The asymptotic region of the potential energy surfaces relevant for the $O(^3P) + SO(X^3\Sigma^-)$ reaction

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Abstract

The potential energy surfaces (PESs) and the spin–orbit couplings for all states of sulfur dioxide correlating with the lowest $O(^3P) + SO(X^3\Sigma^-)$ asymptote have been calculated in the bond formation region employing correlated electronic wavefunctions. The PESs are found to be strongly anisotropic along the bending coordinate. For linear $OS/C_1/C_1/C_1$ approach, the $R$ states lie below the $P$ states; for the $O/C_1/C_1/C_1$ OS orientation the $P/R$ ordering is opposite. For perpendicular approaches their $A_0$ components form avoided crossings. The electron spin quantum number is no longer a good quantum number for geometries where the multiplets come close together.

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1. Introduction

Several theoretical studies dealt with the potential energy surfaces (PESs) of the electronic states of SO$_2$, required for understanding of the formation and the photodissociation of sulfur dioxide [1–17].

Recently, based on ab initio calculations, a global single-valued ground state PES of SO$_2$ has been reported by Rodrigues et al. [1]. The PES has four minima [1,3–5] two in bent OOS, one in ring SO$_2$ structure [4] and the global SO$_2$ minimum. Ivanic et al. [4] showed that, on the ground state PES, interconversion between the open $C_{2v}$ structures and closed ring isomer proceeds via a $C_{2v}$ transition state, and that the $X^1A_1$ and the next $^1A_1$ intersect conically.

The energy diagram for several singlet and triplet intermediates and transition states involved in the $S(^3P) + O_2(X^3\Sigma^-)$ and $O(^3P) + SO(X^3\Sigma^-)$ reactions was published by Lu et al. [5].

The PESs of the first two excited singlet states $A^1A_2$ and $B^1B_1$ cross and are vibronically coupled by the antisymmetric stretching mode [6,7]. The PESs for these states [6] have been used by Mueller and Koeppel [18] to interpret the complex absorption vibronic bands between 260 and 340 nm. The $C^1B_2 \leftarrow X^1A_1$ electronic transition begins at 240 nm, with predissociation into $O(^3P) + SO(^3\Sigma^-)$ occurring above a threshold at approximately 219 nm [19]. In this region, the second asymptote $O(^1D) + SO(^3\Sigma^-)$ is not energetically accessible.

Previously, Kamiya and Matsui [7] and Weis and Rosmus [6] found a crossing between the $^1B_2$ and $^1A_1$ states. This $^1A_1$ and the $B^1B_1$ states correlate with the first $^1\Pi$ state, which opens the path towards the lowest dissociation asymptote.

So far, the most extensive study of the PESs for electronic states of SO$_2$ has been published by Katagari et al. [8], which have been used to interpret the dissociation mechanism of the $C^1B_2$ state. It has been shown experimentally that in both triplet fragments O and SO the spin polarization occur [9–12] which has been attributed to the crossing of the $^1A'$ state with the $C^1B_2$ state. It has been suggested that the dissociation...
may occur through one, or more, of the following pathways: (i) an internal conversion to quasi-bound continuum levels of the 1'A state; (ii) vibronic coupling with the 3'A state; (iii) spin–orbit coupling with the repulsive 2'A state. Interestingly, the analysis of the spectra and ab initio calculations [20–22] lead to the conclusion that the PES of the C state has a double minimum in the antisymmetric stretching coordinate with a barrier of about 140 cm\(^{-1}\) to \(C_{2v}\) saddle point. Using adiabatic ab initio PESs the bound vibrational state of the \(C^1B_2\) electronic state, and the absorption and emission spectra of the \(C^1B_2 \leftrightarrow X^1A_1\) system were found to be in rather good agreement with the experiments [16,17].

The nine adiabatic surfaces and 27 spin-states resulting from the lowest \(O(3P) + SO(3\Sigma^-)\) asymptote have been investigated for large atom–diatom distances. For the \(O \cdot SO\) orientation our results are in a good qualitative agreement with the adiabatic PESs of Rodriguez et al. [1] and Katagari et al. [8]. However, for the collinear and perpendicular \(O \cdot OS\) orientations we find that the mixing among the singlet, triplet and quintet states is strong and the spin quantum numbers loose their significance. This is directly related to the near degeneracy and crossing of the spin multiplets in the bond formation region. The order of the \(\Pi/\Sigma (s = 1, 3, 5)\) states in the linear \(O \cdot SO\) structure is reversed in \(O \cdot OS\) structure. Therefore, for perpendicular approaches all \(\alpha\) states correlating with \(\Pi\) or \(\Sigma\) states form avoided crossings. The results are compared with the shapes of similar asymptotic PESs for ozone [23,24].

2. Electronic structure calculations

The full valence CASSCF by internally contracted MRCI approach available in the MOLPRO program [25] has been used to map the asymptotic region for all states of sulfur dioxide correlating with the \(O(3P) + SO(3\Sigma^-)\) asymptote. Internal coordinates were used. We define the coordinates used in the present work in Fig. 1. The investigated region comprised valence angles between 0° and 180° and \(R_{O-O}\) and \(R_{S-O}\) distances between 4 and 7 bohr. The diatomic SO distance (\(R_1\) in Fig. 1) was kept fixed at 2.7 bohr in all computations. The spd subset of the standard correlation consistent generally contracted aug-cc-pVQZ basis set of Dunning et al. [26,27] was used in all computations (131 contractions in \(\alpha\) and 50 in \(\alpha^\prime\) for \(C_3v\) symmetry). The following scheme, based on previous experiences with ozone [28], was adapted to reduce convergency problems in the computations of the full valence CASSCF [29,30] wavefunctions: starting from the Restricted Hartree–Fock (RHF) wavefunctions of the singlet ground state the CASSCF computations were first performed with 11 lowest \(\alpha\) and 2 lowest \(\alpha^\prime\) molecular orbitals closed; in the next step with 12 \(\alpha\) and 1 \(\alpha^\prime\) molecular orbitals were closed. The natural orbitals from these wavefunctions were used in the subsequent full valence state averaged CASSCF computations (for each multiplet \(2 \times \alpha\) and \(\alpha^\prime\) states with equal weights). Following numbers of CSFs were taken as reference wavefunctions in the subsequent internally contracted MRCI [31,32] computations: 8029 \((2 \times 1\alpha')\), 7701 \((1\alpha')\), 11529 \((2 \times 3\alpha')\), 11637 \((3\alpha')\), 4182 \((2 \times 5\alpha')\) and 4398 \((5\alpha')\). Only the valence electrons were correlated. In these large scale computations the number of internally contracted configurations ranged between 9.9 millions \((\alpha)\) and 5.2 millions \((\alpha')\). Since the dynamical correlation is very important for the electronic problem of sulfur dioxide, also the Davidson corrected MRCI energies were calculated. Neither the size-extensivity nor basis superposition corrections were considered at the present stage. It should be noticed that crossings with states resulting from higher asymptote occur for higher energies. Also the path to related to the \(S + O_2\) reaction has not been investigated in the present work.

Due to its importance in the asymptotic region also the spin–orbit coupling has been investigated. All spin multiplets resulting from the first dissociation asymptote were optimized in state averaged CASSCF computations and these wavefunctions were employed to calculate the coupling elements in the basis of the resulting 27 spin states. We used the Cartesian representation of the spin–orbit operator, the matrix elements were explicitly evaluated from the high-spin components of the two interacting multiplets summing over all one- and two-electron contributions following the scheme of Berning et al. [33], as implemented in MOLPRO program. More details can be found in [23], in which we showed that in the bond formation region interactions are dominated by the spin–orbit coupling in the \(3P\) ground state and are much less geometry dependent than the atom–diatom electrostatic interactions. For separated O atom with
the present ansatz (no higher electronically excited states considered) the fine structure levels in O(3P) are calculated to be 0.0 (0, 0, \( J = 2 \)), 151.50 (158.265, \( J = 1 \)), and 227.25 (226.977, \( J = 0 \)) in cm\(^{-1}\) (experimental values in parentheses [34]). Using the MRCI approach described in previous Section we have calculated the potential energy and electric dipole moment functions of the electronic ground state of the SO molecule and used this information to obtain the vibrational wavefunctions by the Numerov procedure. This allowed to calculate the electric dipole moment in the vibrational ground state \( l_0 = 0.571 \) a.u. (exp. \( l_0 = 0.598(8) \) a.u. [35]). The MRCI quadrupole moment for O(3P) has been calculated to be \( Q_{xx} = Q_{yy} = 0.47572 \) a.u., \( Q_{zz} = 0.95144 \) a.u. Both values can be useful for comparison with multipole expansions of the long range parts of the PESs.

3. Results

In Fig. 2, the collinear cuts for the O···SO and O···OS orientations of the \(^{3}\Pi\) and \(^{1}\Sigma\) states calculated by full valence CASSCF-MRCI with the Davidson correction are compared with similar cuts for ozone molecule. In the O···OS bond formation region (middle panel), like in ozone (upper panel), the cluster of the \(^{3}\Pi\) states lie energetically lower than the cluster of the \(^{1}\Sigma\) states and all potentials are repulsive. The ordering of the states is \(^{3}\Pi\), \(^{1}\Pi\), \(^{3}\Sigma^+, \Sigma^+, \) and \(^{1}\Sigma^+\). An opposite pattern is calculated for the O···SO approach. The \(^{3}\Sigma\) states lie in collinear orientation lower than the \(^{1}\Pi\) states. The lowest \(^{1}\Sigma^+\) state correlates with the \(^{1}A_1\) state of SO\(_2\), and, as reported by Rodriguez et al. [1] and Katagiri et al. [8], the minimal energy path has no barrier for angles smaller than 180\(^\circ\). Some of the potentials are attractive for \( R_{SO} \) smaller than about 4.5 bohr and all are repulsive for \( R_{SO} \) larger than about 4.5 bohr (Fig. 2 lower panel). As discussed in the Introduction, the \(^{1}A'\) component of the \(^{3}\Pi\) state forms an avoided crossing with the \(^{3}B_2\) (\(^{2}A'\)) state opening the path for dissociation.

When the new bond starts to be formed, approximately around 7 bohr, the PESs become anisotropic. In Fig. 3, we show cuts through the CASSCF potentials along the valence angle for \( R_{OO} = 5.0 \) bohr (O···OS), and \( R_{SO} = 5.9 \) bohr (O···SO), relative to the energy of \(^{3}\Sigma^+\) state at \( R_{SO} = 8.5 \) bohr at linearity. Again for O···OS orientations the potentials resemble those calculated for ozone. The \(^{3}\Pi\) states split in their two Renner–Teller components. The singlets and triplets form bent/bent pairs whereas the \( A' \) and \( A'' \) components emerging from the \(^5\Pi\) state possess linear minima. All multiplets cross for valence angles around 155\(^\circ\) and again for angles close to 100\(^\circ\). In the cluster of \(^{1}\Sigma\) states the crossings occur for angle around 145\(^\circ\). All \( A' \) states correlating with \(^{3}\Pi\) or \(^{1}\Sigma\) states form avoided crossings and lie

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energetically close for valence OSO angles around 100° for \( s = 5 \), around 80° for \( s = 3 \) and around 70° for \( s = 1 \). The cuts along the valence angle coordinate for the O··SO orientation are very different. Only the \(^3A''\) and \(^3A'\) components of the \( \Pi \) states are attractive and cross the quintet and triplet \( \Pi' \) states. The cut for the lowest \(^1\Sigma^+\) state has a local minimum around 115°.

We have calculated also the PESs between the \( \Pi/\Sigma \) cluster ordering in the O··SO structure to the \( \Sigma/\Pi \) ordering in the O··SO structure. The cuts through the PESs for \( R_{\text{c.m.}} = 7.7 \) bohr relative to the center of mass of SO for angles between 0° and 180° are shown in Fig. 4. All \(^1A'\) states form avoided crossings near the perpendicular O··SO arrangements.

In the bond formation region the near degeneracy of many states will lead to complex vibronic, electronic spin and other angular momenta couplings. In this Letter, we present only part of the results obtained for spin–orbit mixings related to singlet states. The symmetry relations between spin–orbit matrix elements for states resulting from the \(^3P + ^3\Sigma^-\) asymptote were discussed in our publication on ozone [23]. Also in the present case the important spin–orbit matrix elements are dominated by the atomic term and are approximately isotropic for the region between the perpendicular and linear O··OS orientations. In the O··SO structures they are stronger quenched. The strengths of the spin–orbit mixing depends on the energy difference and as a consequence the spin quantum numbers can lose their meanings not only at very long atom–diatom distances, but also in the PESs regions where the electrostatic interaction leads to anisotropic potentials. Although the spin–orbit matrix elements depend only weakly on the bending angle, the strengths of the couplings between singlet, triplet and quintet states arising from the spin–orbit interactions is anisotropic. This is illustrated in Fig. 5 where we plot the largest percentage of the \( S = S_z = 0 \) component of the eigenvectors of \( A' \) and \( A'' \) symmetry and compare them with similar results for ozone. The eigenvectors were obtained by diagonalizing the full Hamilton matrix including spin–orbit interactions between the 27 components.

Fig. 3. Angular dependence of the nine lowest potential energy surfaces of ozone and sulfur dioxide obtained from full valence CASSCF calculations. The \( R_i \) diatom distances were fixed at values given in caption of Fig. 1. Upper panel: ozone for \( R_{\text{OO}} = 4.9 \) bohr, middle panel: SO··O for \( R_{\text{OO}} = 5 \) bohr, lower panel: O··SO for \( R_{\text{SO}} = 5.9 \) bohr.

Fig. 4. Angular dependence of the nine lowest potential energy surfaces of sulfur dioxide for \( R_{\text{c.m.}} = 7.7 \) bohr (\( R_1 = 2.7 \) bohr).
The singlet characters are almost entirely preserved in the O\(\cdot\)SO orientation for valence SOO angles between 0° and about 80° and this part is not shown. For the O\(\cdot\)OS orientations (valence SOO angles between 180° and 90°) the singlet basis functions have in all eigenvectors smaller weights than about 50%. It should be noted that all interactions entering the spin–orbit matrix are responsible for sometimes irregular shapes of these curves. We have performed similar calculations for all three secondary minima [1,3–5] on the adiabatic ground state PES with both sets of differing geometries published previously. For all three minima the \(S = S_z = 0\) component has weights larger than 95%.

4. Conclusions

The aim of the present Letter was to investigate the anisotropies and regions of vibronic and angular momenta couplings close to the lowest dissociation asymptote of SO\(_2\). We found that: (i) for the collinear OS\(\cdot\)O approach the lowest singlet state retains its singlet character in the formation of the open C\(_2v\) ground state and the \(1,3,5\Sigma\) cluster of states is separated from similar higher lying \(1,3,5\Pi\) cluster; (ii) the order of \(\Sigma/\Pi\) clusters is reversed in collinear O\(\cdot\)OS approach leading to a very similar PESs we found previously for ozone [23]; the PESs are considerably anisotropic along the bending coordinate, with \(\Pi\) states split into Renner–Teller pairs; (iii) like in ozone crossings occur between adiabatic PESs of the \(\Pi\) states with different multiplicity; (iv) particularly for the O\(\cdot\)OS orientations the spin–orbit mixings are large. As a consequence, in the bond formation region the molecular electron spin quantum numbers lose their significance for the collinear O\(\cdot\)OS and perpendicular O\(\cdot\)SO approaches. The alignments in fine structure components observed in O(3\(P_{J}\)) and SO(X 3\(\Sigma^{-}\)) after photodissociation of the C\(_1B_2\) state can result also from long range couplings. The present note suggests that a simple adiabatic model using only the lowest singlet PES is likely to be not fully adequate for a realistic description of O + SO collisions and SO\(_2\) dissociation.

References


Fig. 5. Percentage of \(S = S_z = 0\) spin components of the eigenfunctions after diagonalization of the spin–orbit matrix for the 27 spin states correlating with the lowest dissociation asymptote as a function of the OOS angle for the lowest singlet \(A^1\) and \(A^0\) states. Upper panel: ozone for \(R_{OO} = 4.9\) bohr and \(R_1 = 2.288\) bohr, lower panel: SO\(\cdot\)O for \(R_{OO} = 5.9\) bohr and \(R_1 = 2.7\) bohr.
[25] Molpro is a package of ab initio programs written by H.-J. Werner, and P.J. Knowles. Further information can be obtained from: <http://www.molpro.net/>.