



H⁺ + O₂ system revisited: four-state quasidiabatic potential energy surfaces and coupling potentials

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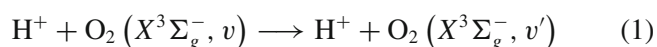
Abstract. The global adiabatic and quasidiabatic potential energy surfaces for the ground and first three excited ($1 - 4^3A''$) electronic states of H⁺ + O₂ system are reported on a finer grid points in the Jacobi coordinates using Dunning's *cc-pVTZ* basis set and internally contracted multi-reference (single and double) configuration interaction method. *Ab initio* procedures have been used to compute the corresponding quasidiabatic surfaces and radial coupling potentials which are relevant for the dynamical studies of inelastic vibrational excitation and charge transfer processes. Nonadiabatic couplings arising out of relative motion of proton and the vibrational motions of O₂ between the adiabatic electronic states have also been analyzed.

Keywords. Potential energy surface; quasidiabatization; coupling potentials; nonadiabatic coupling matrix elements.

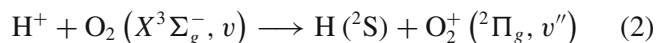
1. Introduction

The proton collisions with molecules are of fundamental importance in several areas of astrophysics, atmospheric chemistry and chemical physics.¹

Experiments^{1,2} reveal that among several diatomics (H₂, N₂, CO, NO, etc.) the energy transfer processes are quite effective in the H⁺ + O₂ system. The following two dominant collision processes take place: the inelastic vibrational excitation (IVE),



and the vibrational charge transfer (CT) collisions



The H⁺ + O₂ system exhibits a direct curve crossing between the ground state (GS) correlating to the CT channel (Eq. 2) and the first excited state (ES) correlating to the IVE channel (Eq. 1), in the collinear and perpendicular geometries. The direct curve crossing becomes an avoided crossing in the off-collinear geometries leading to the conical intersection³ between the GS and the first ES potential energy surfaces (PESs) in the full dimensional nuclear configuration space. The CT channel is exoergic by 1.52 eV as compared to the IVE channel. The experimental data for the H⁺ + O₂ system became available² as early as 1986 for both the

channels at the center of mass collision energy, $E_{cm} = 23$ eV. Unlike the H⁺ + H₂ and the H⁺ + N₂ systems where ground state potential energy surface (PES) is well separated energetically from the low-lying excited states the H⁺ + O₂ system demands inclusion of other low-lying ESs as they are highly coupled through the Landau-Stueckelberg type of coupling.⁴⁻⁶ *Ab initio* calculations of H⁺ + O₂ system in restricted geometry was first reported⁷ to characterize the energies and geometries of bound HO₂⁺ ion using single configuration self consistent field (SCF) method and a double zeta plus polarization (DZ+P) basis set to study the lowest three ($^3A''$, $^1A'$, $^1A''$) states. Another set of restricted geometry calculations were reported⁸ predicting the geometric structure and vibrational frequencies of HO₂⁺ based on configuration interaction (CI) level of theory using DZ+P basis set. Just recently, ground electronic PES for the HO₂⁺ system has been reported⁹ at MRCI/cc-pVXZ ($X = T, Q$) level extending the accuracy at the full CI limit. The experimental observations of large vibrational excitations of O₂ as compared to other diatoms (H₂, N₂, CO, NO) upon collisions with H⁺ at $E_{cm} = 9.5$ eV was qualitatively explained^{10,11} in terms of intermediate charge transfer by computing the adiabatic PECs in restricted geometry. Subsequently, there have been few studies reporting full three dimensional *ab initio* GS and the first ES PESs of H⁺ + O₂ system. For instance, Grimbert *et al.*¹² reported PESs using model projected valence bond (MPVB) calculations. Almost at

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the same time Schneider *et al.*¹³ constructed these PESs using semi-empirical *diatomics-in-molecule* (DIM) formalism.

1.1 Present focus

The incoming IVE channel, $\text{H}^+ + \text{O}_2(X^3\Sigma_g^-)$, corresponds to $1^3\Sigma^-$ and $1^3A''$ states in the collinear and off-collinear geometries, respectively. The first CT channel, $\text{H}(^2S) + \text{O}_2(^1\Pi_g)$ corresponds to the $1^3\Pi$ state in the collinear geometry which splits into $1^3A'$ and $2^3A''$ states in off-collinear geometries. For collision energies in the range $E_{cm} = 9.5 - 23$ eV several low-lying (energetically accessible) states are likely to get involved into the collision dynamics. It is also worth pointing out here that for such collision energies the collision time estimated to be much shorter (two orders of magnitude less) than the rotational time of the target diatom. Therefore, effective nonadiabatic coupling arises largely due to radial (vibrational–translational) motions. In such a situation there would be no coupling between $^3\Sigma^-$ and $^3\Pi$ states, and also between $^3A'$ and $^3A''$ states and nonadiabatic coupling would arise only among $^3A''$ electronic states. PESs.

Early theoretical studies^{14,15} involved quantum dynamics studies under the vibrational close-coupling rotational infinite-order sudden approximation (VCC-RIOSA)¹⁶ using the quasidiabatic PESs of the $1^3A''$ (electronic) ground state (GS) and the $2^3A''$ (first) excited state (ES), which were constructed by the *ab initio* MPVB calculations¹² and by the semi-empirical DIM¹³ approach, respectively. The quantum dynamics results were in overall qualitative agreement with those of experiments. But, there were some noticeable discrepancies. Subsequently, high level *ab initio* computations were performed¹⁷ to obtain the GS and the first ES adiabatic and quasidiabatic PESs. The quasidiabatic PESs were constructed using the *ab initio* procedures.¹⁸ However quantum dynamics calculations under the VCC-RIOSA scheme showed little improvement. The existing discrepancy could be arising due to non-inclusion of further energetically accessible low-lying excited electronic states which could possibly get involved during the collision dynamics at the experimental collision energy. Therefore, in a subsequent *ab initio* study¹⁹ adiabatic as well as quasidiabatic PESs were computed for the GS and the lowest three ESs ($1-4^3A''$) and the quantum dynamics calculations could reproduce some of the experimental findings. Yet, some of the quantitative discrepancies between theory and experiment still remained to be explained. Therefore, further improvement in the theoretical treatment was desirable to unravel the complexity of the collision process in the

system. The considered steps for further improvement could involve the following: (i) inadequacy of the constructed quasidiabatic PESs and the coupling potentials, (ii) non-inclusion of further low-lying ESs in the dynamical treatment, (iii) inadequacy of VCC-RIOSA framework and (iv) the presently available four-state PESs should involve further computations of more energy points over refined grid of angular approaches of H^+ .

It is important to note that nonadiabatic processes play a crucial role in many chemical processes and construction of accurate (quasidiabatic) PESs and coupling potentials is of paramount importance.^{20–22} Several prescriptions have been suggested in the literature^{18,23–45} to construct quasidiabatic PESs and coupling potentials. A brief discussion is given in the following section. For the $\text{H}^+ + \text{H}_2$ system, quasidiabatic PESs and potential couplings were obtained using *ab initio* procedures¹⁸ and quantum dynamics within VCC-RIOSA yielded results in excellent quantitative agreement with those of the experiments for the system^{46–48} in the collision energy range $E_{cm} = 9.5-23.0$ eV, thus providing confidence in *ab initio* procedures to obtain quasidiabatic PESs and the potential couplings. The $\text{H}^+ + \text{H}_2$ system effectively involves the ground and first excited electronic states which asymptotically correlate to $\text{H}^+ + \text{H}_2(X^1\Sigma_g^+)$ and $\text{H}(^2S) + \text{H}_2(^2\Sigma_g^+)$, respectively. Based on computations of several computed structural parameters of the HO_2^+ system reported earlier^{17,18} we believe that an overall good representation of quasidiabatic PESs and potential couplings has been achieved for the title system in the present MRCI/cc-pVTZ computations. However, it must be noted that the topology of quasidiabatic PESs and their potential couplings could be sensitive to the accuracy achieved in the computations. It is also worth mentioning here that adiabatic and quasidiabatic PESs for the H_3^+ have also been obtained recently^{49,50} for the lowest three singlet electronic states in the hyper spherical coordinates by computing nonadiabatic coupling matrix elements (NACME) and by satisfying the curl condition and solving the adiabatic-to-diabatic equation, followed by the coupled three-dimensional time-dependent wave packet studies.

The decoupling of the angular momenta in the VCC-RIOSA scheme is based on the fact that collision time is much (approximately two orders of magnitude) shorter than the rotational time of the target diatom. Therefore, for $E_{cm} = 9.5-23$ eV it is expected to be valid.

It could be likely that some more energetically accessible low lying ESs could get involved in the dynamics process. In view of the fact that collision outcomes are observed experimentally^{1,2} only for the IVE ($\text{H}^+ + \text{O}_2(X^3\Sigma_g^-)$) and the first CT ($\text{H}(^2S) + \text{O}_2(^1\Pi_g)$)

channels, which asymptotically correlate with the first ES ($2^3A''$) and the GS ($1^3A''$) respectively, and there were no hints in the experiments of any outcomes in other electronically excited state channels for collision energies in the range 9.5 – 23.0 eV, the inclusion of further low-lying ESs beyond the third ES ($4^3A''$) in calculations is expected to bring any significant influence on the collision attributes. Therefore, inclusion of four lowest electronic states ($1-4^3A''$) would be sufficient to capture the collision dynamics at the experimental collision energies. In the earlier study,¹⁹ PESs for these lowest four electronic states were computed in the Jacobi scattering coordinates. (R, r, γ) where r is the internuclear distance of O_2 , R is the vector connecting center of mass of O_2 and the projectile (H^+/H) and γ is the angle between these two vectors, defined by $\gamma = \cos^{-1} \left(\frac{\vec{R} \cdot \vec{r}}{|\vec{R}| |\vec{r}|} \right)$. The angular approaches of H^+ were taken at 15° interval between 0° and 90° . It is important to note that the construction of multi-state quasidiabatic surfaces is a painstaking task and often becomes intractable due to the convergence problems at both MCSCF and MRCI levels. The reason behind this is the involvement of further low-lying excited states at some configurations. Since the collision attributes (and particularly differential cross sections (DCS)) crucially depend on the anisotropy of the internuclear potential it is important that the angular dependence of the PESs is represented well. Therefore, in the present study we undertook further extensive *ab initio* calculations by computing PESs at γ -values from 7.5° to 82.5° with an interval of 7.5° and augmented the PESs with previously computed surfaces at the same level of theory and accuracy. We believe that with these additional calculations the PESs for the lowest four electronic states would now be represented sufficiently accurately for the quantum dynamics studies.

In section 3 we present and discuss the refined global adiabatic as well as quasidiabatic PESs in the Jacobi scattering coordinates for the lowest four electronic states. The characteristics of the corresponding quasidiabatic PESs, nonadiabatic coupling elements between the adiabatic states and the coupling potentials of the quasidiabatic states are analyzed. The PESs have been extended in the asymptotic limit in terms of multipolar expansion and described in section 4 followed by a summary and conclusion in section 5.

1.2 Quasidiabatization

The Schrödinger equation for the coupled electronic PESs can be expressed in either adiabatic electronic basis or diabatic electronic basis. In an adiabatic electronic basis $\{\psi_i^a\}$ which also happens to be the set

of eigenfunctions of the electronic Hamiltonian, the potential energy operator is diagonal with the electronic energies (E_i) as the diagonal elements, and the non-adiabatic coupling arises in terms of the derivative term of the type $\langle \psi_i^a | d/dR | \psi_i^a \rangle$ and $\langle \psi_i^a | d^2/dR^2 | \psi_i^a \rangle$ which are referred to as the first and second order NACMEs, respectively. The second order NACMEs are generally negligibly small and therefore they are often ignored. Here R stands for nuclear geometry. Since these couplings occur in the kinetic energy operator (\hat{T}) the first order NACMEs are vector quantities, their numerical evaluation becomes a very difficult and involved task as they become non-local and their magnitudes grow extremely large in magnitude over small regions of non-adiabatic interactions. To circumvent the problem one generally resorts to do calculations in some other electronic basis, namely the ‘diabatic (quasidiabatic) basis’ $\{\psi_i^d\}$, which show no dependence (weak dependence) on nuclear coordinates and thus the first and second order NACMEs become zero (or nearly zero).²³ The connection between the unique adiabatic basis $\{\psi_i^a\}$ and the diabatic basis $\{\psi_i^d\}$ is given by a unitary transformation. For example, for a 2×2 case, the unitary transformation matrix (U) is given by

$$\begin{pmatrix} \psi_1^d(R) \\ \psi_2^d(R) \end{pmatrix} = \begin{pmatrix} \cos \theta(R) & \sin \theta(R) \\ -\sin \theta(R) & \cos \theta(R) \end{pmatrix} \begin{pmatrix} \psi_1^a(R) \\ \psi_2^a(R) \end{pmatrix} \quad (3)$$

with the condition that $\langle \psi_2^d | d/dR | \psi_1^d \rangle = 0$, one can determine U from the knowledge of first-order NACME as

$$\theta(R) = \theta(R_{ref}) + \int_{R_{ref}}^R \left\langle \psi_2^d \left| \frac{d}{dR} \right| \psi_1^d \right\rangle dR \quad (4)$$

However, one generally faces the problem that there is no unique set of diabatic basis. Only for cases, for example, a diatomic case where the NACMEs become exactly zero, there exists a unique set of diabatic basis. The evaluation of first order NACME involves contour integration and for a polyatomic case its evaluation becomes path dependent. Therefore, for a polyatomic case, NACMEs can only be made vanishingly small and therefore it is always possible to have different sets of $\{\psi_i^d\}$ which more or less give nearly vanishing NACME values. These sets of $\{\psi_i^d\}$ are generally called quasidiabatic electronic wavefunctions. For vanishing NACMEs, \hat{T} becomes nearly diagonal. However, since $\{\psi_i^d\}$'s are not a set of eigenfunctions of electronic Hamiltonian, the potential energy (PE) operator \hat{V} becomes non-diagonal. Yet one prefers to carry out dynamics studies in this representation since the non-adiabatic coupling appears in the potential terms which can be evaluated conveniently since they are local in nature.

Several methods to construct a set of quasidiabatic wavefunctions and to derive the potential couplings have been proposed in the literature^{18,23–45}. However, they lack uniqueness and one often faces a serious question whether the constructed electronic PESs and the coupling potentials would yield the quantum dynamics attributes in agreement with the experiments since they crucially depend on the topology of PECs. A natural choice should be based on the method of construction of quasidiabatic PESs which alter their topology only in the interaction regions as compared to those obtained for the unique adiabatic basis and both the quasidiabatic and adiabatic PESs should become identical in the regions away from the nonadiabatic interactions. For details of NACME based diabatization procedure see reference 45 and references therein. An alternative method has been proposed by Werner and coworkers¹⁸ for the construction of quasidiabatic electronic states based on *ab initio* calculations. This method was used to compute the quasidiabatic PESs and the couplings to study the photodissociation dynamics of H₂S to explain the experimental observations. In this method one constructs quasidiabatic electronic wavefunctions in the following way: first calculations are done at a reference point R_{ref} of nuclear arrangement at which both the $\{\psi_i^a\}$ and $\{\psi_i^d\}$ are assumed to be identical since the reference point would be located away from the regions of non-adiabatic interactions. Now another *ab initio* calculation is carried out at slightly displaced nuclear configuration $R + \Delta R$. For this, $\{\psi_i^a\}$'s, E_i 's and Molecular Orbitals (MOs) coefficient would change in comparison with the those obtained at R_{ref} . If one puts a constraint that a $\psi_i^a(R_{ref} + \Delta R)$ must look similar to $\psi_i^a(R_{ref})$ then the former state vector must be rotated to give maximum overlap with the latter. This can be achieved if one maximizes the overlap integral of the MOs (generally the active MOs since the core MOs mostly remain invariant or they change little with R). This constraint leads to determination of \mathbf{U} and $\psi_i^d(R + \Delta R)$ (the rotated vector $\psi_i^a(R_{ref} + \Delta R)$) which yields (almost) same energy value (as compared to that calculated at $R = R_{ref}$) and also shows very weak dependence on R . For a 2×2 case, the maximization of such overlap defined for all pairs of active orbitals $\{\psi\}$, $|\langle \psi_i^a(R_{ref} + \Delta R) | \psi_i^a(R) \rangle|^2 + |\langle \psi_j^a(R_{ref} + \Delta R) | \psi_j^a(R) \rangle|^2 + \dots$, can be achieved by a 2×2 Jacobi rotation technique.⁵¹ The unitary transformation for ψ 's can also be obtained in an alternative way¹⁸ as $\mathbf{T} = \mathbf{S}(\mathbf{S}^\dagger \mathbf{S})^{-1/2}$ where the overlap matrix elements S_{ij} are defined as $S_{ij} = \langle \psi_i^a(R_{ref}) | \psi_j^a(R_{ref} + \Delta R) \rangle$. It has been found¹⁸ that both the approaches lead to identical results. For an m -state (quasi) diabatization, the unitary transformation matrix $\mathbf{U}(m \times m)$ can be obtained by following the block diagonalization

methods^{18,52} of electronic Hamiltonian. If ψ_m^d is the m^{th} state diabatic wavefunction then it can be given as with the condition that $\langle \psi_2^d | d/dR | \psi_1^d \rangle = 0$, one can determine \mathbf{U} from the knowledge of first-order NACME as

$$\psi_m^d = \sum_i^n d_{im} \xi_i^d \quad (5)$$

where m varies from 1 to m . ξ_i^d are the configuration state functions (CSF) in the constructed diabatic electronic wavefunctions and d_{im} 's are the CI coefficients. Similarly, the adiabatic wavefunctions are given as

$$\psi_m^a = \sum_i^n c_{im} \xi_i^a \quad (6)$$

The relationship between the coefficient matrix $\mathbf{C}(n \times m)$ and $\mathbf{D}(n \times m)$ matrices is given by

$$\mathbf{D} = \mathbf{C} \mathbf{U} \quad (7)$$

\mathbf{U} can be obtained as $\mathbf{U} = \mathbf{W}(\mathbf{W}^\dagger \mathbf{W})^{-1/2}$ with $\mathbf{W} = \mathbf{C}^\dagger \mathbf{D}_{ref}$. This scheme is implemented in the MOLPRO suit of *ab initio* programs.⁵³ It is important to note that quasidiabatic PESs and coupling potentials do depend on the level of computational accuracy. We believe that the achieved accuracy in the present calculations would describe them quite satisfactorily and adequately.

2. Computational details

Ab initio calculations of adiabatic and quasidiabatic PESs for the H⁺ + O₂ system have been carried out for the triplet spin state using the MOLPRO[®] 2010.1 suite of programs⁵³ in the Jacobi coordinates (R, r, γ) as defined above in Section 1.1. Calculations were carried out using internally contracted multireference configuration interaction with single and double excitations (*ic*-MRD-CI)^{54–56} method and Dunning's⁵⁷ correlation consistent polarized valence triple zeta (*cc*-*p*VTZ) basis set. The *ab initio* surfaces are now obtained on an extended and refined grid (~ 11000 data points) for a total of 13 γ -values with inclusion of earlier calculated data points. The grid points in the scattering coordinates depend on the approach of H⁺ towards the molecular target, defined by γ which is equally spaced from 0° to 90° with the step of 7.5° interval. For example, for $\gamma = 7.5^\circ$, $R = 1.8 - 7.0(0.2)$, $8-15(1.0)$, $\gamma = 45^\circ$, $R = 0.8-7.0(0.2)$, $8-15(1.0)$ and $\gamma = 90^\circ$, $R = 0.2-7.0(0.2)$, $8-15(1.0)$. The grid along r varies from 1.5 to 3.5 with an interval of 0.1. The values are expressed in Bohr and the number in the parenthesis denotes step size in the stated interval. This grid pattern assures the proper inclusion of the interaction region in the scattering calculations for all angular approaches of H⁺. The equilibrium bond distance (r_{eq}) of the diatom (O₂) was fixed at the optimized value $r_{eq} = 2.293a_0$ which is close

to the experimental value.⁵⁸ The complete set of *ab initio* data over the computed grid points is available upon request.

Diabatic reference geometry was fixed far away from nonadiabatic region at $R = 15.0a_0$ throughout the entire calculations such that both adiabatic and diabatic potential energy curves (PECs) become identical. All calculations were performed in the C_{2v} and C_s abelian subgroups. For example, the molecule in the linear geometry ($\gamma = 0^\circ$ and $\gamma = 180^\circ$) belongs to the point group of $C_{\infty v}$ but the calculations were done only in C_{2v} group which is its abelian subgroup. Calculations in the off-collinear and perpendicular geometries were performed under C_s and C_{2v} point groups, respectively. Based on the chosen basis set *ab initio* program generated 74 molecular orbitals (MOs) of which lowest nine are occupied in the Hartree-Fock (HF) level. The ground state electronic configuration of the nine occupied HF orbitals in its increasing order of energy is given as follows: $(1\sigma)^2, (2\sigma)^2, (3\sigma)^2, (4\sigma)^2, (5\sigma)^2, (1\pi)_{xy}^2, (1\pi)_{xz}^2, (2\pi)_{xy}^1, (2\pi)_{xz}^1$ for the linear geometry, ($\gamma = 0^\circ$), $(1a')^2, (2a')^2, (3a')^2, (4a')^2, (5a')^2, (6a')^2, (1a'')^2, (7a')^1, (2a'')^1$ for the off-collinear geometry and $(1a_1)^2, (1b_2)^2, (2a_1)^2, (2b_2)^2, (3a_1)^2, (4a_1)^2, (1b_1)^2, (3b_2)^1, (1a_1)^1$ for the perpendicular geometry ($\gamma = 90^\circ$). The numbers as superscript of parenthesis denotes the number of electrons. Electrons in the first two orbitals were treated as core electrons at the multi configuration self consistent field (MCSCF)^{59,60} level of calculations and the electrons in the remaining orbitals were involved in the excitation. The considered active space was $[3-9a', 1-2a'']$ and the lowest four roots $[1-4^3A'']$ were calculated with equal weightage. In all calculations the energy threshold was kept at 0.32×10^{-6} a.u. compared to the default value of 1×10^{-6} a.u. in MOLPRO[®]. The computed structural parameters and energetics for O_2 , O_2^+ and HO_2^+ were earlier found in very good agreement with experimental⁵⁸ as well as theoretical results.⁶¹ Therefore, we believe that with the adopted threshold value, the obtained PESs would be quite adequate for the dynamical studies. Four roots of $^3A''$ states typically consisted of 21477678 uncontracted configuration state functions (CSF) and they were internally contracted to 642952 configurations.

3. Results and Discussions

3.1 Adiabatic potential energy surfaces

Here we examine the characteristics of the GS and the lowest three ESs in terms of potential energy curves (PECs), coupling potentials and NACMEs. The GS and the lowest three PESs respectively correlate to four different channels in the asymptotic limit: $\{H^+ + O_2(X^3\Sigma_g^-, v')\}$, $\{H(^2S) + O_2^+(X^2\Pi_g, v')\}$, $\{H(^2S) + O_2^+(^4\Pi_u, v')\}$ and $\{H(^2S) + O_2^+(^2\Pi_u, v')\}$. These asymptotic correlations are presented in Figure 1 for $\gamma = 7.5^\circ$. At extended R , PECs correlating to $H + O_2^+$ asymptotes

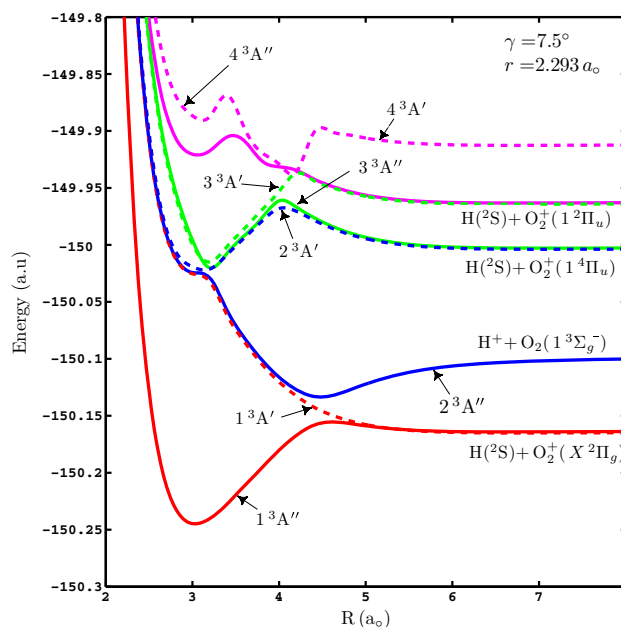


Figure 1. *Ab initio* adiabatic PECs for the lowest four roots of A' (dashed lines) and A'' (solid lines) states for the off-collinear ($\gamma = 7.5^\circ$) geometry as a function of R with $r = r_{eq} = 2.293a_0$ for the $H^+ + O_2$ system. The rich nonadiabatic coupling in the interaction region is evident from appearance of various avoided crossings.

show small shallow well suggesting the presence of charge transfer complex, HO_2^+ in the excited states. The PECs for both $^3A'$ and $^3A''$ are shown. In collinear geometries the incoming channel $\{H^+ + O_2(X^3\Sigma_g^-)\}$ and the exoergic CT channel, $H(^2S) + O_2^+(X^2\Pi_g)\}$ correlates to $1^3\Sigma^-$ and $1^3\Pi$ states, respectively. The spatial degeneracy of the $1^3\Pi$ state is lifted for off-collinear approaches giving rise to $1^3A'$ $1^3A''$ states.

We consider the nonadiabatic coupling arising out of the radial motions in view of the fact that rotational period of the diatom ($\sim ps$) is three orders of magnitude less as compared to a typical collision time ($\sim fs$) in the considered collision energy and interaction potential range. Therefore, there we ignore the coupling between Σ and Π states. There is a direct curve crossing between $\Sigma^- - \Pi$ symmetries in collinear ($\gamma = 0^\circ$) and perpendicular ($\gamma = 90^\circ$) geometries along the radial coordinates (R and r). The Σ^- state in the collinear geometry correlates with A_2 symmetry in the perpendicular geometry and Π state correlates with the degenerate B_1 and B_2 symmetries. In the off-collinear geometry the degeneracy of Π -state is lifted into A' and A'' states where as Σ^- correlates to A'' state. For off-collinear geometries the GS corresponds to A'' state (originating from Σ^- and B_2 symmetries in the collinear and perpendicular configurations, respectively) with triplet spin symmetry. There

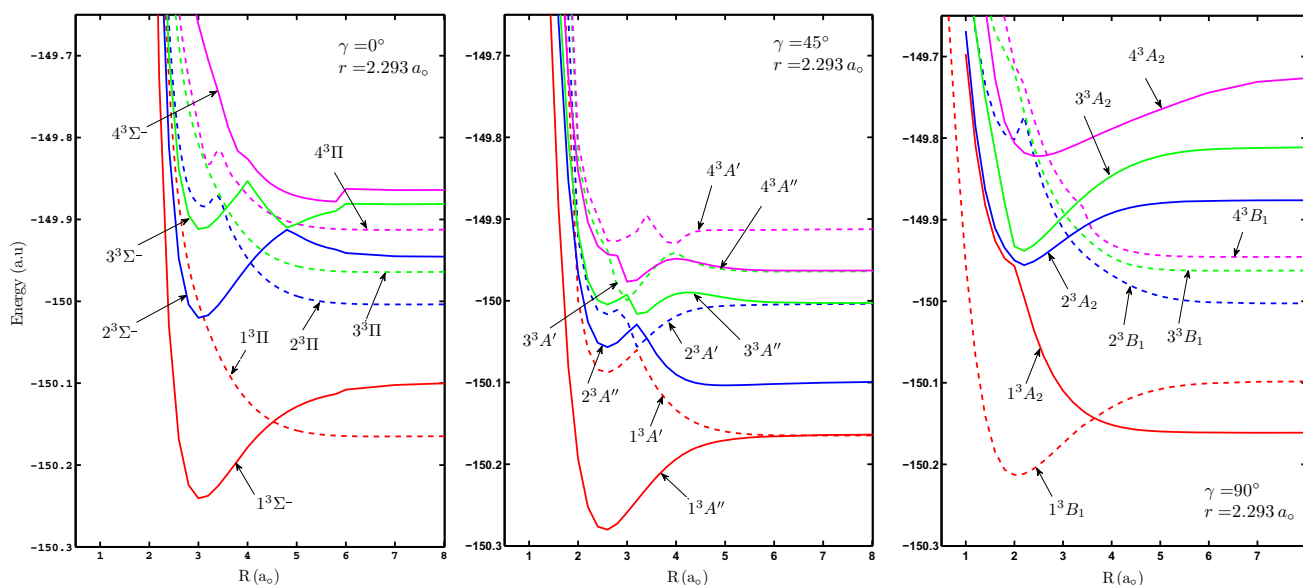


Figure 2. *Ab initio* adiabatic PECs for the collinear ($\gamma = 0^\circ$), off-collinear ($\gamma = 45^\circ$) and perpendicular ($\gamma = 90^\circ$) geometries as a function of R fixed at $r = r_{eq} = 2.293a_0$ for the ground and lowest seven excited states of $H^+ + O_2$ system. Note that the avoided crossing for off-collinear geometry becomes direct curve crossing in collinear and perpendicular geometries.

exists no coupling between the A'' and A' symmetries along the radial coordinates R and r .

As an illustration, the lowest four adiabatic PECs for the $^3\Sigma^-$ and $^3\Pi$ symmetries in the collinear geometries ($\gamma = 0^\circ$), A' and A'' symmetries in the off-collinear geometries ($\gamma = 45^\circ$) and B_1 and A_2 symmetries in the perpendicular geometries ($\gamma = 90^\circ$) as a function of the radial coordinate R fixed at $r = r_{eq} = 2.293a_0$ is shown in Figure 2. One can see the direct curve crossing between $^3\Sigma^- / ^3\Pi$ symmetries at $\gamma = 0^\circ$ and B_1 / A_2 symmetries at $\gamma = 90^\circ$ and the avoided crossing between A' / A'' symmetries at $\gamma = 45^\circ$. A number of avoided crossings are also seen among excited states at $\gamma = 45^\circ$. Experimental measurements reported the collision attributes for the IVE channel, ($H^+ + O_2 (^3\Sigma_g^-)$) and the CT channel ($H(^2S) + O_2^+(^2\Pi_g)$) and there were no hints of collision outcomes in the second and third ESs. Therefore, in the present study we have considered the computation of the electronic states pertaining to the lowest four states of A'' symmetry only and these PESs would be sufficient for the dynamics study for experimental collision energies in the range $E_{cm} = 9.5\text{--}23$ eV. All the four lowest adiabatic surfaces in the off-collinear geometry show various avoided crossings along R as well as r coordinate, and therefore they must be included in the dynamics calculations. Most of these crossings are actually cuts through the conical intersections of the PESs. One can also see the existence of Landau-Zener type of coupling between $1^3A''\text{--}2^3A''$, $2^3A''\text{--}3^3A''$ and $3^3A''\text{--}4^3A''$ along the R -coordinate.

3.2 Quasidiabatic potential energy surfaces

The adiabatic and quasidiabatic PECs for off-collinear geometries as a function of R with $r = r_{eq} = 2.293a_0$ for $\gamma = 7.5^\circ\text{--}82.5^\circ$ are shown in Figure 3. Both adiabatic and quasidiabatic PECs merge at large R values. The avoided crossings appear generally at two regions of R . For example, at $\gamma = 82.5^\circ$ (the upper right panel of Figure 3), the avoided crossing between GS and first ES PEC appears near $R = 3.5a_0$ whereas the avoided crossing between excited states is located in the neighborhood of $R = 2.3a_0$. The diabatic PECs exhibit direct crossings as shown on the right panel.

All the GS PESs are attractive in nature representing a stable state. Unlike the GS PES, the excited states are mostly repulsive with some shallow wells located at extended R values. Beyond $R = 8a_0$ the surfaces are almost flat. Representative plots for both adiabatic and quasidiabatic PESs for the lowest four states are shown in Figure 4 for $\gamma = 7.5^\circ$ as a function of R and r .

3.3 Nonadiabatic couplings and coupling potentials

It would be worthwhile to analyze the NACMEs which arise as the first and second derivative couplings in the adiabatic representations. Generally the second-order NACMEs are found very small in magnitude and therefore they are mostly ignored. As an illustration, the computed first-order NACMEs are shown as a function of R fixed at $r = r_{eq} = 2.293a_0$ for the off-collinear

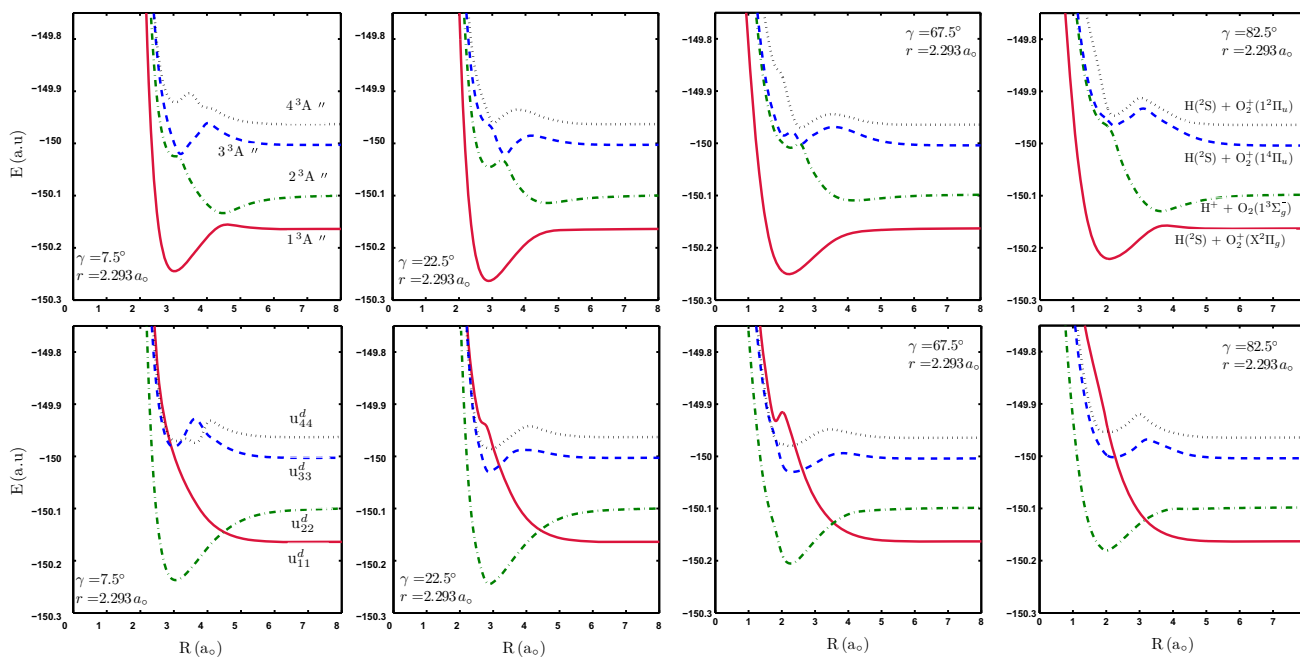


Figure 3. Adiabatic (top panel) and quasidiabatic (bottom panel) PECs of $1 - 4^3A''$ states as a function of R at fixed $r = r_{eq} = 2.293a_0$ for the off-collinear approach of $\gamma = 7.5^\circ, \gamma = 22.5^\circ, \gamma = 37.5^\circ$ and 82.5° for the ground state and lowest three excited states of $H^+ + O_2$ system. The asymptotic correlation is shown for $\gamma = 82.5^\circ$.

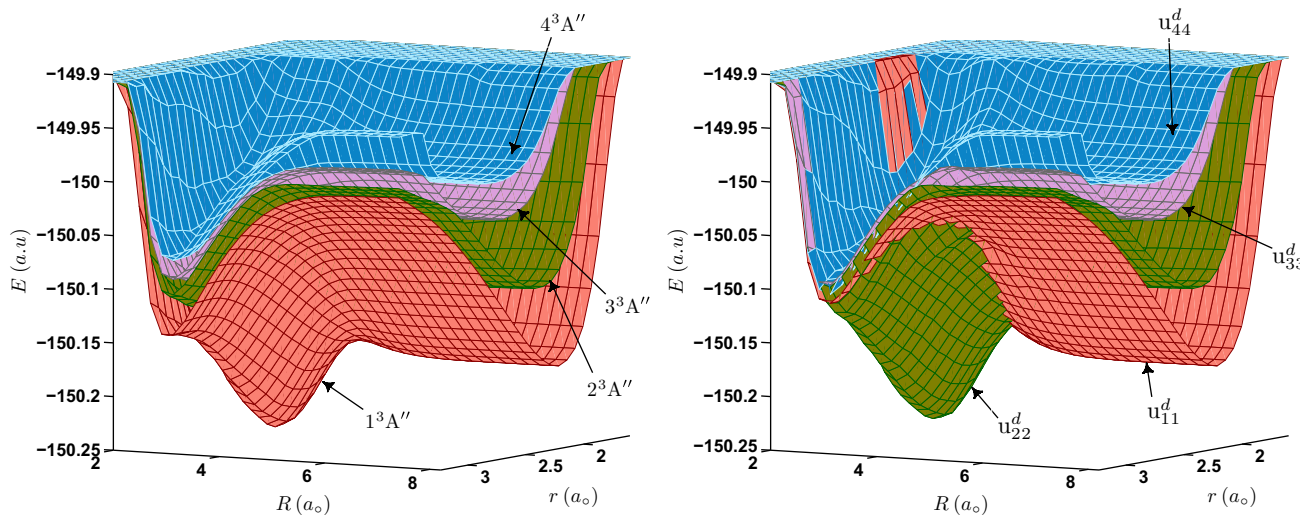


Figure 4. The lowest four PESs of $^3A''$ symmetry of $H^+ + O_2$ system at $\gamma = 7.5^\circ$. Left panel: adiabatic PESs. Right panel: quasidiabatic PESs.

angular approach for $\gamma = 7.5^\circ$ and 82.5° for the lowest four electronic states are shown in Figure 5 (top panel). As expected, the NACME values decay to zero for R values away from the nonadiabatic interactions for all angular approaches. Generally NACMEs grow up near avoided crossings. It is clear that the magnitude of NACME between GS and first ES (τ_{12}) is the highest in all angular approaches and it shows a maximum in the range $3 \leq R \leq 5$. Other NACME values like τ_{13} and τ_{24} also shows their strength in the regions of avoided

crossings. It should also be noted that the magnitude of τ_{12} is larger in near-collinear approaches ($\gamma = 7.5^\circ$ and $\gamma = 82.5^\circ$) when compared to the other angular approaches.

The nonadiabatic behavior can also be assessed in terms of potential coupling between different surfaces. For illustration, the variation of coupling potentials (u_{ij}^d ($i = 1, 2, j = 2, 3, 4$)) as a function of R with $r = r_{eq}$ for the lowest four states for $\gamma = 7.5^\circ$ and 82.5° are shown in the bottom panel of Figure 5. In the regions

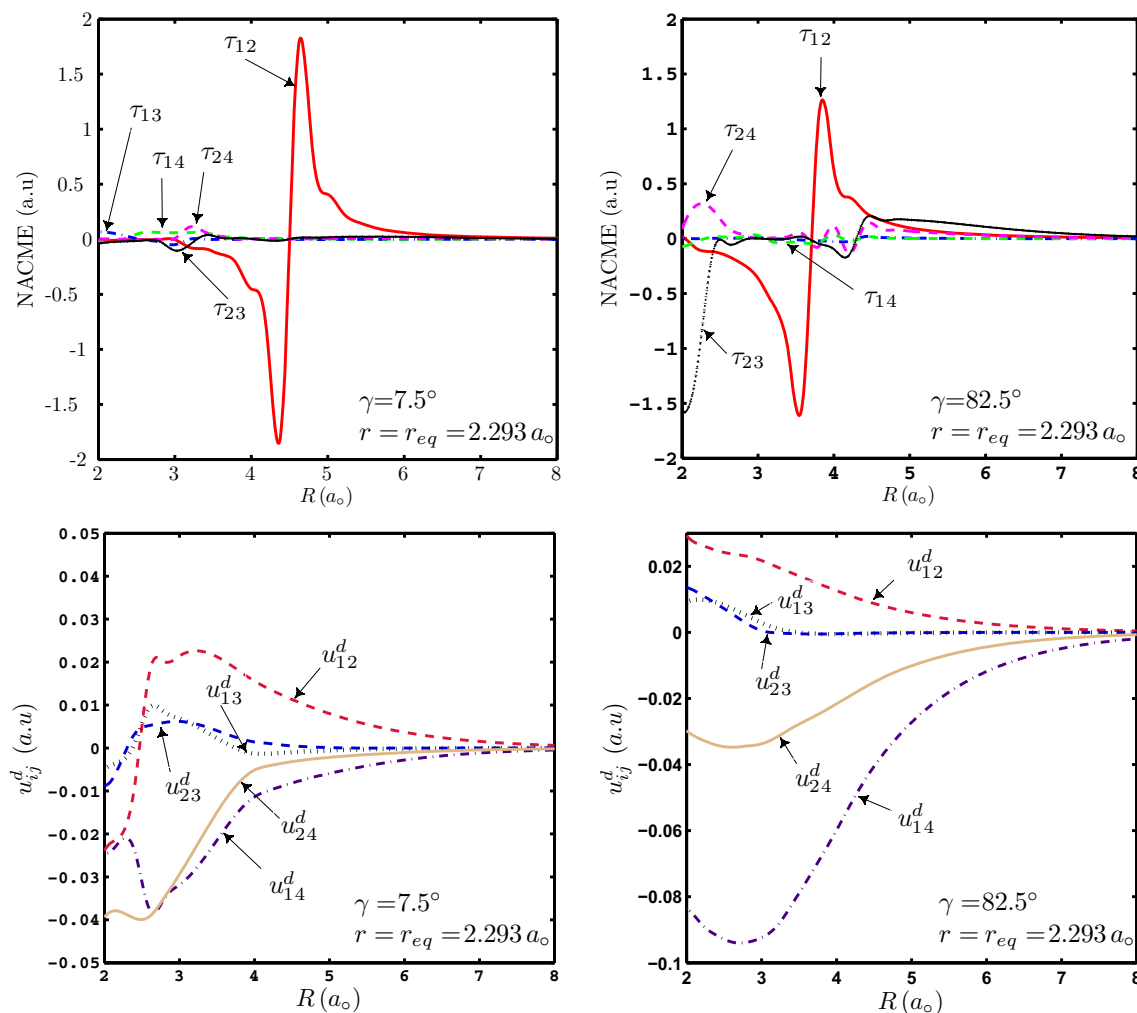


Figure 5. Top panel: The first-order nonadiabatic coupling matrix elements as a function of R fixed at $r = r_{eq} = 2.293a_0$ for $\gamma = 7.5^\circ$ and 82.5° orientations between the lowest four electronic states of $\text{H}^+ + \text{O}_2$ system. Bottom panel: The variation of coupling potential u_{ij}^d with R fixed at $r = r_{eq} = 2.293a_0$ for $\gamma = 7.5^\circ$ and 82.5° of $\text{H}^+ + \text{O}_2$ system.

of avoided crossings quasiadiabatic PECs of the GS and first three excited ESs show a smooth behavior. From the Figure 5 (bottom panel), it is clear that the coupling pattern is mostly similar in trend in going from $\gamma = 7.5^\circ$ to $\gamma = 82.5^\circ$.

4. Asymptotic interaction potential

The long range interaction potential V_{as} for the $\text{H}^+ + \text{O}_2$ system ($R > 15a_0$) was constructed by multi-polar expression as

$$V_{as}(R, r; \gamma) \sim \frac{Q(r)}{R^3} P_2(\cos \gamma) - \frac{\alpha_0(r)}{2R^4} - \frac{\alpha_2(r)}{2R^4} P_2(\cos \gamma) \quad (8)$$

where V_{as} is the asymptotic long range potential, $Q(r)$ is the quadrupole moment, $\alpha_0(r)$ and $\alpha_2(r)$ are the dipole polarizability components and the P_i 's are Legendre polynomials. We computed the $Q(r)$, $\alpha_0(r)$ and $\alpha_2(r)$ as a function of internuclear distance (r) of $\text{O}_2(X^3\Sigma_g^-)$ and was fitted them with the following functional form

$$x(r) = \sum_{i=0}^N C_x(i) \left(\frac{1}{r}\right)^i \quad (9)$$

where x stands for $Q(r)$ or $\alpha_0(r)$ or $\alpha_2(r)$ and C_x are the coefficients used in the fitting and are used to generate asymptotic PESs correlating to the IVE channel, $\text{H}^+ + \text{O}_2(X^3\Sigma_g^-)$. These coefficients are shown in Table 1. For the VCT channels, $\text{H}(^2\text{S}) + \text{O}_2^+(X^2\Pi_g)$, $\text{H}(^2\text{S}) + \text{O}_2^+(X^4\Pi_u)$ and $\text{H}(^2\text{S}) + \text{O}_2^+(X^4\Sigma_g^-)$, the asymptotic potential is modeled as charge (O_2^+ being a point

Table 1. Values of coefficients (in a.u.) used in Eq. 8 for the generating Q , α_0 and α_2 as a function of r .

$C(i)$	Q	α_0	α_2
$C(0)$	0.95×10^2	0.71×10^2	0.63×10^2
$C(1)$	-0.20×10^4	-0.37×10^3	-0.48×10^3
$C(2)$	0.18×10^5	0.80×10^3	0.12×10^4
$C(3)$	-0.88×10^5	-0.95×10^3	-0.16×10^4
$C(4)$	0.26×10^6	0.70×10^3	0.12×10^4
$C(5)$	-0.47×10^6	-0.33×10^3	-0.60×10^3
$C(6)$	0.53×10^6	1.00×10^2	0.18×10^3
$C(7)$	-0.33×10^6	-0.19×10^2	-0.35×10^2
$C(8)$	0.88×10^5	1.00×10^1	0.38×10^1
$C(9)$		-0.91×10^{-1}	-0.18×10^0

charge) - polarizability (of H) interactions. The polarizability of the H-atom ($\alpha_0 = 2.737$ a.u.) is used to generate the asymptotic potentials. These computed asymptotic potentials have been connected smoothly to the respective interaction potentials in order to obtain the global PESs for all γ . The coupling PESs become zero for all r for $R > 15a_0$.

5. Conclusions

Ab initio computations were undertaken to obtain the electronic GS and the lowest three ESs at MRCI/cc-pVTZ level of accuracy for the $H^+ + O_2$ system. The richness and complexities of nonadiabatic interactions among them have been examined in terms of first order nonadiabatic coupling matrix elements. For computational feasibility and numerical convenience the corresponding quasidiabatic PESs have also been obtained along with potential coupling using *ab initio* procedures. In the present study the existing four-state *ab initio* PESs have been further refined with inclusion of $\sim 5,000$ computed *ab initio* data points, particularly over angular intervals so that the anisotropy of the interaction potential is well represented. This was essential since the collision attributes such as DCS and vibrational transition probabilities crucially depend on it particularly in view of processes involving multi-electronic excitations.

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