Calculations for XeO$_n$ ($n = 2$−4): Could the Xenon Dioxide Molecule Exist?[†]

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Pseudopotential ab initio calculations of the potential energy surface of the XeO$_2$ molecule have been carried out and a local minimum has been located. Geometries of the experimentally known XeO$_3$ and XeO$_4$ species have also been optimized, and the vibrational frequencies calculated for all three species. The possibilities for synthesizing XeO$_2$ are discussed in the light of these results.

1. Introduction

Two xenon oxides, XeO$_3$ and XeO$_4$, are known in the bulk.[1,2] The gas-phase monoxide, XeO, is known to have a repulsive $^1\Pi$ ground state.[3] No evidence is available for a xenon dioxide, XeO$_2$. In fact, a photodissociation experiment on xenon tetroxide using 200−300 nm UV light[4] gives no trace of the dioxide. Therefore, it is interesting to try to determine by ab initio calculations whether the xenon dioxide is thermodynamically stable or not.

The available data for XeO$_3$ and XeO$_4$ are collected in Table 1. They can be used for calibration of the theoretical methods used. For completeness, we also included some high-level computational data on the $^1\Sigma$ excited XeO.[3]

Xenon dioxide was first mentioned as a component in the hypothetical experimentally obtained complex XeO$_2\cdot$2H$_2$O in the paper by Bartlett and Rao[5] in 1963. Since then, scattered evidence for the species with the XeO$_2$ stoichiometry has been put forth several times.[6,7] Naumkin and Knowles found loosely bound minima on the Xe−O$_2$ potential energy surface using empirical potentials.[8]

For the latest reviews on rare-gas chemistry, see Holloway and Hope[9] or Pettersson et al.[10]

2. Methodology

At least three independent sets of effective core potentials (ECPs) are available for xenon: the Hay and Wadt parametrization,[11] the Nicklass et al. parametrization,[12] and the one by LaJohn et al.[13] The first two belong to the large-core, eight-valence-electron category, replacing the core electrons up to and including the 4d, with the electrons on the 5s and 5p orbitals modeled explicitly. The third one is of the small-core kind, where the 4d electrons are also included explicitly in the calculation. All sets of ECPs come with the corresponding basis sets. All three parametrizations were tried for the purposes of the present work, and very similar results were obtained. The Nicklass ECPs and basis sets were used for the results reported here, because of their quadruple-ζ quality, the Hay and Wadt basis sets being of double-ζ quality. The basis sets included with the LaJohn parametrization are of quadruple-ζ quality, and

the inclusion of core electrons increases the size of the computational system without significant increase in accuracy.

The Nicklass basis set for xenon was augmented with three d and one f set of polarization functions, with the exponents 0.4460, 0.2322, and 0.1208 for the d and 0.5157 for f, respectively.[12] For the oxygen atoms, the 6-311G* and the aug-ccPVTZ basis sets were tried, and the latter gave much better accuracy for heats of formation of XeO$_3$ and XeO$_4$. Because of computational limitations, the geometries and vibrational frequencies of XeO$_3$ and XeO$_4$ were calculated using the 6-311G* basis set, followed by single-point calculations with the aug-ccPVTZ basis to obtain more reliable energetic values for the tri- and tetroxide.

Electron correlation was accounted for by using the coupled clusters model including the single and double excitations and the triple excitations perturbatively (CCSD(T)).

All calculations were performed assuming either bent C_{2v} O−Xe−O, or a linear $C_{\infty v}$ Xe−O−O structure for the XeO$_2$ molecule. The linear structure did not yield any minima in the covalently bound region and is not discussed further. The experimentally known pyramidal C_{3v} structure for XeO$_3$ and the tetrahedral T_d geometry for XeO$_4$ were used. The minima were confirmed by calculating the Hessians and checking that no negative eigenvalues were present. Some potential energy surfaces were also generated by a sequence of independent single-point calculations.

As already mentioned, single-point vibrational frequency calculations were performed at the stationary points. The reported vibrational frequencies are unscaled values, as printed by the Gaussian program.

The Gaussian94[14] and Gaussian98[15] packages were used for the calculations.

3. Results and Discussion

Calibration of the Method. The main results of the calculations are presented in Tables 2 and 3. The geometries (Xe−O distances R, and O−Xe−O angles), heats of formation, and vibrational frequencies (ν) of XeO$_3$ and XeO$_4$ are experimentally known[2] and the calculations served mostly as calibration points for the methodology used. The calculated Xe−O bond lengths are within 2 pm of the experiment, and the O−Xe−O angle in XeO$_3$ is within 4° from the measured value. The vibrational frequencies are typically underestimated by up to 13%; an average scaling factor of 1.05 is suggested on the basis of these figures.

Calculations for XeO$_n$ (n = 2−4)

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TABLE 1: High-Level Computational Data on XeO and Experimental Data on XeO$_3$ and XeO$_4$[a]

compound	ΔH_f, kJ/mol	ΔH_{atom}, kJ/mol	R, pm	O−Xe−O, deg	ν, cm^{-1}
XeO ($^1\Sigma$)		−118[b]	206[b]		472[b]
XeO$_3$	402(8)[c,d]		176(3)[e]	103(2)[e]	780 (a$_1$), 344 (a$_1$), 833 (e), 317 (e)[f]
	528(50)[g]	219[b,g]			770 (a$_1$), 311 (a$_1$), 820 (e), 298 (e)[h]
XeO$_4$	643[i]		173.6(2)[j]	109.5	773 (a$_1$), 877, 305.7 (t$_2$)[k]
	685[g]	311[b,g]			808 (a$_1$), 272 (e), 901, 309 (t$_2$)[l]

[a] See text for the definition of the symbols. [b] Reference 3. [c] Reference 16. [d] Solid-state value. A sublimation enthalpy of 126(42) kJ/mol is quoted in ref 17. [e] Solid-state X-ray diffraction,[21] average values. [f] Raman data in aqueous solution.[22] [g] Estimated gas-phase value. [h] Infrared data of the solid.[23] [i] Solid-state value[17] [j] Gas-phase electron diffraction.[24] [k] Gas-phase.[25] For solid-state data, see the same reference. [l] Harmonic gas-phase frequencies.[26]

TABLE 2: Main Geometric Parameters, Heats of Formation and Atomization of the XeO$_n$, n = 2−4, Molecules As Calculated at the CCSD(T) Level of Theory

	R(Xe−O), pm		O−Xe−O, deg		ΔH_f, kJ/mol		ΔH_{atom}, kJ/mol	
system	calc	expt	calc	expt	calc	expt	calc	expt
XeO$_4$	175.8	173.6	109.5	109.5	706	685	236	311
XeO$_3$	177.6	176	106.6	103	560	528	147	219
XeO$_2$	185.0		111.8		487		−15	

TABLE 3: Vibrational Frequencies of the XeO$_n$, n = 2−4, Molecules As Calculated at the CCSD(T) Level of Theory

molecule	method	
XeO$_4$	calc	e 265, t$_2$ 311, a$_1$ 757, t$_2$ 863
	exp	e 272, t$_2$ 309, a$_1$ 808, t$_2$ 901
XeO$_3$	calc	e 280, a$_1$ 315, a$_1$ 757, e 846
	exp	e 317, a$_1$ 344, a$_1$ 780, e 833
XeO$_2$	calc[a]	a$_1$ 205, a$_1$ 647, b$_2$ 703
	calc[b]	206, 668, 716

[a] 6-311 g* oxygen. [b] aug-ccPVTZ oxygen.

The heats of formation posed a greater challenge and eventually turned out to be the main reason for choosing the particular basis set used. The reported experimental values[16,17] are for solid XeO$_3$ and XeO$_4$, while the calculations are performed for isolated molecules (gas phase). The enthalpy of sublimation of XeO$_3$ is estimated by Gunn[17] at 126(42) kJ/mol. No energy of sublimation of XeO$_4$ was available to us; thus we estimated a value of 42 kJ/mol (10 kcal/mol) by analogy with other similar compounds, notably the likewise tetrahedral, "heavy" OsO$_4$. The energy of sublimation of the nonpolar XeO$_4$ is expected to be lower than that of the polar XeO$_3$ with dipole−dipole intractions between the molecules.

In Tables 1 and 2 the heats of formation (ΔH_f) correspond to the reaction Xe + $^n/_2$O$_2$ → XeO$_n$, while the heats of atomization (ΔH_{atom}) correspond to the atomization reactions XeO$_n$ → Xe + nO. All energies of multiatom species, calculated as part of this work, include the zero-point vibrational corrections; thus the heats of formation correspond to 0 K.

When the sublimation enthalpies are taken into account, the calculated heats of formation of the known oxides agree with experiment within 32 kJ/mol, and the atomization energies within 75 kJ/mol. We thus conclude that the chosen model is usable for predicting the properties of the so far unobserved XeO$_2$ species.

The O$_2$ molecule was calculated to have the O- - -O distance of 121.3 pm (triplet state), within 0.6 pm of the experimental value of 120.75 pm.[18]

Geometry and Energy of XeO$_2$. From most starting configurations, a dissociative behavior of the XeO$_2$ molecule was observed. Only when provided with a starting geometry fairly close to the local minimum on the singlet surface, would the optimization converge to that minimum. Energetically, the minimum is located 487 kJ/mol above the triplet O$_2$ molecule and singlet Xe atom, and essentially at the same energy level (15 kJ/mol above) as the Xe atom and two O atoms. Additionally, the minimum is on a slope of the potential energy surface, separated from the dissociative configuration by a barrier at most 115 kJ/mol high (determined by analysis of grid point data). It is not excluded that dissociation channels with even lower barriers could have escaped our attention. Also, the points near the transition state region have a multireference character (The T_1 diagnostic[19] is 0.13); thus the height of the barrier might be much different. At the geometry of the singlet local minimum, the triplet state is 254 kJ/mol higher in energy. The T_1 diagnostic

values for the local minima of all species checked were below 0.044, typically in the 0.030−0.037 region.

The dipole moment of XeO$_2$ is calculated as 3.93 D, using the SCF electron density. For comparison, the calculated dipole moment of XeO$_3$ is 4.15 D. Such a high dipole might increase its stability in polar solvents, just like the case for XeO$_3$, which is used as an oxidizer in the form of aqueous solutions in dilute acids. The experimental ΔH_f of XeO$_3$(aq) is 418(1) kJ/mol.[20] This is only slightly (16(9) kJ/mol) above the solid-state value in Table 1. The system is one of the strongest oxidants in aqueous media but has high kinetic stability.

Note the monotonic increase of R and the monotonic decrease of the largest vibrational frequency in Tables 1−3 for XeO$_n$ when n decreases from 4 to 1. This reflects the weakening of the Xe−O chemical bond as the number of oxygen atoms decreases.

On the basis of these results, one should probably not expect XeO$_2$ to be accessible as a stable isolated species at room temperature. It is possible, however, that matrix or other low-temperature methods of preparation would allow one to detect it.

4. Conclusions

On the basis of the calculations, the XeO$_2$ system has a local minimum on the potential energy surface, separated from the dissociative configurations by a reasonably high barrier. It is therefore thinkable that, under carefully selected conditions, preparation of this species may be experimentally possible.

References and Notes

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