



Xenon oxides, sulfides, and oxysulfides. A theoretical ab initio investigation



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ABSTRACT

We present ab initio RCCSD(T)/aug-cc-pV5Z results on the closed shell systems XeO_nS_m with $n, m = 0, 1, 2, 3, 4$ and $1 \leq n + m \leq 4$, a total of 14 molecules. Geometrical parameters, binding and atomization energies, dipole moments and harmonic frequencies are provided for all title species. Moreover, the bonding mechanisms, as well as, the possibility of isolating some of them are discussed.

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1. Introduction

Xenon is, perhaps, the most reactive element among rare gases due to the effective shielding of its valence electrons by the inner ones. Xenon oxides, fluorides and oxyfluorides were synthesized in the early sixties [1–4]. The preparations of XeO_3 [5] and of XeO_4 [6,7] were reported in 1963 and 1964, respectively. XeO_3 forms non-volatile colorless crystals, while XeO_4 is a yellow solid at low temperature and unstable at room conditions. Both are highly explosive. Several experimental studies were carried out in order to determine the structure [8,9], vibrational spectra [10–12], and enthalpies of formation [13–15] of these compounds.

Bartlett and Rao [16], in 1963, speculated the discovery of xenon dioxide in the experimentally obtained $\text{Xe}(\text{OH})_4$ (or $\text{XeO}_2 \cdot 2\text{H}_2\text{O}$) white solid which also was explosive above $\sim 30^\circ\text{C}$. Very recently, Brock and Schrobilgen [17] announced the synthesis of a bright yellow solid with the XeO_2 stoichiometry. They used Raman spectroscopy and isotopic enrichment techniques to show that this solid consisted of “polymerized” XeO_2 . However, the observation of molecular XeO_2 still remains uncertain.

Now, concerning the XeO diatomic, a green emission band system was observed [18–20], which was attributed, to the xenon monoxide $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ transition. Both states involved in this transition are excited states of the system. As shown by Dunning and Hay [21], in the first theoretical work on rare gas oxides, the XeO ground state is of $^3\Pi$ symmetry. This state together with a

$^3\Sigma^-$ state, stem from the $\text{Xe}(^1\text{S}) + \text{O}(^3\text{P})$ asymptotic channel. They are of repulsive character and cross the potential energy curve (PEC) of the first bound $1^1\Sigma^+$ state, emerging from the $\text{Xe}(^1\text{S}) + \text{O}(^1\text{D})$ asymptote. In 1980 Langhoff [22] studied the spin–orbit coupling between $1^1\Sigma^+$ and the $^3\Sigma^-$, 3Π states for all rare gas monoxides in order to determine the efficiency of the collisional quenching $\text{Rg} + \text{O}(^1\text{D}) \rightarrow \text{Rg} + \text{O}(^3\text{P})$. A more thorough study of the low-lying electronic states of XeO and XeS was reported by Yamanichi et al. [23]. These workers used the MRSDCI methodology coupled with double- ζ quality basis sets to construct PEC's of nine electronic states. For the $1^1\Sigma^+$ state of XeO they computed a binding energy of 0.77 eV.

The first theoretical investigation concerning XeO_n systems, with $n = 2, 3, 4$, was published in 2000 by Pyykkö and Tamm [24]. These authors focused mainly on the possibility of isolation of XeO_2 . They employed the CCSD(T) method in conjunction with triple- ζ bases and obtained results for XeO_3 and XeO_4 in relatively good agreement with existing experimental data. Concerning XeO_2 , they computed a slightly negative atomization energy but they claimed that XeO_2 might be observed at low temperature due to the kinetic stability brought about by a barrier of, at most, 115 kJ/mol.

In the same year, Ball [25] examined theoretically the possibility of stable binary and ternary xenon–oxygen–sulfur compounds. He performed HF, DFT, and MP2 calculations on the series XeO_3 , XeO_2S , XeOS_2 , and XeS_3 . For all species he found local minima with real harmonic frequencies and he also computed the corresponding enthalpies of formation. It must be noted that none of the xenon sulfides or the mixed Xe–O–S systems has been, so far,

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synthesized. The only xenon sulfide detected was XeS. Its near-IR emission spectrum was recorded in rare-gas matrices by Taylor and Walker [26], in 1979. As in the case of XeO, the luminescence observed, was attributed to the $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$ transition. Yamanishi et al. [23] showed theoretically that XeO and XeS have very similar PEC profiles and the binding energy of the $1^1\Sigma^+$ state of XeS is less than half that of XeO.

Now, in the present paper we carry out a systematic high level ab initio study of the lowest closed shell state of all possible XeO_n - S_m species, i.e. with $n, m = 0, 1, 2, 3, 4$ and $1 \leq n + m \leq 4$, a total of 14 different molecular systems. Our goal was to provide very accurate theoretical results concerning the structural properties and energetics of these systems. We present geometrical parameters, binding and atomization energies, dipole moments and harmonic frequencies for all species studied. Moreover, we discuss on their bonding mechanism and, also, on the possibility of isolating some of them.

2. Computational outline

Through all calculations we employed the restricted coupled-cluster singles and doubles with a perturbation treatment of triples, RCCSD(T), methodology.

For the Xe atom we used the augmented quintuple- ζ correlation consistent small core pseudopotential basis set of Peterson et al. [27], aug-cc-pV5Z-PP, contracted as (17s14p14d4f3g2h) \rightarrow [8s8p6d4f3g2h]. This basis set replaces the [Ar]3d¹⁰ core of Xe with a relativistic potential and comprises 139 spherical Gaussians. The corresponding aug-cc-pV5Z bases of Dunning were, also, used for oxygen [28] and sulfur [29].

We have correlated at the RCCSD(T) level all valence electrons, namely $\text{Xe}(5s^25p^6) + \text{O}(2s^22p^4)$ or $\text{S}(3s^23p^4)$. This computational scheme yields the following absolute atomic energies: $\text{Xe}(^1S) - 328.49903 E_h$, $\text{O}(^3P) - 75.00041 E_h$, $\text{O}(^1D) - 74.92095 E_h$, $\text{S}(^3P) - 397.67143 E_h$, $\text{S}(^1D) - 397.62425 E_h$. Thus, the $\text{O}(^1D) \rightarrow \text{O}(^3P)$ and $\text{S}(^1D) \rightarrow \text{S}(^3P)$ energy separations were found 2.162 and 1.284 eV, respectively, slightly greater than the experimental [30] 1.958 and 1.121 eV values. These differences are due to our single reference description of the 1D state. All D_0 values reported here were corrected for this small asymptotic error.

The basis set superposition errors calculated by the counterpoise method, never exceeded the $4 \times 10^{-4} E_h$ value.

Harmonic frequencies were calculated using the corresponding aug-cc-pVTZ-PP [27] for the Xe atom and aug-cc-pVTZ [28,29] for O and S, in order to make tractable the time consuming numerical Hessian computations. For Xe the average isotopic atomic mass was used.

Table 1
Energies E (E_h), geometrical parameters (\AA , deg), binding energies D_0 (kcal/mol), atomization energies ΔH_{atom} (kcal/mol), dipole moments μ (D), net Mulliken charges q (e), and harmonic frequencies ω_e (cm^{-1}) of the lowest closed singlet state of XeO_n , $n = 1-4$.^a

Species	$-E$	$r(\text{Xe}-\text{O})$	$\angle\text{O}-\text{Xe}-\text{O}$	D_0^b	ΔH_{atom}^c	μ	q_{Xe}	ω_e
$\text{XeO}(^1\Sigma^+)$	403.482597	1.923	–	33.7	–10.6	3.8	+0.87	594
$\text{XeO}_2(^1A_1)$	478.506480	1.840	112.1	92.2	1.9	3.9	+1.96	a_1 198, a_1 681, b_2 728
$\text{XeO}_3(^1A_1)$ (expt)	553.579031	1.779 (1.760) ^d	106.8 (103) ^d	180.2	44.7 (52.5 \pm 12) ^e	3.5	+3.12	e 262, a_1 304, a_1 777, e 852 (e 317, a_1 344, a_1 780, e 833) ^f
$\text{XeO}_4(^1A_1)$ (expt)	628.624297	1.757 (1.736) ^g	109.47 (109.47) ^g	251.4	70.7 (84.4) ^h	0.0 (0.0)	+4.00	e 253, t_2 304, a_1 774, t_2 868 (e 267, t_2 306, a_1 776, t_2 879) ⁱ

^a Net Mulliken charges are from HF calculations, harmonic frequencies are obtained at the RCCSD(T)/aug-cc-pVTZ level. All other numbers are at the RCCSD(T)/aug-cc-pV5Z level.

^b With respect to $\text{Xe}(^1S) + n\text{O}(^1D)$.

^c With respect to $\text{Xe}(^1S) + n\text{O}(^3P)$.

^d Solid state crystallographic average values, Ref. [8].

^e Thermochemical data assuming a sublimation enthalpy 30 ± 10 kcal/mol, Ref. [13].

^f Raman spectrum of aqueous solution, Ref. [10].

^g Ref. [9].

^h Enthalpy of formation from thermochemical studies, Ref. [14], and assuming a 119 kcal/mol binding energy for O_2 .

ⁱ Gas phase, Ref. [12].

All dipole moments were evaluated through the finite field approach by applying a 5×10^{-6} a.u. electric field.

In the case of the XeO and XeS diatomics, we performed also MRCI calculations which consisted of single and double replacements out of a CASSCF space defined by allotting 10 [O or S($2p^4$) + Xe($5p^6$)] electrons to 10 orbitals. The Xe $5s^2$ and O or S $2s^2$ electrons were correlated at the CISD level. The MRCI spaces ranged from 1.6×10^9 to 3.1×10^9 configuration functions (CF) internally contracted to $\sim 15 \times 10^6$ – 27×10^6 CFs. Size non-extensivity errors were corrected using multireference Davidson correction (MRCI + Q).

The MOLPRO 2010.1 code [31] was used through all our calculations.

3. Results and discussion

3.1. Oxides

Table 1 summarizes our results concerning the lowest closed singlet state of each of the $\text{XeO}(^1\Sigma^+)$, $\text{XeO}_2(^1A_1)$, $\text{XeO}_3(^1A_1)$, and $\text{XeO}_4(^1A_1)$ systems. For the XeO species we also present, in Fig. 1, potential energy curves of the lowest three electronic states, $^3\Pi$, $^3\Sigma^-$, and $^1\Sigma^+$. As we can see from this figure, the first two states, stemming from the ground state atomic asymptote, are of repulsive nature with only very weak van der Waals interactions at 3.596 \AA ($D_e = 125 \text{ cm}^{-1}$) and 4.150 \AA ($D_e = 64 \text{ cm}^{-1}$), respectively. The first bound electronic $^1\Sigma^+$ state correlates adiabatically to the $\text{Xe}(^1S) + \text{O}(^1D)$ channel and crosses the $^3\Pi$ and $^3\Sigma^-$ PEC's at $r(\text{Xe}-\text{O}) = 2.188$ and 2.401 \AA , respectively. From Table 1 we have for this state: $r_e = 1.923 \text{ \AA}$, $D_0 = 33.7 \text{ kcal/mol}$, and $\omega_e = 594 \text{ cm}^{-1}$. Our numbers are in serious disagreement with the corresponding $r_e = 2.06 \text{ \AA}$, $D_0 = 17.8 \text{ kcal/mol}$, and $\omega_e = 472 \text{ cm}^{-1}$ values by Yamanishi et al. [23]. This discrepancy is due to the fact that the basis sets used by these authors (double- ζ and large core for Xe) are rather poor. We were able to reproduce their results with the same basis sets. The atomization $\text{XeO}(^1\Sigma^+) \rightarrow \text{Xe}(^1S) + \text{O}(^3P)$ process is exothermic by 10.6 kcal/mol. This process contributes to the quenching mechanism $\text{Xe} + \text{O}(^1D) \rightarrow \text{XeO}(^1\Sigma^+) \rightarrow \text{Xe} + \text{O}(^3P)$ and is regulated by the efficiency of the spin-orbit coupling to generate the necessary intersystem crossing. The interaction $\text{Xe}(^1S) + \text{O}(^1D)$ can be depicted by the valence bond-Lewis (vbl) diagram of Scheme 1.

In this scheme, only the first term of the $|^1D; M_L = 0\rangle = \frac{1}{\sqrt{6}}(2|p_x^2 p_y^2| - |p_x^2 p_z^2| - |p_y^2 p_z^2|)$ atomic wavefunction of oxygen is shown. As we can see, an electron pair is transferred from Xe towards the empty p_z orbital of O to form a dative bond. This mechanism does not imply any electron recoupling and this

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