

Ground and excited state adiabatic ${}^2A''$ and ${}^2A'$ potential energy surfaces of the $(\text{Kr}-\text{O}_2)^+$ cluster ion

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The seven lowest adiabatic potential energy surfaces (PES) of the $(\text{Kr}-\text{O}_2)^+$ cluster ion in each of the ${}^2A''$ and ${}^2A'$ symmetries are calculated. The computational method involves configuration interaction calculations in a basis of a thousand projected valence-bond state functions. It resorts to diagonal corrections of the Hamiltonian matrix prior to configuration interaction and makes use of an l -dependent pseudopotential for Kr. The results are characterized by the shallowness of the $1\ {}^2A''$ potential well and the absence of wells in the other PES investigated. The $1\ {}^2A''$ equilibrium characteristics differ significantly from those proposed in other work. Notable effects on all the PES are observed when the O–O bond is stretched beyond $2.5a_0$. No $1\ {}^2A' - 2\ {}^2A'$ (nor $1\ {}^2A'' - 2\ {}^2A''$) pseudocrossings are found that could explain, on the basis of mere electronic structure arguments, the available thermal energy charge transfer data. A $2\ {}^2A'' - 1\ {}^2A'$ crossing actually exists but the related Coriolis coupling mechanism cannot be invoked for low energy <1 eV encounters. This draws attention to alternative more subtle dynamic charge transfer mechanisms possibly involving quartet-doublet spin–orbit transitions and/or (near) degeneracies of rovibronic, instead of mere electronic, energy levels. Evidence is shown for pseudocrossing mechanisms of population sharing between the $2,3A''$ and $2A'$ states. Similar evidence is shown for an $\text{O}_2(X\ {}^3\Sigma_g^-) \rightarrow \text{O}_2(a\ {}^1\Delta_g)$ excitation involving two electron rearrangement. © 1996 American Institute of Physics. [S0021-9606(96)03101-8]

I. INTRODUCTION

Today's knowledge on (heavy rare-gas O_2)⁺ cluster-ion systems comes mainly from a variety of scattering¹ and photodissociation² experiments. The qualitative and quantitative understanding of the related data calls for a good knowledge of several low lying potential energy surfaces (PES) of these systems. So far, only tentative estimates of these PES exist whose reliability is difficult to assess.^{1–5} These estimates consist of qualitative guesses,^{1,2} fragmentary diatomic in molecules descriptions,³ predictions of asymptotic theory,⁴ or *ad hoc* parametrization.⁵ The need for a better founded determination of the PES of (heavy rare-gas O_2)⁺ systems is the first incentive to undertake the present work.

In a previous contribution⁶ we have reported projected valence bond (PVB) configuration interaction (CI) calculations on the $1\ {}^2A''$ ground state PES of the $(\text{Kr}-\text{O}_2)^+$ system. The present article is devoted to several of its ${}^2A''$ and ${}^2A'$ excited states. The objective of this work is twofold. First, it aims at making available indispensable information for dynamics calculations on^{1,5} (1) $\text{O}_2^+(v=1) + \text{Kr} \rightarrow \text{O}_2^+(v=0) + \text{Kr}$ vibrational quenching and (2) $\text{Kr}^+ + \text{O}_2(v) \rightarrow \text{Kr} + \text{O}_2^+(v)$ or $\text{Kr}^+ + \text{O}_2^*(v')$ vibronic charge transfer and excitation. Second, it allows one to examine, on the basis of quantitative information, the cogency of electronic transition

mechanisms based on PES crossings as invoked in earlier work to interpret experimental findings.^{1,2} Further, it suggests the opening of new investigation tracks. Only adiabatic PES are reported here. At the present stage of our study, regions of strong nonadiabatic behavior that may come into play in eventual electronic transitions are traced by inspecting “pinchings” of the energy differences between states of like symmetry (Sec. III); those pinchings locate zones of avoided PES crossings. Actual $A' - A''$ crossings are also traced owing to their possible implication in inducing electronic transitions via Coriolis coupling.⁷

The present investigation of the $(\text{Kr}-\text{O}_2)^+$ system could not be undertaken without a precursor work⁸ on $(\text{H}-\text{O}_2)^+$ which served as a prototype to evaluate approximate techniques for the determination of the PES of complicated ion-molecule charge transfer systems. One important difficulty of the considered systems arises from the $\text{O}_2^{(+)}$ group which would require tremendous computational effort if it were to be handled by strict *ab initio* means. This is due to the necessity to treat, with the same high accuracy, the ground state and a few low lying valence states of both the neutral and ionized O_2 molecule in the triatomic environment. If this task can, only just, be achieved for the isolated diatomics it becomes prohibitive for systematic studies of the (rare gas O_2)⁺ systems of interest. The approach of Ref. 8 was designed to make quantum chemistry technology manageable in such circumstances at the expense of some compromise with the strict observance of *ab initio*'ism. It resorts to *ad*

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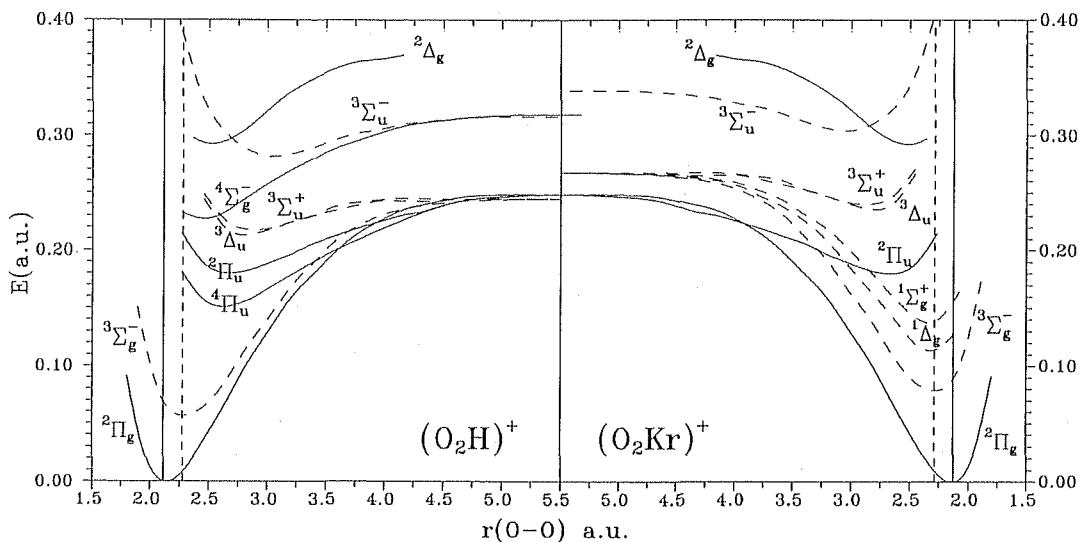


FIG. 1. Comparison of the exact relative energy disposition of the relevant potential energy curves for the $(\text{H}-\text{O}_2)^+$ and $(\text{Kr}-\text{O}_2)^+$ systems for infinite relative atom molecule distance.

hoc corrections of the Hamiltonian matrix prior to CI to palliate known deficiencies of limited basis set (orbital or configuration state function) expansions for the separate atomic or diatomic fragments. Here we use one of the two methods proposed in Ref. 8 to overcome the mentioned difficulties in the treatment of the O_2^+ group. This is done (Sec. II) in combination with a pseudopotential method that drastically simplifies the description of the Kr partner in the system.

Our choice of $(\text{Kr}-\text{O}_2)^+$ as the first system to be investigated among the (rare-gas O_2)⁺ cluster ions has another relation to the work of Ref. 8. Due to the closeness of the ionization potentials (IP) of H and Kr (0.5 and 0.5225 a.u., respectively)⁹ it seemed, at first sight, that the characteristics of the $\text{H}^+ + \text{O}_2 \leftrightarrow \text{H} + \text{O}_2^+$ and $\text{Kr}^+ + \text{O}_2 \leftrightarrow \text{Kr} + \text{O}_2^+$ charge transfer interactions¹⁰ would be similar in the two systems thereby entailing some similarity of their PES. Actually, there are a few specifics of the two systems which let one anticipate significant differences. Electron-electron (Coulomb and Pauli) repulsion between the Kr^+ and O_2^+ ion cores is an important feature that did not exist in the previously studied $(\text{H}-\text{O}_2)^+$ system. This repulsion is expected to manifest itself near $2-3a_0$, that is, right in the region where a sizeable potential well appeared for the lowest states of $(\text{H}-\text{O}_2)^+$. The competition between those repulsions and chemical bond formation as a result of electron transfer and delocalization is a subtle effect that can hardly be estimated on the basis of rough qualitative grounds and thereby justifies calculations such as those reported here. Another aspect of a Kr partner, as compared to an H partner, is that the active atomic electron participating in the charge transfer is one of six equivalent $4p_{\text{Kr}}$ electrons. Two in-plane ($4p_{\text{Kr}}^x, z; a'$) orbitals and one out-of-plane ($4p_{\text{Kr}}^y; a''$) orbital may therefore come into play as compared to the single in-plane ($1s_{\text{H}}$) orbital involved in $(\text{H}-\text{O}_2)^+$. Aside from related geometry effects on chemical bond formation² this has the effect (Sec. II) of increasing the number of states to be con-

sidered in the CI calculation by a factor of 2-3 as compared to what sufficed in $(\text{H}-\text{O}_2)^+$.

In the present paper we consider exclusively doublet spin states of $(\text{Kr}-\text{O}_2)^+$. For the time being, higher spin multiplicities have not been considered because they do not arise from $\text{Kr}(^1\text{S}) + \text{O}_2^+(^2\Pi_g)$, the reactant or product channel of the charge transfer reaction with partners in their ground states. The considered doublet spin multiplicity puts constraints on the states of the separated partners which are allowed to mix at finite atom-molecule separations (Fig. 1). As will be seen in Sec. III—another important difference between $(\text{H}-\text{O}_2)^+$ and $(\text{Kr}-\text{O}_2)^+$ also arises from these constraints especially as concerns the disappearance in the latter case of the $\text{O}_2^+(^4\Pi_u, ^4\Sigma_g^-)$ contributions.

II. TECHNICAL DESCRIPTION OF THE CALCULATIONS

Throughout the present work we have followed one of the two approximate PVB-CI procedures described in Ref. 8. Several details of the procedure have been presented in Ref. 6. Here we outline features of the calculations which differ from those of the $(\text{H}-\text{O}_2)^+$ case.⁸

The first difference with the work of Ref. 8 relates to the single and multielectron nature of H and Kr, respectively. The possibility of handling the few thousand geometries investigated in this work owes to our actual use of a pseudopotential for Kr. The 28 electrons of the Kr^{3+} core are replaced by an l -dependent pseudopotential¹¹ whose form and parametrization have been worked out by Hay *et al.*¹² The computer routines provided by Kolar¹³ have been interfaced with the MOLECULE-ALCHEMY program¹⁴ in order to evaluate the one-electron pseudopotential integrals and merge them with one-electron integral inputs of standard calculations.

Another difference with Ref. 8 relates to the orbital list of the separated partners which is used to build the valence-

bond-type configuration state functions (CSF). Within the PVB framework,¹⁵ these orbitals are Schmidt orthonormalized in the following order:

$$a': 1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, 4s, 3\sigma_g, 1\pi_u, 4p^z, 4p^x, \\ 1\pi_g, \text{VO}(\text{O}_2), \text{VO}(\text{Kr}), \quad (1a)$$

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

In these lists molecular orbital (MO) labels refer to O₂ while atomic orbital (AO) labels refer to Kr. MO's and AO's are obtained from independent self-consistent-field (SCF) calculations on the separate neutral partners in their respective ground states. VO (O₂ or Kr) are corresponding sets of virtual orbitals. The orbital order in Eq. (1) is that of increasing SCF binding energy. Superscripts *z*, *x* refer to 4*p* orbitals lying in the triatomic plane while superscript *y* refers to the corresponding out-of-plane orbital. In the calculations the O₂ molecule lies along the *oz* axis. The changes with respect to the corresponding lists in Ref. 8 are the insertion of the 4*s* AO between the indicated O₂ MO and the appearance of three (4*p^{z,x,y}*) AO's instead of one (1*s_H*) between the 1π_u and 1π_g MO's.

The orbitals are expanded in terms of contracted sets of Gaussian orbitals: Dunning's [11,6/5,4] basis¹⁶ plus polarization ($\zeta_d=0.8$) is used for each O atom while the [3,3/1,1] basis of Hay *et al.*¹² plus polarization ($\zeta_d=0.14$) is used for Kr. CSF's are built from the previous orbital lists to form the basis of a CI calculation. The considered CSF types are as follows.

(1) Full valence CI (FVCI) for the eight outer electrons of O₂ and simultaneous FVCI for Kr⁺. The corresponding arrangements are designated by

$$3\sigma_g^2, 1\pi_u^4, 1\pi_g^2 \rightarrow 3\sigma_g, 1\pi_u, 1\pi_g, 3\sigma_u, \\ 4p^5 \rightarrow 4p.$$

(2) Single excitation of the eight outer electrons of O₂ to virtuals and simultaneous FVCI for Kr⁺:

$$3\sigma_g^2, 1\pi_u^4, 1\pi_g^2 \rightarrow \text{VO}(\text{O}_2), \\ 4p^5 \rightarrow 4p.$$

(3) FVCI of the seven outer electrons of O₂⁺ keeping Kr in its ground state configuration

$$3\sigma_g^2, 1\pi_u^4, 1\pi_g \rightarrow 3\sigma_g, 1\pi_u, 1\pi_g, 3\sigma_u.$$

(4) Single excitations to virtuals of the seven outer electrons of O₂⁺ keeping Kr in its ground state configuration

$$3\sigma_g^2, 1\pi_u^4, 1\pi_g \rightarrow \text{VO}(\text{O}_2).$$

(5) Single excitation of Kr keeping O₂⁺ in its ground state configuration

$$4p^6 \rightarrow \text{VO}(\text{Kr})$$

(6) Single excitations of Kr⁺ keeping O₂ in its ground state configuration

$$4p^5 \rightarrow \text{VO}(\text{Kr}).$$

The total number of CSF's is slightly less than 950 in both ²A'' and ²A' symmetries. Changes with respect to Ref. 8 essentially concern the CSF types (1), (2), and (6) which involve the 4*p*⁵ electrons of the Kr⁺ ion core.

The lack of valence CI for O₂⁺ CSF's of type (5) and (6) is likely to affect the description of O₂⁺+Kr* and O₂+Kr⁺* states when stretching the O–O bond, say, beyond 3*a*₀. Inasmuch as the Kr* and Kr⁺* states lie high up in energy (>10 eV) the aforementioned CSF's come into play only in polarisation distortions of the low lying states of interest when the O–O bond breaks. This means that the reactive part of the PES describing O⋯(O–Kr)⁺ or O⁺⋯(O–Kr) may be inadequately described.

A shift procedure, described in Ref. 8, is applied prior to the CI to diagonal elements of the electronic Hamiltonian matrix in the above PVB-CSF basis. Of the two types of corrections discussed in Ref. 8 only the one which adjusts misplaced energy levels of the separated partners to their exact positions is made. No attempt to correct CSF energies of type (5) and (6) is made for reasons just stated in the preceding paragraph. As pointed out in Refs. 6 and 8, the mentioned shift procedure is intended to palliate the limited size of orbital or CSF expansion bases which makes the calculations tractable. It ensures that the actual shape of the O₂(X³Σ_g⁻) potential curve relative to its O+O asymptote is reproduced and it fixes the relevant Kr⁺+O₂^(*) and Kr+O₂^(*) asymptotes, for infinite intermolecular separation, the closest possible to their exact placing relative to this curve (Fig. 1).

In the reported calculations the spin-orbit effect of Kr has been ignored. Wherever needed when applying the above shift procedure, the Kr ionization potential extracted from the Kr⁺(²P_{3/2,1/2}) limits was taken to be:⁹ IP(Kr)=0.5225 a.u. This exact value of IP(Kr) may be compared with the noncorrected one: 0.513 a.u. resulting from the relevant 17-state CI in the separated partner limit. This comparison is indicative of the size of the shift correction for Kr.

III. RESULTS AND DISCUSSION

To present the results we use the set of Jacobi coordinates representing, respectively, the O–O bond distance (*r*), the Kr–O₂ center of mass to center of mass distance (*R*) and the related (**r**,**R**) angle (*γ*). With this choice *γ*=0° or 180° correspond to collinear geometries while *γ*=90° corresponds to the T-shape geometry. Thus, for symmetry reasons one only needs to investigate the range 0° ≤ *γ* ≤ 90°.

²A' and ²A'' adiabatic PES have been obtained for a few thousand geometries in the following ranges of the *r*, *R*, *γ* coordinates:

$$r(a_0): 1.8, 1.9, 2.05, 2.11, 2.2, 2.28, 2.5, 3, 3.5, 4, 5, 6,$$

$$0 \leq R(a_0) \leq 10 \quad \text{with a step } \Delta R = 0.25a_0,$$

$$0^\circ \leq \gamma \leq 90^\circ \quad \text{with a step } \Delta \gamma = 15^\circ.$$

This *r*, *R*, *γ* grid covers a broader sample of geometries than that considered in our earlier account of the results for the

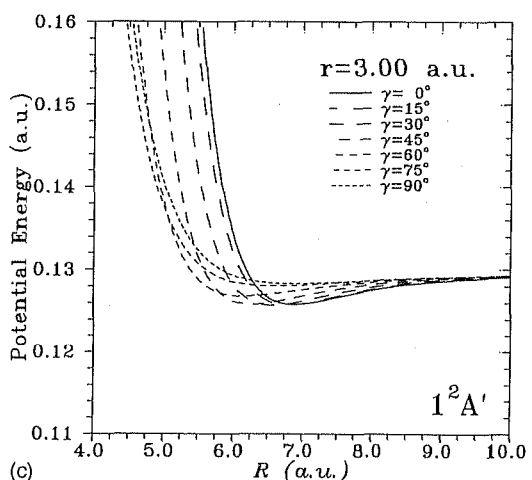
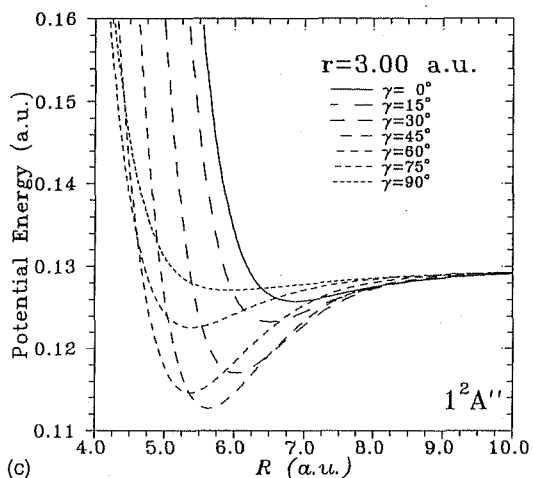
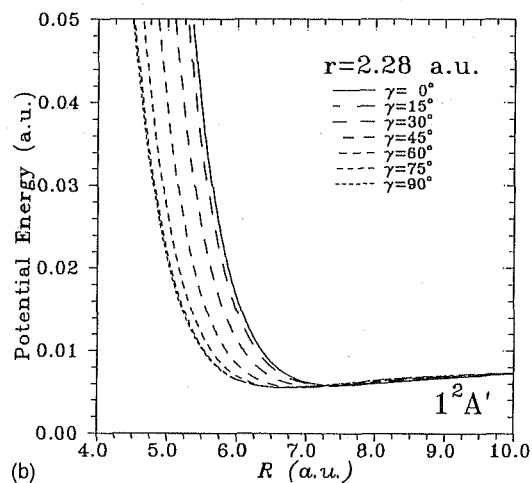
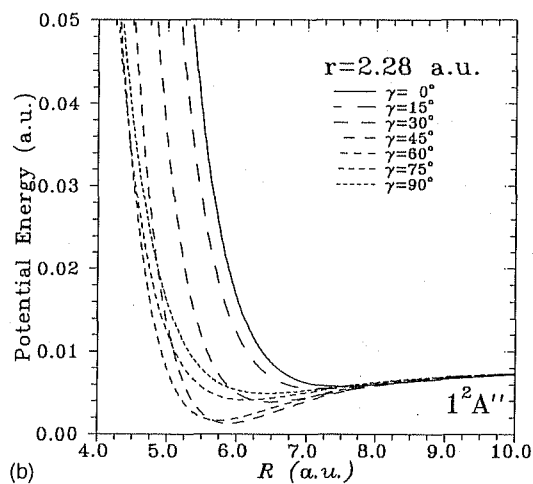
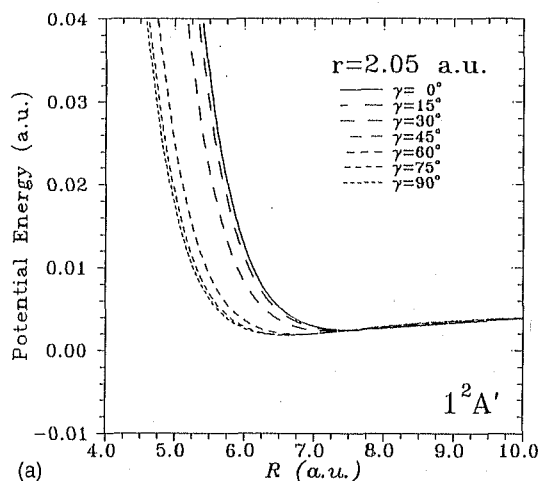
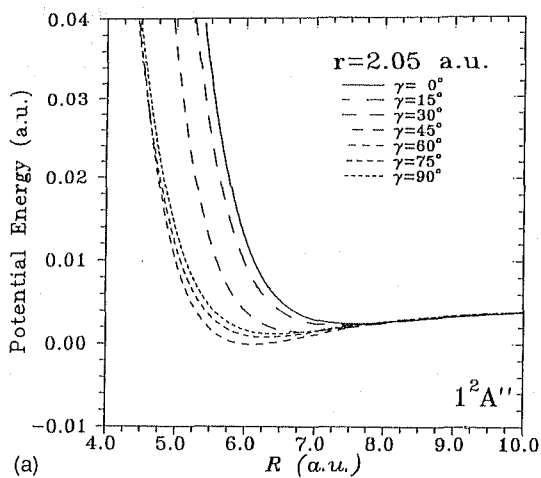


FIG. 2. Cuts of the $1^2A''$ ground state potential energy surface of $(\text{Kr}-\text{O}_2)^+$ for various values of γ and (a) $r=2.05a_0$; (b) $r=2.28a_0$; (c) $r=3a_0$. All curves are referred to the $\text{Kr}+\text{O}_2^+(r=r_e)$ asymptote. These data complement those provided for other r values in Ref. 6.

FIG. 3. Cuts of the $1^2A'$ potential energy surface of $(\text{Kr}-\text{O}_2)^+$ for various values of γ and (a) $r=2.05a_0$; (b) $r=2.28a_0$; (c) $r=3a_0$. The origin of energies is the same as in Fig. 2.

$1^2A''$ ground state.⁶ Samples of the results are presented in Figs. 2–5 for some low lying states in each symmetry. The reported information complements and extends our earlier data of Ref. 6. The PES have been obtained in the general C_s symmetry point group. Accordingly, the calculations do not distinguish symmetries other than $^2A'$ and $^2A''$; hence, for

the limiting geometries, $C_{\infty v}$ ($\gamma=0^\circ$) and C_{2v} ($\gamma=90^\circ$), states of different symmetries which correlate with one of the two C_s irreducible representations are not allowed to cross. Throughout, the cuts of the PES displayed for fixed r and γ are obtained as three-dimensional cubic spline interpolations of the data in the above grid. The contour plots or perspec-

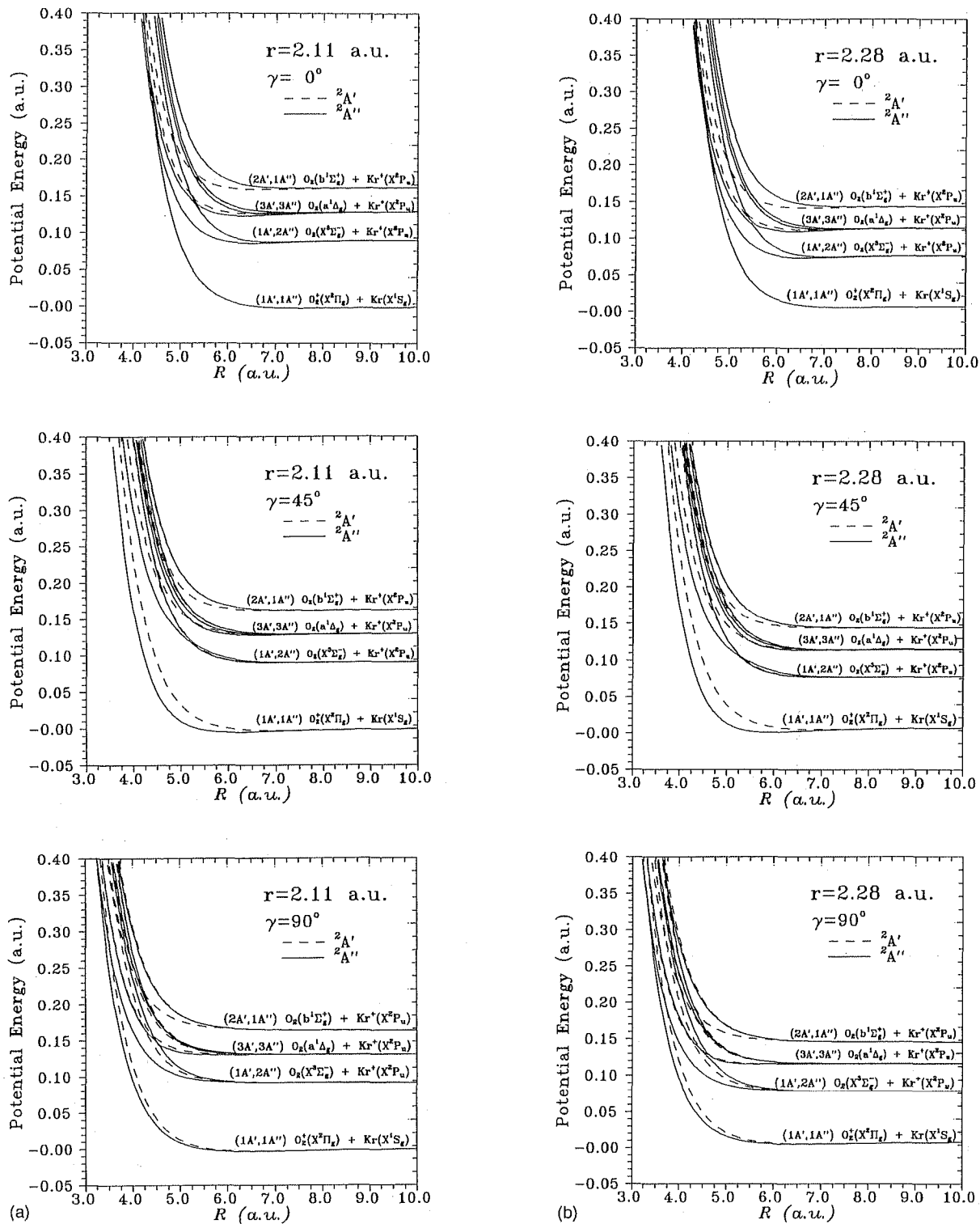


FIG. 4. Cuts of the seven lowest ${}^2A''$ (solid lines) and ${}^2A'$ (dashed lines) potential energy surfaces of $(\text{Kr}-\text{O}_2)^+$ for fixed r and γ : (a) $r=2.11a_0$; (b) $r=2.28a_0$; (c) $r=2.5a_0$. For each bond distance r , plots are displayed for $\gamma=0^\circ$, 45° , and 90° as indicated. The numbers of A' and A'' states converging towards each separated partner limit are indicated in brackets. The labeling of the states used in text refers to their increasing energy order in each symmetry. The origin of energies is the same as in Fig. 2.

tive views show the results from three-dimensional β -spline interpolations through the data points.

It is first remarked that the cuts of the PES for fixed r and γ (Figs. 2–4) are generally much flatter than what is

observed in the $(\text{H}-\text{O}_2)^+$ system and that the potential walls rise at comparatively much larger distances. This is primarily attributable to the electronic cloud accompanying the Kr^+ ion (as compared with a bare proton): electron–electron

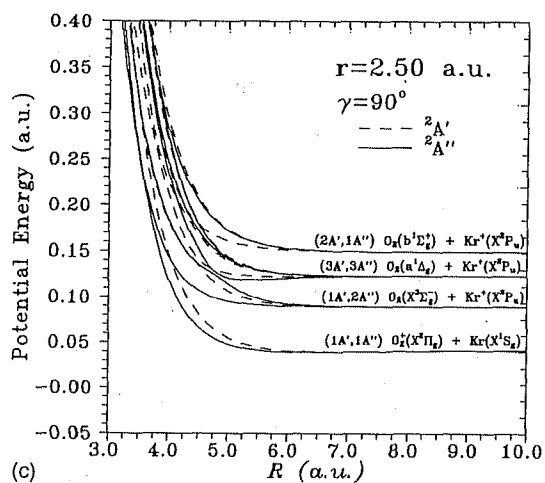
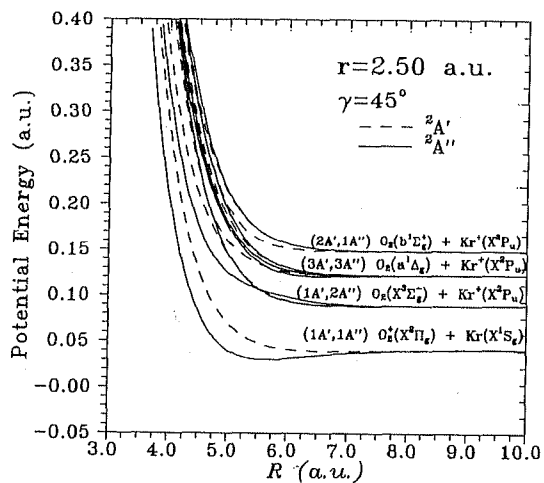
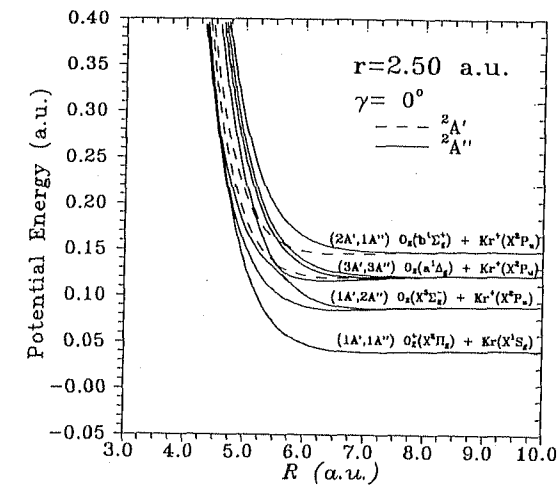


FIG. 4. (Continued.)

(Coulomb and Pauli) repulsion, that does not exist with a proton, thereby appears between the Kr^+ and O_2^+ cores.

For elongated O–O bonds ($r \geq 2.5a_0$) potential wells become apparent in the fixed- r , γ cuts of the $1,2A''$ PES [Figs. 2(c), 3(c), and 4(c)]. Stretching the O–O bond has two ef-

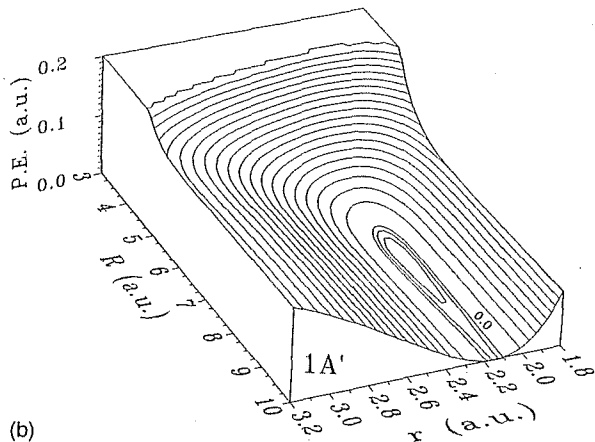
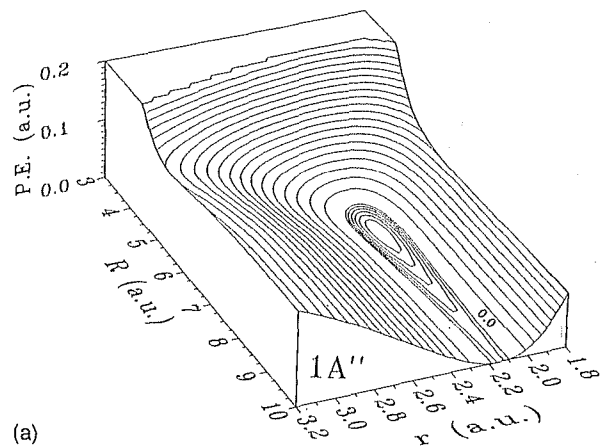


FIG. 5. Perspective views of cuts of the $1^2A''$ and $1^2A'$ PES for $(\text{Kr}-\text{O}_2)^+$ for $\gamma=51^\circ$. Contour lines for negative values of the potential start at -0.005 a.u. and are spaced by 0.001 a.u. Contour lines for positive values of the potential are spaced by 0.01 a.u. The origin of energies is the same as in Fig. 2.

fects in this respect: (i) it reduces the mentioned electron-electron repulsions, and (ii) it modifies the $\text{O}_2 \rightarrow \text{O}_2^{+(*)}$ ionization energies in such a way that the $\text{Kr}^+ + \text{O}_2$ and $\text{Kr} + \text{O}_2^{+(*)}$ levels come nearer to each other.

The latter effect favors adiabatic $\{1\pi_g, 1\pi_u, \text{ and } 3\sigma_g \rightarrow 4p\}$ electron transfer. The latter has been recognized to play an important role in the appearance of potential wells in the $(\text{H}-\text{O}_2)^+$ system. Yet, it should be kept in mind that spin-multiplicity conditions put constraints on the aforementioned electron transfer. An example is provided by the states which correlate with $\text{Kr}(^1S) + \text{O}_2^{+(*)}(a^4\Pi_u, b^4\Sigma_g^-)$. These states are incompatible with the considered doublet spin multiplicity and therefore do not participate in $\{1\pi_u \text{ or } 3\sigma_g\} \rightarrow 4p$ electron transfer (Fig. 1). Comparison with the $(\text{H}-\text{O}_2)^+$ system indicates that this constraint contributes to the observed flatness of the present doublet PES. In this respect the $1^4A''$ PES is predicted to be sensibly more attractive than the lowest $2^2A''$ state correlating to the same asymptote $\text{Kr}^+ + \text{O}_2$, due to both the more favorable electron transfer and to electron–electron exchange stabilization (Hund's rule).

The perspective views in Figs. 5(a) and 5(b) provide overall pictures of the $1^2A''$ and $1^2A'$ PES for $\gamma=51^\circ$. They show at once a tendency of the O_2^+ potential well to widen with the approach of a Kr atom. This tendency is stronger for the $1^2A''$ than for the $1^2A'$ state and corresponds to the bond elongation effect discussed earlier. The $1^2A'$ PES is globally repulsive; that is, no point on it lies below the asymptotic $Kr+O_2^+(X^2\Pi_g)$ potential minimum. Moreover, for $r\leq 3a_0$, all fixed- r, γ cuts of the $1^2A'$ PES are repulsive. On the other hand, the $1^2A''$ surface is slightly attractive; its minimum relative to the bottom of the asymptotic $Kr+O_2^+(X^2\Pi_g)$ curve is found by interpolation to lie at

$$R_m = 5.86a_0, \quad r_m = 2.16a_0, \quad \gamma_m = 51^\circ,$$

$$V_m = -0.173 \text{ eV}.$$

These equilibrium geometry parameters slightly differ from those reported earlier⁶ by us due to our present use of a broader grid of sample geometries. We are thus inclined to consider the aforementioned estimates as being more accurate. Actually, these new values do not change the conclusions drawn in our preliminary account⁶ of the $1^2A''$ results as to the way they compare with estimates inferred from photodissociation data:² $V_m^{\text{exp}} = -0.33 \pm 0.1 \text{ eV}$. With today's experience with the computational scheme of Sec. II we can hardly ascertain an accuracy of a tenth of an eV on V_m . Still, it may be pointed out that the work of Jarrold *et al.*² could not guarantee the vibrational state assignment on which the determination of V_m^{exp} was based. Thus, reiterating our earlier claim in Ref. 6, it is not excluded with the data at hand that a shift of the vibrational state assignments of Ref. 2 by one unit (0.196 eV) could reconcile their estimate with the present one.

The general characteristics of the presently calculated $1^2A''$ PES also differ considerably from the one constructed empirically to fit the $O_2^+(v=1)+Kr \rightarrow O_2^+(v=0)+Kr$ vibrational quenching data.^{1(c),1(d),5} This could suggest⁶ that the $1^2A''$ PES alone may not be sufficient to reproduce these data thereby implying the participation in this process of $1^2A'', v_{1A'}. j_{1A''} - 1^2A', v_{1A'}. j_{1A'}$ rovibronic transitions induced by Coriolis coupling.⁷

Figures 4(a)–4(c) show some characteristics of higher excited doublet states. For $r < 2.8a_0$, the lowest six states, in each of the $2A'$ and $2A''$ symmetries are correlated with $Kr^+ + O_2(X^3\Sigma_g^-, a^1\Delta_g, \text{ and } b^1\Sigma_g^+)$ asymptotes. For larger bond distances the $Kr + O_2^+(A^2\Pi_u)$ asymptote mixes in. A conspicuous feature of the results is the $2^2A' - 3^2A'$ pseudointersection and the corresponding $3^2A'' - 4^2A''$ one. These are best seen near colinear and T-shape geometries. The $2^2A'$ and $3^2A''$ states both correlate with $Kr^+ + O_2(X^3\Sigma_g^-)$ while the $3^2A'$ and $4^2A''$ states correlate with $Kr^+ + O_2(a^1\Delta_g)$. The mentioned pseudointersections thus reveal possible $O_2(X^3\Sigma_g^- \rightarrow a^1\Delta_g)$ excitation mechanisms in $Kr^+ + O_2(X^3\Sigma_g^-)$ collisions. Since we are considering states that have the same total spin of the overall $(Kr-O_2)^+$ system, the spin change of the O_2 molecule in the latter mechanisms have to involve two-electron rearrangements of the dominant PVB CSF's in the pseudocrossing CI

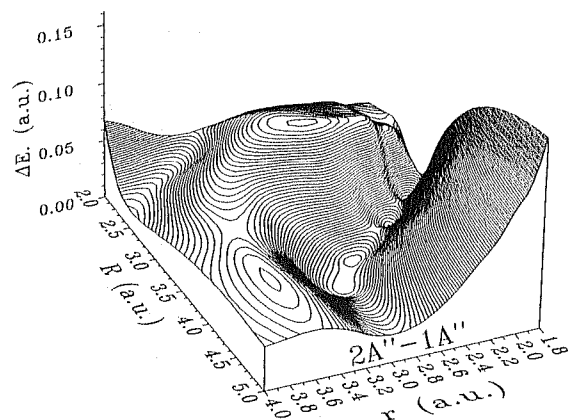


FIG. 6. Perspective view of the $2^2A'' - 1^2A''$ energy difference for $(Kr-O_2)^+$ for $\gamma=90^\circ$.

states; in such a two-electron rearrangement one spin orbital changes on the atom and one spin orbital changes on the molecule. In view of the energy position of the $2^2A' - 3^2A'$ and $3^2A'' - 4^2A''$ pseudointersections near colinear and T-shape geometries [Figs. 4(a)–4(c)], the aforementioned excitation mechanisms are expected to have their center of mass threshold energy near 1 eV.

Following an assumption made by Jarrold *et al.*² to explain the $Kr^+ + O_2(X^3\Sigma_g^-) \rightarrow Kr + O_2^+(X^2\Pi_g)$ charge transfer reaction, we have looked for the eventual existence of a pseudointersection between the $1^2A'$ and $2^2A'$ PES. The fixed- r, γ cuts of the PES [Figs. 4(a)–4(c)] show no indication of $1^2A' - 2^2A'$ nor of $1^2A'' - 2^2A''$ pseudocrossings in an energy range that could be relevant to thermal energy charge transfer collisions.^{1(a)} A more systematic search of eventual (pseudo)intersections of PES has been undertaken by inspecting the corresponding energy differences. The smallest energy difference between the lowest two $2A'$ or $2A''$ PES is actually found near $\gamma=90^\circ$. Figures 6 and 7 show related perspective views. Near the O_2 equilibrium bond distance ($r=2.28a_0$), the minimum 1-2 potential energy differences occur for $3a_0 \leq R \leq 3.5a_0$. For larger bond distances this range becomes $3.5a_0 \leq R \leq 4a_0$. In all cases the corre-

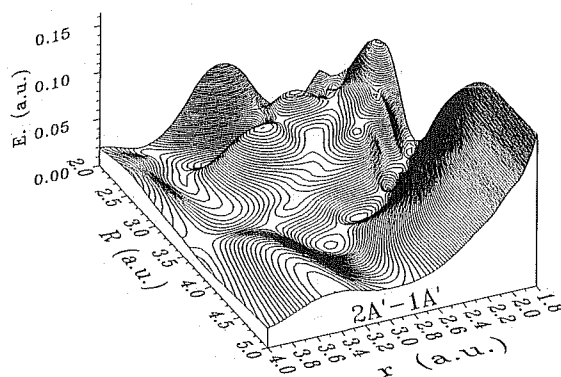


FIG. 7. Perspective view of the $2^2A' - 1^2A'$ energy difference for $(Kr-O_2)^+$ for $\gamma=90^\circ$.

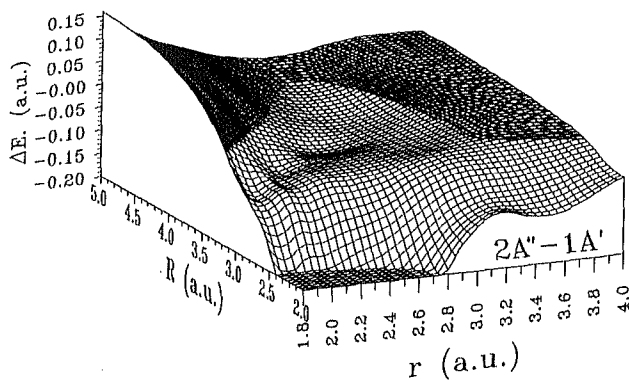


FIG. 8. Perspective view of the $2^2A''-1^2A'$ energy difference for $(\text{Kr}-\text{O}_2)^+$ for $\gamma=90^\circ$.

sponding pinchings are located on the potential walls at energies well above 1 eV relative to the $\text{Kr}^+ + \text{O}_2(X^3\Sigma_g^-)$ asymptote. Hence, we find no support in our calculations to the tentative guess of Ref. 2 as to (i) the behavior of the PES near $\gamma=90^\circ$ [compare Fig. 4(b) and Fig. 10 in Ref. 2], and (ii) the existence of a $1^2A'-2^2A'$ (pseudo)crossing that would act like a funnel for low energy (<1 eV) trajectories to go from the upper $\text{Kr}^+ + \text{O}_2$ channel to the lower $\text{Kr} + \text{O}_2^+$ one.

Our systematic search of (pseudo)intersections actually reveals a real crossing between the $1^2A'$ and $2^2A''$ states. This is best seen in the $75^\circ \leq \gamma \leq 90^\circ$ angular range but is also observed high up on the potential walls for $\gamma \approx 0^\circ$. Figure 8 illustrates some characteristics of this $1^2A'-2^2A''$ crossing at $\gamma=90^\circ$. For $r \leq 3a_0$ its locus $R(r)$ is roughly a linearly increasing function; correspondingly the larger r the lower its location in energy. This crossing may come into play in electronic transitions via Coriolis coupling as a result of the tumbling of the triatomic plane⁷ in the course of a $\text{Kr}^+ + \text{O}_2$ collision. Yet it is noted that for r values around the O_2 equilibrium distance, the required collision energy to reach it lies again above 1 eV.

IV. SUMMARY AND CONCLUDING REMARKS

The present data, together with those reported in Ref. 6, bring out unprecedented information on the low lying doublet states of the $(\text{Kr}-\text{O}_2)^+$ cluster ion. The calculations have covered a broad range of energies with the aim of being useful for future scattering calculations. The results are somewhat counter to earlier views of the PES of this system and therefore their implication in the dynamics.

A remarkable feature of the results is the shallowness of the $1^2A''$ potential well and the absence of wells in the other PES investigated. The $1^2A''$ ground state potential well is half as deep as what has been proposed² and used^{5,17,18} in earlier work; moreover, the corresponding equilibrium geometry differs significantly from the one considered thus far.^{2,5} This suggests that the calculated $1^2A''$ state alone might not be sufficient to account for the vibrational quenching in low

energy $\text{O}_2^+(v=1) + \text{Kr}$ collisions. A model considering the more repulsive $1^2A'$ state may be necessary as well and could come into play⁶ via Coriolis coupling.

Notable effects on all the PES are observed when the O-O bond is stretched beyond $2.5a_0$. An explanation of this effect has been given. Strong vibrational and vibronic phenomena may thereby ensue if the system is likely to explore these regions.

Contrary to qualitative guesses of Ref. 2, no pseudocrossings of doublet states are found that could straightforwardly explain, on the basis of mere electronic structure arguments, the low energy (<1 eV) charge transfer process.^{1(a)} $\text{Kr}^+ + \text{O}_2(X^3\Sigma_g^-) \rightarrow \text{Kr} + \text{O}_2^+(X^2\Pi_g)$. We are thus led to the conclusion that more subtle ro-vibronic transition mechanisms possibly involving also quartet-doublet spin orbit transitions might constitute alternative candidates to explain this process. This constitutes a strong incentive for future work.

The present calculations reveal a $1^2A'-2^2A''$ crossing for $75^\circ \leq \gamma \leq 90^\circ$. The related Coriolis coupling mechanism is switched on at energies above 1 eV. This could explain the observation of a strong reactivity increase for Kr^+ ions colliding with O_2 at relative energies near and above 1 eV.^{1(b)}

Another new feature of the reported PES is that they show evidence for pseudocrossing mechanisms of population sharing between the $2,3A''$ and $2A'$ states. Similar evidence is shown for an $\text{O}_2(X^3\Sigma_g^-) \rightarrow \text{O}_2(a^1\Delta_g)$ excitation involving two electron rearrangement.

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