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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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$_2^+$ ($X ^2Π_g$) molecular cation. On both surfaces weakly bound KrO$_2^+$ complexes were found, namely KrO$_2^+$(X $^2A''$) and KrO$_2^+$(A $^2B_2$), with $D_e/D_h = 0.240 (0.223)$ and $0.135 (0.126)$ eV, respectively. Potential energy curves, slices of the $\tilde X ^2A''$ and $\tilde A ^2A'$ surfaces, are also presented.

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–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 $^2Π_g$) + 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-pVSZ 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 $D_e(n) = p_1 + p_2 \exp(-p_3n)$, 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 \( \text{O}^{+}_{2}(X^{2} \Pi_{g}) \) ion is produced by removing one of the two uncoupled \( \pi_{g} \) electrons from \( \text{O}_{2}(X^{3} \Sigma_{g}^{-}) \). This process requires 12.071 eV \[20\]. Taking into account that the Kr I.P. is 13.996 eV \[21\], the \( \text{O}^{+}_{2}(X^{2} \Pi_{g}) + \text{Kr}(1S) \) asymptotic channel is clearly energetically lower than \( \text{O}_{2}(X^{3} \Sigma_{g}^{-}) + \text{Kr}^{+}(2P) \). Our calculations accurately describe this situation since we found I.P.(\( \text{O}^{+}_{2} \)) = 12.05 eV and I.P.(Kr) = 14.03 eV (which is to be compared to the 14.14 eV weighted average for \( \text{Kr}^{+}(2P_{3/2}) \) and \( \text{Kr}^{+}(2P_{1/2}) \)) at the RCCSD(T)/aug-cc-pV5Z level.

Now, when Kr attacks \( \text{O}^{+}_{2} \), it can give rise to two possible electronic symmetries, \( 2A_{0} \) and \( 2A_{00} \), with the symmetry carrying \( \pi_{g} \) electron of \( \text{O}^{+}_{2} \) 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 \( 2A_{0} \) and \( 2A_{00} \) surfaces. This contrasts the Ramiro-Díaz et al.’s results stating that the \( 2A_{0} \) surface is totally repulsive. At all levels the \( 2A_{00} \) minimum is lower by 0.004 eV than the corresponding \( 2A_{0} \), thus being the ground KrO\(^{+}_{2} \) state, \( \sim X^{2}A_{00}^{0} \). Its binding energy with respect to the \( \text{O}^{+}_{2}(X^{2} \Pi_{g}) + \text{Kr}(1S) \) 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 \( D_{0}(\text{Kr}^{+}/C_{0}\text{O}^{+}_{2}) = 0.223 \) 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 \( \text{O}^{+}_{2} \) on the polarized Kr atom. However, 12.071 eV \[20\].
a pure electrostatic binding mode should lead to a C\textsubscript{2v}, KrO\textsubscript{2} geometry, which is not the case for the $X^2\text{A}^\prime$ 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 0.1 e\textsuperscript{-} is transferred from Kr to the empty in-plane p\textsubscript{g} orbital of O\textsubscript{2}, adding some ‘chemical’ character to the bonding. This electron transfer is favored by a bent C\textsubscript{2v} 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\textsubscript{2}.

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

Now, turning to the $\tilde{A}$–$\tilde{A}$ minimum, we find from Table 1 that a C\textsubscript{2v} geometry is adopted and this state should rather be dubbed KrO\textsubscript{2}($\tilde{A}$ $^2\text{B}_2$). In the present case any electron transfer is blocked by the presence of one electron in the in-plane p\textsubscript{g} orbital of O\textsubscript{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\textsubscript{2} binding energy was found at the CBS limit $D_B = 0.139$ e\textsuperscript{V}, which is lower by 0.1 e\textsuperscript{V} than the corresponding $X^2\text{A}^\prime$ value. The Kr–O distances are much longer, 3.311 Å, while the O–O bond length of 1.117 Å remains practically unchanged.

4. Summary

We studied the interaction of O\textsubscript{2}($X^2\text{I}_\text{g}$) with Kr($^1\text{S}$) 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 $^1\text{A}^\prime$ and $^3\text{A}^\prime$ symmetry. The ground state KrO\textsubscript{2}($X^2\text{A}^\prime$) was found to be bound with $D_B = 0.240$ e\textsuperscript{V} ($D_\theta = 0.223$ e\textsuperscript{V}) at the RCCSD(T)-DKH/aug-cc-pV5Z level of theory. It has a bent C\textsubscript{2v} 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\textsubscript{2}($\tilde{A}$ $^2\text{B}_2$) minimum on the $2\text{A}^\prime$ surface has a binding $D_\theta$ energy of 0.135 e\textsuperscript{V} ($D_\theta = 0.126$ e\textsuperscript{V}) at the RCCSD(T)-DKH/aug-cc-pV5Z level, and a T-shaped C\textsubscript{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.

References