A calculated $(\text{KrO}_2)^+$ ground-state potential energy surface

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Configuration interaction calculations have been undertaken in a basis of a thousand projected-valence-bond state functions for 1400 points of the $(\text{KrO}_2)^+$ ground-state potential energy surface. The calculations involve an l -dependent pseudo-potential for Kr and resort to diagonal corrections of the Hamiltonian matrix prior to CI. The computed dissociation energy (0.13 eV) is smaller than the inferred from photodissociation data (0.33 eV) and the potential surface differs in many respects from the previous empirical ones.

1. Introduction

Interest in the $(\text{KrO}_2)^+$ cluster ion has arisen from a variety of work; photodissociation measurements [1] charge-transfer collision [2], half-collision [1] studies, and the investigation of vibrational deactivation in thermal O_2^+/Kr collisions [3–7]. The rationalization of related data requires a good knowledge of the $(\text{KrO}_2)^+$ ground-state potential energy surface. The first information on characteristics of this potential surface was provided by Jarrold et al. [1] who estimated the dissociation energy, $D_0^0(\text{Kr}-\text{O}_2^+) \approx 0.33$ eV (± 0.1 eV). This value was deduced from the assignment of structures in the product kinetic energy distributions for the photodissociation of $(\text{Kr}-\text{O}_2)^+$ to $\text{Kr}^+ (^2\text{P}_{3/2})$ ions flying off of $\text{O}_2(X^3\Sigma_g^-)$ molecules in specific vibrational states. The geometry of the $(\text{Kr}-\text{O}_2)^+$ ground state was also inferred from the fit by an impulsive model [8] of the photoproducts angular distributions [1];

a bent geometry with a bond angle $135^\circ < \theta(\text{O}-\text{O}-\text{Kr}) \approx 139^\circ < 143^\circ$ was thus proposed. Taking these features into account, empirical potential energy surfaces have thereafter been tried by Tosi et al. [4,5] and later by Ramachandran and Ezra [7] in order to understand the “anomalous” behaviour of the

vibrational quenching in the $5 \times 10^{-3} \text{ eV} < E < 5 \text{ eV}$ energy range [3–7]. The present Letter reports independent information from projected-valence-bond configuration interaction (PVB-CI) calculations on $(\text{KrO}_2)^+$. As briefly recalled in section 2 we follow the procedure of ref. [9] which consists of using configuration interaction (CI) calculations of moderate sizes, < 1000 configuration state functions, preceded by diagonal corrections of the relevant PVB Hamiltonian matrix. The reported results on the $(\text{KrO}_2)^+$ ground state are part of a more extensive set of data on the twenty low-lying A' and A'' states that are relevant for the study of the $\text{Kr}^+ + \text{O}_2 \leftrightarrow \text{Kr} + \text{O}_2^+$ charge transfer. The complete account of the results will be the subject of an other publication.

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2. Method

The $(\text{KrO}_2)^+$ system is described by using a superposition of valence-bond (VB)-type $\text{Kr}^{(*)}-\text{O}_2^{(*)}$ and $\text{Kr}^{(*)}-\text{O}_2^{+(*)}$ configuration state functions (CSF). The considered VB-CSFs are built from occupied and virtual self-consistent field (SCF) orbitals of the neutral species in their ground state. In the PVB method the orbitals are first orthonormalized before building the CSFs [9–11]. Here, the orbitals are orthonormalized by a Schmidt procedure in the following order:

a': $1\sigma_g 1\sigma_u 2\sigma_g 2\sigma_u 4s 3\sigma_g 1\pi_u 4p^x 4p^y$

$-1\pi_g 3\sigma_u \text{VO}(\text{O}_2) \text{VO}(\text{Kr})$,

a'': $1\pi_u 4p^y 1\pi_g \text{VO}(\text{O}_2) \text{VO}(\text{Kr})$.

In this orbital list, diatomic MO labels refer to O_2 while AO labels refer to Kr, $\text{VO}(\text{O}_2 \text{ or Kr})$ is the respective set of virtual orbitals, superscripts z and x refer to the $4p$ orbitals lying in the triatomic plane (zOx). Inner orbitals of Kr do not appear in the list because we use an l -dependent *ab initio* pseudo-potential [12,13] to represent the effect on the Kr^{8+} core.

The SCF orbitals are expanded over contracted Gaussian basis functions (CGTO). Dunning's [11,6/5,4] CGTO basis [14] plus a d polarization orbital ($\zeta_d=0.8$) [15] are used for each O atom while the [3,3/1,1] CGTO basis of Hay et al. [13] plus a d polarization orbital ($\zeta_d=0.14$) are used for Kr. The dipole polarizability of Kr, calculated at the SCF level by placing the atom in the field a bare charge, is thus found to be $\alpha = 14.9$ au, in good accord with the experimental value of 16.75 au [16]. This shows that the reported calculations are able to reproduce, within 10%, the long-range ion-induced-dipole attraction invoked in the discussion of the dynamics of the $\text{Kr}-\text{O}_2^+$ interaction [7,17].

Following the view of our earlier work [9] on $(\text{HO}_2)^+$ the CSFs included in the present PVB-CI scheme aim at describing (i) the interaction between the Kr^+ (or Kr) and O_2 (respectively O_2^+) subsystems, and (ii) the interaction within each subsystem itself. (i) has to do essentially with both the *polarization* of each neutral by the corresponding ion and *electron transfer* from the neutral to the ion. The

latter is the basic constituent of the invoked strong *chemical bonding* between Kr and O_2^+ [7]. The $1\pi_g \leftrightarrow 4p$ (HOMO/LUMO) electron transfer put forward qualitatively by Jarrold et al. [1] is but one of the contributions to this bonding. Our calculations also take provision of CSFs, accounting for $3\sigma_g$ and $1\pi_u \leftrightarrow 4p$ electron transfers which were found to be important in the description of the $(\text{HO}_2)^+$ potential well [9]. (ii) has to do, among other things, with the correct dissociation of the O_2/O_2^+ states into proper atomic states when stretching the O–O bond; it also enables one to describe distortions of the relevant valence shells with a unique set of SCF orbitals. The CSF generation scheme of ref. [9] was designed to cope with these objectives and was thus followed closely. It basically consists of full valence CI+single excitations to virtuals. In this scheme the $3\sigma_u$ orbital is considered to belong to the valence shell of O_2/O_2^+ . All inner orbitals up to $4s$ in the above a' list were fully occupied. Thus the essential difference between the present $(\text{KrO}_2)^+$ CSFs and those described in ref. [9] lies in the electronic configuration of the Kr^+ ion as compared to a bare proton. Therefore only the related alterations need to be specified. These actually concern CSF-types E1 (a), (b) of ref. [9] which describe $\text{Kr}^+-\text{O}_2^{(*)}$. The $\text{O}_2^{(*)}$ excitations in this set – i.e. full-valence CI and one-electron excitations into $\text{VO}(\text{O}_2)$ – are now accompanied by all allowed arrangements of five electrons in the $4p^{x,y}$ orbitals. Moreover, new CSF types are considered which describe the O_2 ground state configuration in the presence of an excited Kr^+ ion, that is, all single excitations $4p \rightarrow \text{VO}(\text{Kr})$ with proper rearrangement of the remaining four electrons in the $4p$ shell. The total number of CSFs is slightly less than 950 CSFs in either A' or A'' symmetries.

Before performing the CI step, diagonal elements of the electronic Hamiltonian in the above PVB-CSF bases are rectified. Of the two types of adjustments discussed in ref. [9] only the one which misplaced energy levels of the separated partners was required. Admittedly these corrections are intended to palliate the limited size of orbital or CSF expansion bases which make the calculations tractable [9]. They are introduced to reproduce the actual shape of an O_2 potential curve (say $\text{O}_2(\text{X } ^3\Sigma_g^-)$) relative to its O+O dissociation limit and to fix the relevant $\text{Kr}^+-\text{O}_2^{(*)}$ and $\text{Kr}-\text{O}_2^{+(*)}$

asymptotes, for infinite intermolecular distances, as possible to their exact placing relative to this curve. By ensuring exact $O_2^{(*)}/O_2^{+(*)}$ equilibrium properties as well as ionization potentials and excitation energies of both partners we are thus confident that the above CSF selection scheme is capable of accounting for the most important effects contributing to the $Kr-O_2^+$ bonding at interparticle distances larger than $4-5 a_0$. The mentioned adjustments are actually carried out along general lines described in ref. [9]. They concern not only states which are easily transcribed from that work by the mere replacement $H^+ \leftrightarrow Kr^+$ but also concern $Kr^+ + O_2^{(*)}$ in low-lying singlet states: $^1\Delta_g$, $^1\Sigma_g^+$, $^1\Sigma_u^+$, $^1\Pi_u$. Wherever needed in these adjustments, the exact Kr ionization potential has been adjusted to remove the $^2P_{3/2}-^2P_{1/2}$ spin-orbit splitting of Kr^+ ,

$$IP(Kr) = \frac{1}{3} [2E(Kr^+ ^2P_{3/2}) + E(Kr^+ ^2P_{1/2})] - E(Kr ^1S).$$

All calculations have been achieved using the joint MOLECULE-ALCHEMY program^{#1} adapted in two ways: firstly by inserting calls to Kolar's program [18] in the one-electron integral evaluation state to compute matrix elements of the Hay et al. [12] pseudo-potentials and secondly by allowing the aforementioned corrections to be made prior to CI.

3. Results

Adiabatic $^2A'$ and $^2A''$ potential energy surfaces (PES) have been computed for eleven O-O bond distances: $r(a_0) = 2.05, 2.11, 2.2, 2.28, 2.5, 3, 3.5, 4, 5, 6, 7$; eighteen Kr-O₂ (center of mass to center of mass) distances: $2.5 a_0 \leq R \leq 9 a_0$ and seven equally spaced relative angles (r, R): $0^\circ \leq \gamma \leq 90^\circ$. The various relative distances and angles used in this paper are defined in fig. 1.

We restrict ourselves in this Letter to the lowest

^{#1} The joint MOLECULE-ALCHEMY program incorporates the MOLECULE integral program and the ALCHEMY chain of programs. MOLECULE was written by D.J. Almlöf at the University of Uppsala, Sweden; ALCHEMY was written by A.D. McLean, M. Yoshimine, P.S. Bagus and B. Liu of the IBM San Jose Research Lab. The interfacing of these programs was performed by U. Wahlgren and P.S. Bagus at IBM.

Fig. 1. Definition of the relative distances and angles used in the text.

potential energy surface which actually correlates with $Kr(4p^6 ^1S) + O_2^+(X ^2\Pi_g)$. As could have been anticipated on qualitative grounds [1], this surface has $^2A''$ symmetry. The minimum of the calculated $1 ^2A''$ surface is found, by interpolation of the calculated points, to lie at

$$R_m = 5.89 a_0, \quad r_m = 2.11 a_0,$$

$$\gamma_m = 49.8^\circ \quad (\text{that is } \theta_m(O-O-Kr) = 121.4^\circ),$$

$$V_m = -0.133 \text{ eV}.$$

The potential minimum V_m is measured relative to the bottom of the $Kr-O_2^+$ asymptotic curve ($R \rightarrow \infty$, $r_c = r_m$, $\forall \gamma$). A perspective view of the ground-state PES at $\gamma = 45^\circ$ is presented in fig. 2. Fig. 2 clearly shows a broadening of the O_2^+ well with the approach of the Kr atom. This feature is most pronounced for $30^\circ \leq \gamma \leq 60^\circ$ but is also perceptible at

Fig. 2. Perspective view of a cut of the $1 ^2A''$ ground state potential energy surface of $(KrO_2)^+$ for $\gamma = 45^\circ$. The origin of energies is taken to be the $Kr + O_2^+(r=r_c)$ asymptote. Contour lines for negative values of the potential start at -0.005 au and are spaced by 0.001 au. Contour lines for positive values of the potential are spaced by 0.01 au.

Fig. 3. Cuts of the $1^2A''$ ground state potential energy surface of $(\text{KrO}_2)^+$ for various values of γ and (a) $r=2.11 a_0$ and (b) $r=2.5 a_0$. All curves are referred to the $\text{Kr} + \text{O}_2^+$ ($r=r_e$) asymptote.

the other angles. Figs. 3a and 3b display slices of the $1^2A''$ PES for two bond distances $r=2.11 a_0$, and $2.5 a_0$ (respectively) and given values of γ . It is clearly seen that the previously mentioned broadening of the O_2^+ well arises from the deepening of the interaction potential,

$$U(R, r, \gamma) = V(R, r, \gamma) - V(R \rightarrow \infty, r, \forall \gamma),$$

when the Kr atom approaches a stretched O_2^+ molecule ion. Obviously, it is this bond length depen-

Fig. 4. Contour plots of cuts of the $1^2A''$ ground state potential energy surface of $(\text{KrO}_2)^+$ for $r=2.28 a_0$. An (R, γ) polar representation is used where $\gamma=0$ along the abscissa axis and $\gamma=90^\circ$ along the ordinate axis. The scales on the axes are in atomic units of distance. (a) Present calculation, (b) empirical surface of ref. [4].

dence that causes vibrational transitions to occur. Figs. 3 and 4a illustrate the strong anisotropy of the calculated potential energy surface.

Considering our R, r, γ grid the above value of $|V_m|$

should be close to the actual minimum of the $1^2A''$ PES. This value differs from that proposed by Jarrold et al. [1] (0.33 ± 0.1 eV) by nearly one vibrational quantum of O_2 (0.196 eV) [19]. This indicates that a shift of the vibrational state assignments of ref. [1] by one unit can eliminate the mentioned discrepancy; this possibility is not excluded by the data at hand. The discrepancy of $\approx 18^\circ$ between the calculated bond angle $\theta_m(O-O-Kr) = 121.4^\circ$ and that proposed by Jarrold et al. [1] (139°) should not be taken too seriously in view of the approximations that were required to extract the latter value from the photodissociation data.

In conclusion, it will be interesting to see to what extent the presently calculated PES, which differs markedly in many respects from the previously used empirical potentials [4–7] (see e.g. fig. 4), is able to account for the $O_2^+(\nu=1) + Kr$ deactivation data [3–7] and to what extent the neglect of the $1^2A'$ potential is thereupon legitimate.

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