Ab initio investigation of the lowest $\tilde{X}\ ^2A''$ and $\tilde{A}\ ^2A'$ potential energy surfaces of the $Kr-O_2^+$ cationic system

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ARTICLE INFO

ABSTRACT

High level ab initio RCCSD(T) calculations were used to explore the $\tilde{X}\ ^2A''$ and $\tilde{A}\ ^2A'$ potential energy surfaces stemming from the interaction of $Kr(^1S)$ with the O_2^+ $(X\ ^2\Pi_g)$ molecular cation. On both surfaces weakly bound KrO_2^+ complexes were found, namely $KrO_2^+(\tilde{X}\ ^2A'')$ and $KrO_2^+(\tilde{A}\ ^2B_2)$, with $D_e(D_0) = 0.240$ (0.223) and 0.135 (0.126) eV, respectively. Potential energy curves, slices of the $\tilde{X}\ ^2A''$ and $\tilde{A}\ ^2A'$ surfaces, are also presented.

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1. Introduction

The interaction of the Kr atom with the diatomic cation O_2^+ has been the object of several experimental scattering works [1–6]. Some of them deal with the photo-induced charge transfer reaction [1–3] $Kr + O_2^+ \rightarrow Kr^+ + O_2$ and the photodissociation of the KrO_2^+ complex [4], while others investigate the vibrational quenching [5,6] of O_2^+ by Kr. Many theoretical studies [7–14] have been carried out in order to elucidate the mechanisms of the O_2^+ vibrational relaxation through collisions with Kr atoms. Of course, an accurate potential energy surface describing the $Kr\cdots O_2^+$ interaction is a prerequisite for such theoretical studies. In 1987, Tosi et al. [7] devised a semi-empirical potential energy surface combining experimental data by Jarrold et al. [4], and they used it in classical trajectory calculations. A slightly different, also semi-empirical, potential was proposed by Ramachandran and Ezra [9] in 1992. The first ab initio potential energy surfaces for the $Kr-O_2^+$ system were presented in two Letters by Ramiro-Diaz et al. [15,16]. These authors carried out projected VB-CI calculations in conjunction with relatively small basis sets, with pseudopotentials on Kr, to produce seven low-lying surfaces in each of the two, $^2A'$ and $^2A''$, possible symmetries of the KrO_2^+ system. They concluded that all potential energy surfaces, except for the ground $\tilde{X}\ ^2A''$, are globally repulsive. For the ground state they found a minimum corresponding to a KrO_2^+ complex with a binding energy $D_e(Kr-O_2^+) = 0.173$ eV. This value is approximately half the experimental one deduced by photodissociation data [4]. In 1999, Craimer et al. [13] used the Ramiro-Diaz et al. potentials to study the vibrational relaxation of O_2^+ colliding with Kr. They employed the coupled states

approximation (CSA) taking into account the two lowest electronic states of KrO_2^+, $\tilde{X}\ ^2A''$ and $\tilde{A}\ ^2A'$. This work resulted in rate constants which were an order of magnitude lower than the experimental data and the need for more accurate ab initio potential energy surfaces was pointed out as a conclusion.

In the present Letter, our goal was to re-explore the first $^2A''$ and $^2A'$ surfaces of KrO_2^+ by using high level ab initio calculations and to characterize possible minima on them. We also constructed potential energy curves corresponding to the $O_2^+(X\ ^2\Pi_g) + Kr(^1S)$ interaction. As we shall see some interesting results differing from the data in Refs. [15,16] were obtained.

2. Computational outline

Through all this study we employed the restricted coupled cluster singles and doubles with a perturbation treatment of triples technique, RCCSD(T), to perform all electron calculations. We used the correlation consistent basis sets [17,18], aug-cc-pVnZ, augmented with diffuse functions. Full geometry optimizations were carried out using the n = D, T, Q (double, triple, and quadruple-ζ) bases. Calculations at the aug-cc-pV5Z level were done using the geometries optimized with the quadruple-ζ basis set. The binding energies D_e of the minima found were corrected for the basis set superposition error (BSSE). The corrected D_e values were used to obtain the complete basis set (CBS) limit through the extrapolation formula $D_e(n) = p_1 + p_2 \exp(-p_3 n)$, where n is the basis set cardinal number and p_1, p_2, p_3 fitting parameters.

Relativistic corrections were included by using a Douglas–Kroll–Hess (DKH) Hamiltonian of 8th order as it is implemented in the MOLPRO program.

The potential energy curves were constructed using the aug-cc-pVQZ basis sets. All our calculations were performed using the MOLPRO 2006.1 code [19].

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3. Results and discussion

The $O_2^+(X\,^2\Pi_g)$ ion is produced by removing one of the two uncoupled π_g electrons from $O_2(X\,^3\Sigma_g^-)$. This process requires

Table 1
Absolute energies $E(E_h)$, geometrical parameters r_{O-O} (Å), R (Å), and θ (degrees) (for definition see inset of Fig. 1), Net Mulliken charges on Kr q_{Kr} (+e), and Kr–O_2^+ binding energies D_e (eV) of the KrO$_2^+$ $\bar{X}\,^2A''$ and $\bar{A}\,^2A'$ states and for different basis sets.

Basis set	E	r_{O-O}	R	θ	q_{Kr}	D_e
$\bar{X}\,^2A''$						
aug-cc-pVDZ	−2901.708510	1.138	3.390	45.6	0.08	0.207
aug-cc-pVTZ	−2901.957699	1.130	2.981	53.8	0.10	0.225
aug-cc-pVQZ	−2902.018074	1.124	2.996	54.1	0.10	0.236
aug-cc-pV5Z[a]	−2902.037204	1.124	2.996	54.1	0.10	0.239
CBS						0.239
DKH/aug-cc-pVQZ[b]	−2938.344043	1.125	2.983	54.0	0.09	0.240
DKH/aug-cc-pV5Z[a,b]	−2938.365282	1.125	2.983	54.0	0.10	0.240
$\bar{A}\,^2A'$ ($\bar{A}\,^2B_2$)						
aug-cc-pVDZ	−2901.704649	1.130	3.332	90.0	0.02	0.090
aug-cc-pVTZ	−2901.953521	1.121	3.258	90.0	0.01	0.127
aug-cc-pVQZ	−2902.014286	1.117	3.264	90.0	0.02	0.137
aug-cc-pV5Z[a]	−2902.033457	1.117	3.264	90.0	0.01	0.138
CBS						0.139
DKH/aug-cc-pVQZ[b]	−2938.340131	1.117	3.258	90.0	0.02	0.133
DKH/aug-cc-pV5Z[a,b]	−2938.361410	1.117	3.258	90.0	0.02	0.135

[a] Single point calculations using geometries optimized with the aug-cc-pVQZ basis sets.
[b] RCCSD(T) calculations using a Douglas–Kroll–Hess Hamiltonian.

12.071 eV [20]. Taking into account that the Kr I.P. is 13.996 eV [21], the $O_2^+(X\,^2\Pi_g)$ + Kr(^1S) asymptotic channel is clearly energetically lower than $O_2(X\,^3\Sigma_g^-)$ + Kr$^+(^2P)$. Our calculations accurately describe this situation since we found I.P.(O_2) = 12.05 eV and I.P.(Kr) = 14.03 eV (which is to be compared to the 14.14 eV weighted average for Kr$^+(^2P_{3/2})$ and Kr$^+(^2P_{1/2})$) at the RCCSD(T)/ aug-cc-pV5Z level.

Now, when Kr attacks O_2^+, it can give rise to two possible electronic symmetries, $^2A'$ and $^2A''$, with the symmetry carrying π_g electron of O_2^+ in and out of the molecular (OOKr) plane, respectively. We searched for minima on both surfaces and our results are summarized on Table 1.

As a first observation, we see that bound KrO$_2^+$ complex structures were found on both $^2A'$ and $^2A''$ surfaces. This contrasts the Ramiro-Diaz et al.'s results stating that the $^2A'$ surface is totally repulsive.

At all levels the $^2A''$ minimum is lower by $\sim$0.004E_h than the corresponding $^2A'$, thus being the ground KrO$_2^+$ state, $\bar{X}\,^2A''$. Its binding energy with respect to the $O_2^+(X\,^2\Pi_g)$ + Kr(^1S) fragments was found 0.239 eV at the highest level of our calculations and it is identical with the estimated CBS limit. Including relativistic corrections does not practically affect this result as we obtain a binding energy of 0.240 eV and a very similar geometry at both aug-cc-pVQZ and aug-cc-pV5Z levels (see Table 1). This value is larger than the previously calculated of 0.173 eV [16]. Our D_e was further corrected for the zero point energy (ZPE) to obtain a D_0(Kr–O_2^+) = 0.223 eV which can be considered in fair agreement with the experimental estimation of 0.33 ± 0.1 eV by Jarrold et al. [4].

The weak bonding of Kr–O_2^+ is primarily attributed to electrostatic forces exercised by O_2^+ on the polarized Kr atom. However,
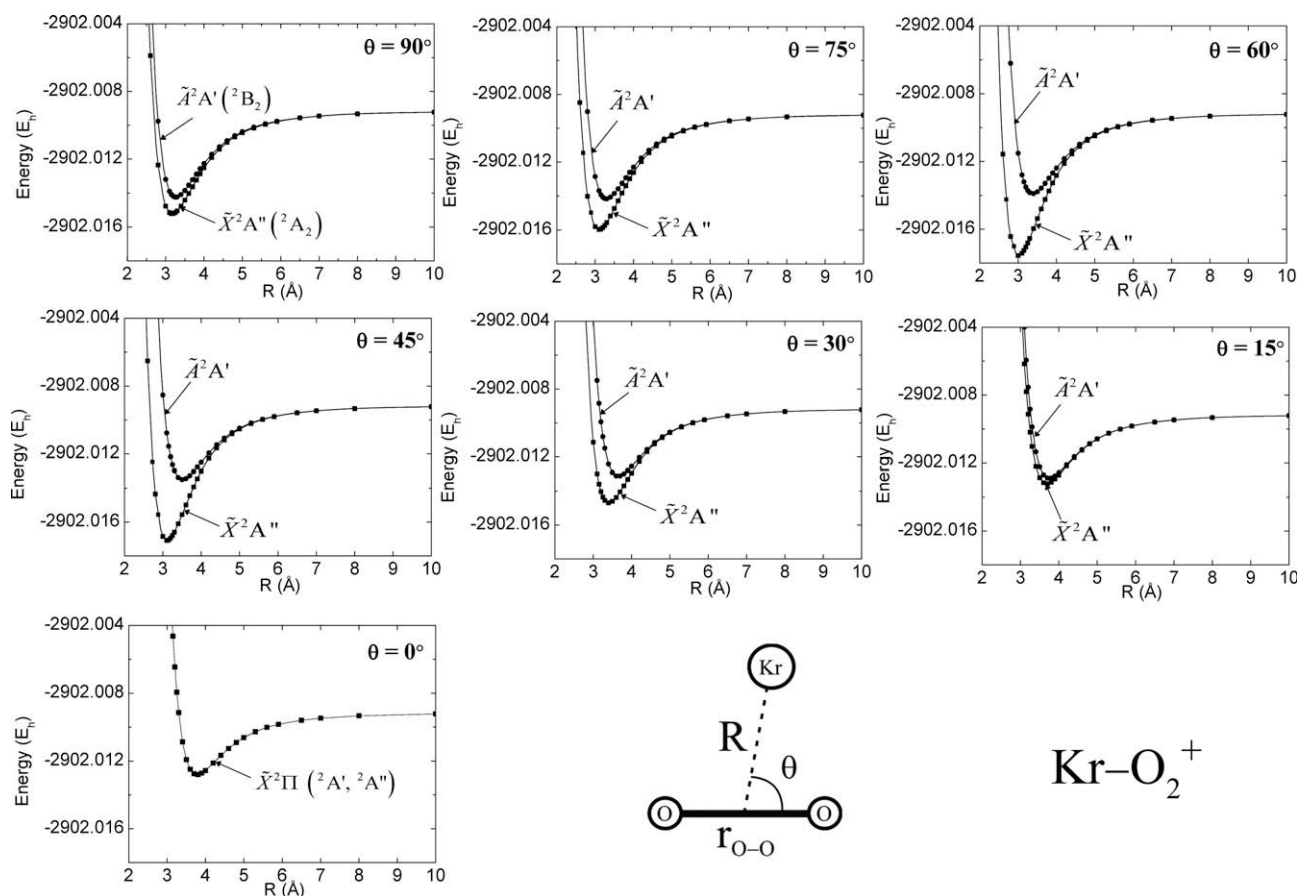
Fig. 1. Potential energy curves, cuts of the KrO$_2^+$ $\bar{X}\,^2A''$ and $\bar{A}\,^2A'$ surfaces resulting from the interaction of Kr(^1S) + $O_2^+(X\,^2\Pi_g)$, for different angles θ (see inset of attack. The r_{O-O} bond distance was always kept at the value 1.112 Å.

a pure electrostatic binding mode should lead to a C_{2v} KrO_2^+ geometry, which is not the case for the $\tilde{X}$ $^2A''$ minimum as we can see from Table 1. If we take a look at the Mulliken population analysis we find that approximately a population of $0.1e^-$ is transferred from Kr to the empty in-plane π_g orbital of O_2^+ adding some 'chemical' character to the bonding. This electron transfer is favored by a bent C_s geometry, the final configuration being the result of a balance between the two contributions, electrostatic and 'chemical'. The shortest Kr–O distance was found to be 2.705 Å at the aug-cc-pVQZ level, while the O–O distance is r_{O-O} = 1.124 Å very slightly longer than the corresponding calculated 1.112 Å value for the free O_2^+.

The skew geometry found above suggests a symmetric double minimum structure of the corresponding potential energy surface with a saddle-point of C_{2v} symmetry between the two minima. Indeed, a transition state was optimized at the aug-cc-pVQZ level with geometrical parameters r_{o-o} = 1.117 Å, R = 3.170 Å, and θ = 90.0°. The barrier for interconversion between the two minima was found 0.076 (aug-cc-pVQZ) and 0.075 eV (aug-cc-pV5Z). Taking into account and the ZPE correction these values become 0.059 and 0.058 eV, respectively.

Now, turning to the $\tilde{A}$ $^2A'$ minimum, we find from Table 1 that a C_{2v} geometry is adopted and this state should rather be dubbed $KrO_2^+(\tilde{A}\ ^2B_2)$. In the present case any electron transfer is blocked by the presence of one electron in the in-plane π_g orbital of O_2^+, thus rendering the bonding purely electrostatic. This is obvious from the net Mulliken charges on Kr, Table 1, which are almost zero. The $Kr-O_2^+$ binding energy was found at the CBS limit D_e = 0.139 eV, which is lower by 0.1 eV than the corresponding $\tilde{X}$ $^2A''$ value. The Kr–O distances are much longer, 3.311 Å, while the O–O bond length of 1.117 Å remains practically unchanged with respect to the free O_2^+ calculated value. Relativistic corrections yielded D_e values of 0.133 (aug-cc-pVQZ) and 0.135 eV (aug-cc-pV5Z) while leaving the geometry practically unchanged, Table 1. Including the ZPE corrections we finally obtain D_0 = 0.124 and 0.126 eV, respectively.

This short study concludes with the potential energy profiles of Fig. 1 representing the approach of the Kr atom to the $O_2^+(X\ ^2\Pi_g)$ entity for different angles of attack $\theta \equiv$ O(center of O–O)Kr (see inset of Fig. 1). For all curves the O–O bond distance was kept at the free O_2^+ equilibrium value of 1.112 Å. We can see that the two surfaces, $^2A''$ and $^2A'$, never cross, with the $^2A''$ one always being below $^2A'$. A degeneracy for the collinear, θ = 0°, approach is observed. In fact, the two states, $^2A'$ and $^2A''$, emerge as the two components of a Renner–Teller splitting of the linear KrO_2^+ $^2\Pi$ state when the molecule moves away from linearity. For all curves presented, and on the basis of the T1 diagnostic which always remained <0.02, we did not observe any avoided crossings with higher states of same symmetry.

We must note here that the potentials presented were not corrected for BSSE. At this level (aug-cc-pVQZ) the BSSE was calculated to be $\sim 1.5 \times 10^{-4} E_h$ (= $\sim$0.004 eV), which is $\sim$2% of the calculated binding energies and, in our opinion, cannot seriously affect the reliability of the potentials. This reliability was tested in ion mobility calculations employing a non-equilibrium molecular dynamics method described in Ref. [22] and very promising results to be published were obtained [23]. Numerical values of the potentials are available upon request.

4. Summary

We studied the interaction of $O_2^+(X\ ^2\Pi_g)$ with $Kr(^1S)$ using all electron RCCSD(T) calculations and high quality basis sets. Our results revealed the possibility for the system to form weakly bound complexes, evolving on the two possible potential energy surfaces of $^2A''$ and $^2A'$ symmetry. The ground state $KrO_2^+(\tilde{X}\ ^2A'')$ was found to be bound with D_e = 0.240 eV (D_0 = 0.223 eV) at the RCCSD(T)-DKH/aug-cc-pV5Z level of theory. It has a bent C_s geometry with the shortest Kr–O distance being 2.691 Å, the O–O bond slightly elongated by 0.01 Å, and the angle OOKr = 116.3°. The KrO_2^+ ($\tilde{A}$ $^2B_2$) minimum on the $^2A'$ surface has a binding D_e energy of 0.135 eV (D_0 = 0.126 eV) at the RCCSD(T)-DKH/aug-cc-pV5Z level, and a T-shaped C_{2v} geometry with the Kr–O distances 3.306 Å and the O–O distance practically unaffected.

Potential energy curves were constructed for different angles of approach for the two symmetries.

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