-1}$  [15]).

The Kohn–Sham (KS) orbitals were, until recently, considered to be pure mathematical constructs useful only to obtain the electron density. However, it has been demonstrated recently that, within the exact exchange–correlation potential theory, the calculated excitation energies obtained as the difference of KS orbitals represent a reliable estimate of excitation energy [26]. We obtained a rather close correlation between TD DFT excitation energy (the band in which the HOMO–LUMO transition dominates) and the difference of KS frontier orbitals energies (obtained by the B3LYP procedure), which is worth-noting. It might, for example, be useful for estimates of color with rather extensive oligomers where spectra calculations would be too demanding. Clearly, when proceeding along these lines, we cannot get information about the intensity of electronic transitions.

We assume that electronic spectral data could help with structure elucidation of isomers in the region of oligomers. For example, the two isomers of  $(\text{MgO})_2$  possessing  $D_{2h}$  symmetry differ in positions of the longest wavelengths by about  $8200 \text{ cm}^{-1}$ . The two most stable tetramers  $(\text{MgO})_4$  ( $T_d$  and  $D_{4h}$  symmetry) and hexamers  $(\text{MgO})_6$  ( $D_{3d}$  and  $D_{2h}$ ) have the first bands mutually shifted by about  $8000$  and  $3700 \text{ cm}^{-1}$ , respectively. We also performed the harmonic vibrational analysis (the B3LYP procedure) for the aforementioned clusters to establish the nature of the located stationary points. Moreover, it appears that the positions and intensities of vibrational modes can also serve as a reliable tool for distinguishing isomers.

### 3.2. Ionization potentials, electron affinities, and population analysis

Vertical and adiabatic IP's and EA's were calculated by means of H.F., MP2, and B3LYP procedures with DZ and TZ basis sets. We have already dealt with  $(\text{BeO})_n$  ( $n = 1$  through 6). Generally speaking IP and

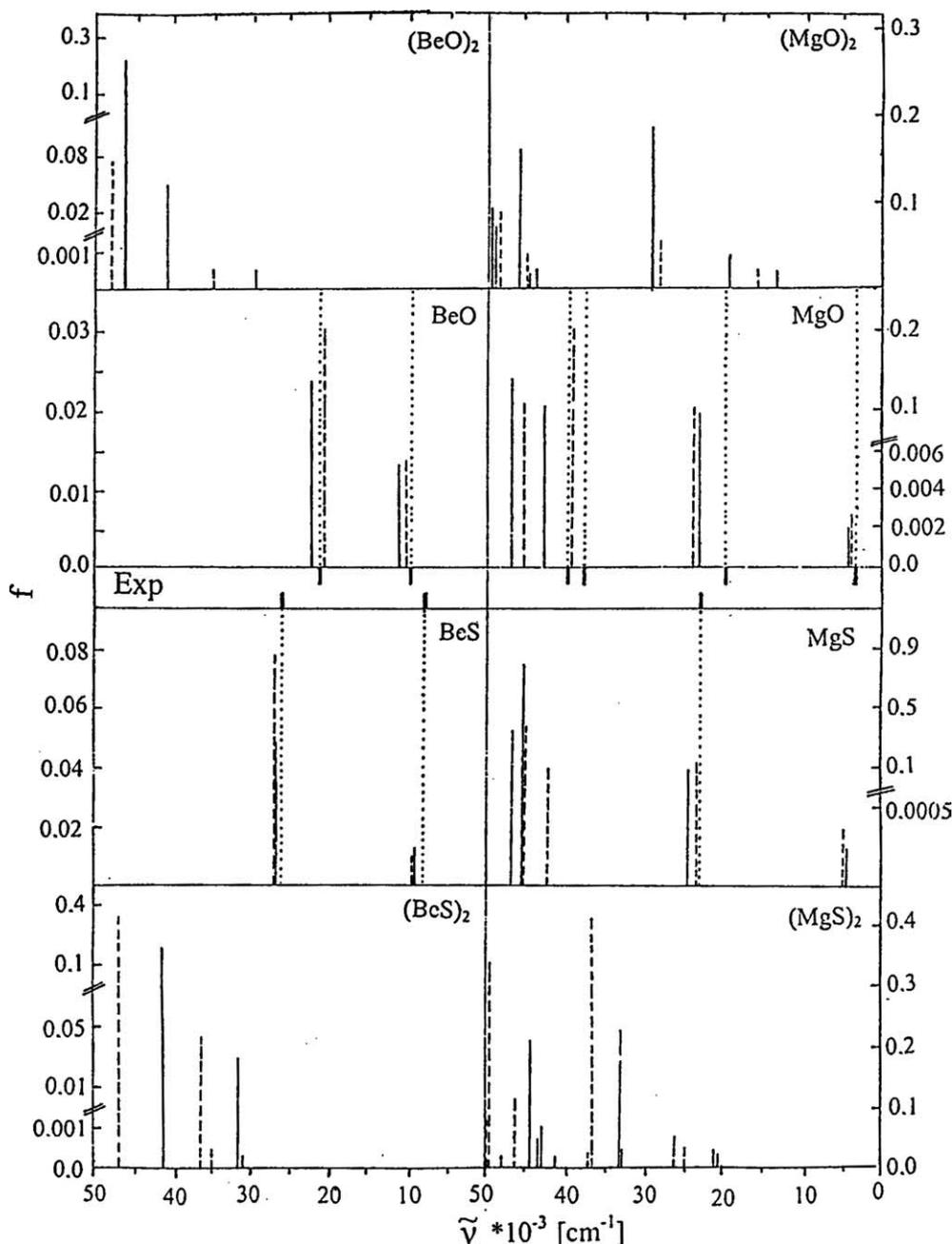


Fig. 1. Calculated positions of vertical transition,  $T_v$ , and oscillator strengths ( $f$ ) of BeO, MgO, BeS, MgS and the dimers ( $D_{2h}$  symmetry) thereof: TD-B3LYP/cc-pVDZ (—) and SAC-CI(SD)/cc-pVDZ (---). Experimental adiabatic band positions,  $T_e$ , are available only for monomers [29] and are indicated in the central part of this Figure. For the sake of easy orientation their positions are visualized by dotted lines.

EA changed ( $n$  having gone from 1 to 6) from 10 to 11.5 eV and from 2 to  $-1.5$  eV, respectively. Positive EA indicates high Lewis acidity which agrees with published observations [31]. The situation is analogous to BeS, MgO and MgS. The shifts of IP and EA values correspond with the observed reactivity decrease of clusters when their size increases [6]. Passing from BeO to BaO is associated with the monotonous decrease of IP, which agrees with experimental values [27–29] except for MgO. The shifts (going from BeO to BaO) are as fol-

lows: DFT 9.46–6.25; MP2 9.43–6.31; and experimental data 10.1–6.46 eV. In the case of MgO, our B3LYP/SDD and MP2/SDD results differ by about 1.3 eV from the experimental value. The discrepancy is reduced significantly when performing an extrapolation of MP2/cc-pVXZ ( $X = D, T, Q, 5$ ) ionization potentials to a CBS limit (8.28 and  $8.76 \pm 0.22$  eV [28] for extrapolated and experimental values, respectively).

The population analysis can be useful when interpreting chemical reactivity. We have tested results of the

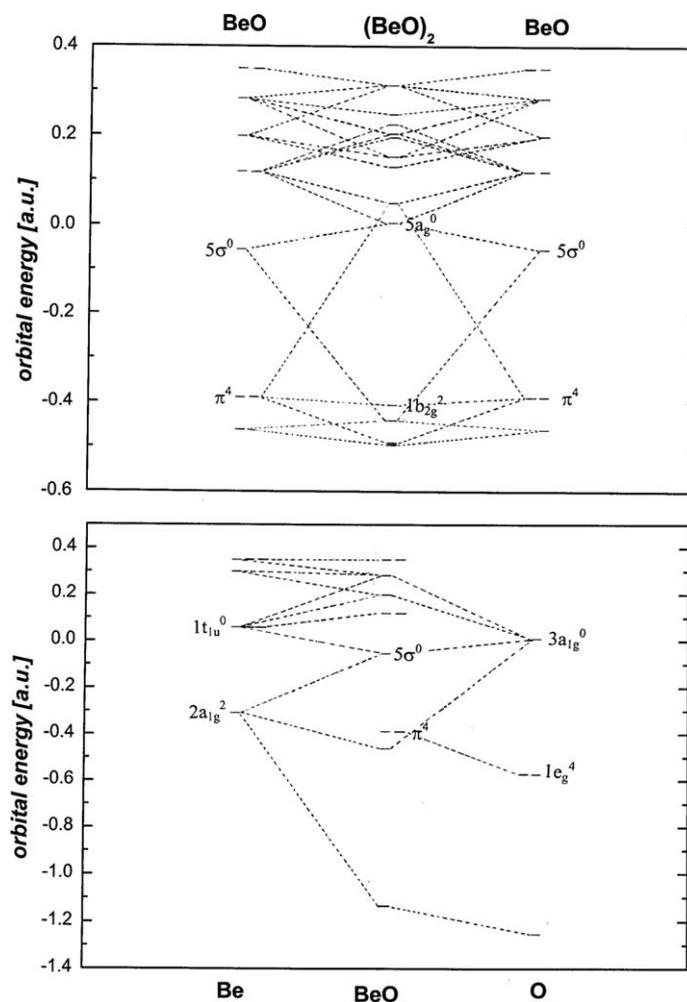


Fig. 2. Correlation diagram of formation of  $(\text{BeO})_2$  and  $\text{BeO}$  from the respective subunits (HF/cc-pVDZ orbital energies were used).

Mulliken and natural bond order (NBO) analysis for  $\text{BeO}$ ,  $\text{BeS}$ ,  $\text{MgO}$ ,  $\text{MgS}$  and for their most stable (rhombic) dimers. One has to keep in mind that the Mulliken/NBO analysis under/overestimates the partial atomic charges, and therefore these values represent limits for more realistic electron density distributions. The NBO analysis emphasizes the single bond character for  $\text{MgO}$  and  $\text{MgS}$ . A slightly more ionic character seems to be associated with  $\text{BeO}$  and  $\text{BeS}$ . An analysis of one-electron density matrices (within the complete active space of the SCF method) confirms that all four diatomics under study are not quite appropriately described by a single configuration function. It concerns mainly  $\text{MgO}$  (77%  $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 2\pi^4 6\sigma^2$ ; 12%  $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 2\pi^4 7\sigma^2$ ). This multireferential character of the wavefunction is supported by our computed electronic spectra where, unexpectedly, we observed a long wavelength for the first allowed electronic state transitions. All these observations indicate a singlet biradical character of  $\text{MgO}$ ,  $\text{MgS}$ , which manifests itself in their enhanced reactivity. We note that the multireferential

character and the single bond character are reduced with the growing cluster size. This is in agreement with the observed hypsochromic shift in electronic spectra.

### 3.3. Formation of $\text{BeO}$ and $(\text{BeO})_2$

Energy changes,  $\Delta E_1$  and  $\Delta E_2$ , accompanying processes  $\text{Be}(^1\text{S}) + \text{O}(^1\text{D}) - \text{BeO}(X^1\Sigma^+)$  (1) and  $2\text{BeO}(X^1\Sigma^+) - (\text{BeO})_2(^1A_g)$  (2) were calculated at the MP2, CCSD(T), and B3LYP levels. Realized calculations permitted extrapolations to CBS limits (reaction (1): DZ through 5Z, reaction (2): TZ and QZ). We obtained with the methods mentioned (in kcal/mol) for process (1)  $-177$ ,  $-159$ ,  $-182$  (experiment  $-153$  [13]) and for process (2)  $-159$ ,  $-164$  and  $-162$ , respectively. The agreement between the CCSD(T) and experimental  $\Delta E_1$  values, as well as the mutual approach of the calculated  $\Delta E_2$  values are noteworthy. Stepwise extension of the dimer to higher oligomers leads to species of the following symmetry with energy changes (kcal/mol):  $D_{3h}$  ( $-178$ ),  $D_{4h}$  ( $-155$ ),  $D_{5h}$  ( $-145$ ) and hexamer  $D_{3d}$

(–133). In all instances, absolute minima on the respective potential energy surfaces are presented.

#### 4. Conclusions and outlook

As is known at chemical laboratories, the second group oxides (white powders BeO through BaO) differ dramatically from monomeric forms and their oligomers. High reactivity and remarkable electronic spectra are especially worth citing. Very high, positive electron affinity of BeO explains its reactivity with rare gas atoms and H<sub>2</sub>; this means that it is an extremely strong Lewis acid. Except for BaO, the oxides exert the first electronic transition in the near IR region, while with MgO even in IR (about 3500 cm<sup>-1</sup>). In the latter case the electronic transition and the valence vibration are only about 1500 cm<sup>-1</sup> apart and therefore the use of the Born–Oppenheimer approximation need not be straightforward. Essentially all the molecules formed by the combination of IIa and VIa atoms (and their oligomers) have remarkable properties. These aspects remain preserved to a limited extent when passing from monomers to oligomers. The first absorption band exerts a hypsochromic shift, the IP increases, and EA decreases. When fixed on a proper holder, these oligomers might be useful not only in catalysis, but also in, e.g., the realm of molecular electronics and as promising materials for lasers.

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