

Formation and Characterization of the XeOO⁺ Cation in Solid Argon

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Since the report of the first stable xenon-containing compound,¹ XePtF₆, a large number of chemically bound noble gas (Ng) complexes have been prepared,^{2–7} and noble gas chemistry has aroused great current interest.^{8–14} For xenon oxides, XeO₄ and XeO₃ exist in the bulk¹⁵ but are thermodynamically unstable, decomposing explosively into their elements. So far, there is no evidence for the existence of XeO₂, which was shown to be a local minimum from theoretical calculation,¹⁶ whereas the XeO₂⁺ cation was observed in previous mass spectrometric studies.^{17,18} Here we report a matrix infrared spectroscopic and theoretical characterization of an unusual XeOO⁺ cation, a species that we show to have a direct xenon–oxygen bond and significant Xe + O₂⁺ binding energy.

The XeOO⁺ cation was prepared either by co-condensation of the reactive species generated by laser ablation of different transition metals (Ti, V, Nb, and Ta) with dioxygen and xenon mixtures in excess argon or by condensation of high-frequency discharged O₂/Xe/Ar mixtures onto a 12 K CsI window as described elsewhere.¹⁹ Infrared spectra were recorded on a Bruker IFS 113V spectrometer at 0.5 cm⁻¹ resolution using a DTGS detector. In both the discharge and laser ablation experiments, besides the known absorptions of O₃, O₃⁻, O₄⁻, and O₄⁺,²⁰ an unknown common absorption at 1507.9 cm⁻¹ was observed. This band appeared on sample deposition, slightly decreased on annealing, and disappeared upon broadband irradiation with a high-pressure mercury arc lamp (250 < λ < 580 nm). When CCl₄ was added to serve as an electron trap,²¹ the intensity of the new product absorption increased relative to the other neutral species, while the O₃⁻ and O₄⁻ anions were eliminated. These results suggest that the new absorption is due to a cationic species.

Isotopic substitutions (¹⁸O₂, ¹⁶O₂ + ¹⁸O₂, and ¹⁶O₂ + ¹⁶O¹⁸O + ¹⁸O₂) were employed for product identification based on isotopic shifts and absorption splitting. The infrared spectra in the 1520–1410 cm⁻¹ region with different isotopic samples are shown in Figure 1. When an ¹⁸O₂/Xe/Ar sample was used (Figure 1, spectrum b), the analogous band was observed at 1422.8 cm⁻¹. The ¹⁶O/¹⁸O isotopic frequency ratio of 1.0598 is characteristic of an O–O stretching vibration. The mixed ¹⁶O₂ + ¹⁸O₂ spectrum (Figure 1, spectrum c) indicates that only one O₂ unit is involved in this mode. Four absorptions at 1507.9, 1466.5, 1465.6, and 1422.8 cm⁻¹ with approximately 1:1:1:1 relative intensities were observed in the spectrum with the ¹⁶O₂ + ¹⁶O¹⁸O + ¹⁸O₂ (1:2:1) sample (Figure 1, spectrum d), which implies that the two O atoms are slightly inequivalent. In contrast, no analogous band was seen in the experiment with the O₂/Kr/Ar sample, suggesting participation of a Xe atom in this species. Accordingly, we assign the 1507.9 cm⁻¹ band to the O–O stretching mode of a XeOO⁺ cation, which is valence isoelectronic with the ClOO and BrOO neutral molecules observed at 1442.5 and 1485.1 cm⁻¹ in solid argon.²²

To validate the experimental assignment, we performed ab initio coupled cluster and density functional theory (DFT) calculations

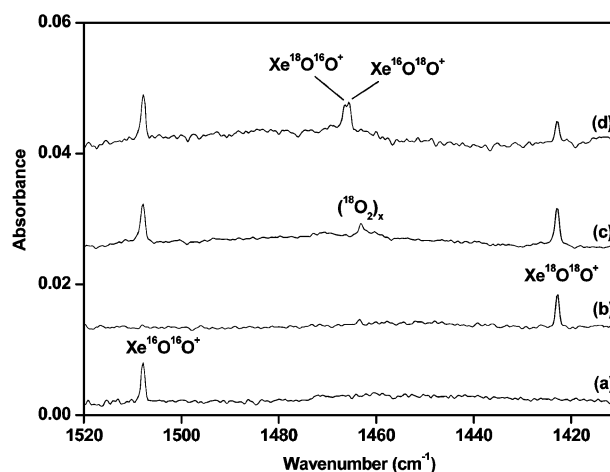


Figure 1. Infrared spectra in the 1520–1410 cm⁻¹ region from co-deposition of the species generated by laser ablation of transition metal with O₂/Xe mixtures in excess argon at 12 K: (a) 1.0% ¹⁶O₂ + 1.0% Xe/Ar, (b) 1.0% ¹⁸O₂ + 1.0% Xe/Ar, (c) 0.75% ¹⁶O₂ + 0.75% ¹⁸O₂ + 1.0% Xe/Ar, and (d) 0.4% ¹⁶O₂ + 0.8% ¹⁶O¹⁸O + 0.4% ¹⁸O₂ + 1.0% Xe/Ar.

Table 1. Bond Lengths (Å), Bond Angles (degree), Vibrational Frequencies (cm⁻¹), ¹⁶O/¹⁸O Isotopic Frequency Ratio, and Dissociation Energies (kcal/mol) of XeOO⁺ Calculated at Various Levels of Theory

	Xe–O	O–O	∠XeOO	ν ₁	ν ₂	ν ₃	16/18	BE
LDA	2.536	1.158	120.9	1703	360	161	1.0608	44.6
BLYP	2.768	1.177	122.5	1594	278	97	1.0608	40.2
PW91	2.673	1.168	121.6	1650	309	120	1.0608	40.5
B3LYP	2.759	1.155	122.0	1698	278	110	1.0608	32.6
B3PW91	2.728	1.149	121.6	1740	289	113	1.0608	30.8
X3LYP	2.698	1.151	121.5	1722	297	123	1.0608	32.8
PBE0	2.695	1.146	121.2	1754	299	124	1.0608	30.0
BHLYP	2.629	1.140	120.6	1735	315	146	1.0608	23.5
CCSD	2.653	1.134	118.8	1712	337	172	1.0608	10.2
CCSD(T)	2.545	1.162	119.3	1588	361	175	1.0608	14.9
Expt.				1507.9			1.0598	

of XeOO⁺ via the NWChem program.^{23,24} The calculations suggest that the monoxenon complex XeOO⁺ accounts for the observed IR absorption, whereas the Xe_nOO⁺ species with n ≥ 2 do not fit. The optimized geometries, vibrational frequencies, ¹⁶O/¹⁸O isotopic frequency ratio, and dissociation energies of XeOO⁺ for the asymptotes Xe + O₂⁺ at various levels of theory are listed in Table 1, which shows that accurate prediction of the structure, frequencies, and dissociation energies of XeOO⁺ requires high-level electron correlation calculations with triple-excitation contribution. The cation has a doublet ground state (²A'') exhibiting a bent Xe–O–O structure with C_s symmetry to minimize the exchange repulsion between the lone pairs of Xe and O atoms. In fact, the linear structure is a transition state, lying 11.8 kcal/mol higher in energy than the bent structure. At the CCSD(T) level, the Xe–O and O–O distances in the bent structure are 2.545 and 1.162 Å, respectively,

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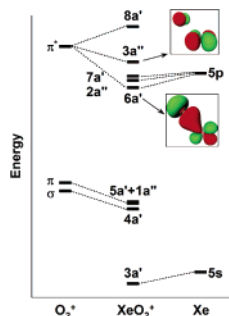


Figure 2. Molecular orbital energy levels of the XeOO^+ cation showing the in-plane and out-of-plane interaction between the π^* orbitals of O_2^+ and the 5p lone pair orbitals of Xe. The frontier electron configuration is $(6a')^2 (2a'')^2 (7a')^2 (3a'')^1$, and the insets depict the 3D contours of the bonding $6a'$ and nonbonding $3a''$ orbitals.

with the $\angle\text{XeOO}$ angle of 119° . The Xe–O distance is slightly longer than the corresponding distances in xenon oxides and HXeO ,^{16,25} but is 1.1 \AA shorter than the sum of the van der Waals radii of Xe and O atoms,²⁶ indicating significant Xe–O bonding. Indeed, the O–O distance is 0.05 \AA longer in XeOO^+ than in the free O_2^+ , implying electron donation from Xe to O_2^+ to form a Xe–O dative bond. From the molecular orbital (MO) analysis shown in Figure 2, the ground state of O_2^+ has an empty and a singly occupied π^* MO pair. By interacting with the in-plane and out-of-plane Xe 5p lone pair orbitals, the former forms a doubly occupied Xe–O ($p-\pi^*$) bonding σ orbital ($6a'$), and the latter forms a singly occupied nonbonding ($p-\pi^*$) π orbital ($3a''$). The 3D MO contour surface of the in-plane bonding orbital ($6a'$ in Figure 2) indicates that the XeOO^+ species indeed possesses a direct Xe–O bond, which is consistent with the significant binding energy of this species (see below). The calculated O_2 and Xe fragment charges are $+0.45$ and $+0.55 e^-$, respectively, at the B3LYP level of theory, and the spin density is mainly distributed at the O_2^+ fragment. We also calculated the symmetric OXeO^+ isomer with a bent C_{2v} structure, which is found to be a local minimum lying 89.3 kcal/mol higher than the asymmetric XeOO^+ cation at the CCSD(T) level.

The CCSD(T) O–O stretching frequency of 1588 cm^{-1} in the gas phase is quite close to the experimental value in the Ar matrix, particularly when considering the existence of the *charge-induced dipole matrix effects* in the latter. Similar calculations on O_2 yield an O–O stretching frequency in excellent agreement with experiment.²⁴ The Xe–O stretching (ν_3) and bending (ν_2) modes are predicted to absorb below 400 cm^{-1} with very low IR intensities. The O–O frequencies are considerably overestimated by nearly all the DFT calculations.

The XeOO^+ cation is formed via an ion-molecular reaction during the concurrent co-deposition process. Although the O_2^+ cation cannot be detected with infrared absorption spectroscopy, its participation is confirmed by reactions with O_2 to form O_4^+ . Upon adding xenon in the reagent gas, the XeOO^+ cation was formed, while the O_4^+ cation absorptions were barely observed. This suggests that XeOO^+ has a binding energy higher than that of O_2-O_2^+ , which was experimentally determined to be $9.7 \pm 0.7 \text{ kcal/mol}$.²⁷ Consistent with this assessment, the binding energy (or dissociation energy) of XeOO^+ with respect to $\text{Xe} + \text{O}_2^+$ is predicted to be around 15 kcal/mol with respect to CCSD(T) , a remarkable binding energy for noble gas systems.^{28,29} Again, the binding energy is significantly overestimated by the DFT methods using different levels of exchange–correlation functionals. The dissociation energy of XeOO^+ is remarkably larger than those of the isoelectronic ClOO (4.8 kcal/mol) and BrOO (1.8 kcal/mol) because of both weakly covalent interaction and charge-induced dipole interaction in the former.³⁰

In summary, we have identified an asymmetric open-shell cation species, XeOO^+ , which involves direct Xe–O bonding. This new species was prepared either by co-condensation of the reactive species generated by laser ablation of different transition metals with dioxygen and xenon mixtures in excess argon or by condensation of high-frequency discharged $\text{O}_2/\text{Xe}/\text{Ar}$ mixtures. Through quantum chemistry calculations, it is discovered that the XeOO^+ cation involves a ($p-\pi^*$) σ bond and is remarkably more stable than the $\text{Xe} + \text{O}_2^+$ reactants.

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Supporting Information Available: Complete ref 23 and total electronic energies (in hartrees) and geometries (as Cartesian coordinates) of XeOO^+ from all methods used. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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