

Diabatic potential energy surfaces of $H^+ + CO$

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Abstract. *Ab initio* adiabatic and diabatic surfaces of the ground and the first excited electronic states have been computed for the $H^+ + CO$ system for the collinear ($\gamma = 0^\circ$) and the perpendicular ($\gamma = 90^\circ$) geometries employing the multi-reference configuration interaction method and Dunning's *cc-pVTZ* basis set. Other properties such as mixing angle before coupling potential and before coupling matrix elements have also been obtained in order to provide an understanding of the coupling dynamics of inelastic and charge transfer process.

Keywords. *Ab initio* potential energy surfaces; non-adiabatic coupling; diabaticization; mixing angle.

1. Introduction

Non-adiabatic phenomena are ubiquitous in nature. Ion–molecule collisions (reactions) often lead to such processes. Proton collisions with simple molecules are of fundamental importance in several areas of chemical physics and astrophysics. Being electronically structureless particle, proton can penetrate the molecular electronic charge cloud rather deeply. As a result, quite often the low-lying excited electronic state (ES) potential energy surfaces (PES) interact with the ground electronic state (GS) PES, leading to inelastic and charge transfer (CT) process.

State-selected beam experiments^{1,2} coupled with proton energy-loss spectroscopy in the collision energy range 0–30 eV show a marked selectivity for vibrational excitation in diatomic molecules. For example, experiments done on N_2 , CO, NO with protons show that the amount of vibrational excitation in these molecules is quite low and that it increases in the order $N_2 < CO < NO$. On the other hand, it is comparatively large for H_2 and even larger for O_2 .

It is clear that the long range interaction potential expressed in terms of charge-quadrupole, charge-dipole, etc. does not seem to play a dominant and decisive role in the dynamics of energy transfer processes. At closer approaches the valence forces play a significant role. The measured selectivity for vibrational a excitations has been explained by the theoretical studies for the $H^+ + H_2$, $H^+ + O_2$, $H^+ + N_2$

systems. In the $H^+ + H_2$,³ there is an avoided crossing between the GS PES and the first ES PES which asymptotically correlates with the $H + H_2^+$. In the $H^+ + O_2$ system⁴ there is a direct curve crossing between the GS PES ($H^+ + O_2$) and the ES PES ($H + O_2^+$). Interestingly, in the $H^+ + N_2$ system,⁵ the low-lying ES PESs are found to be well separated from the GS PES.

In the $H^+ + CO$ system, the asymptotic CT channel, $H(^2S) + CO^+(1^2\Sigma^+)$ is endoergic (≈ 0.42 eV) as compared to the asymptotic $H^+ + CO(1^1\Sigma^+)$ channel². Therefore, it is expected that probability of the CT processes would be less, and that they would be accessible mostly by the Rosen–Zener–Demkov type of coupling.⁶ This is confirmed by the experimentally observed total Differential Cross Section (DCS) for proton and H-atom detection in the $H^+ + CO$ scattering at $E_{lab} = 30$ eV where the CT was found to be almost an order of magnitude less probable than that of elastic and vibrational excitations. Just recently, Potential Energy Curves (PEC) for the GS and several low lying ESs were reported by our group⁷ as a function of R (defined in figure 1) for collinear and perpendicular geometries with r fixed at r_{eq} . A preliminary time-dependent wave packet study involving the two- and three-states was also reported there.

It is important to point out here that bound molecular ions such as HCO^+ and HOC^+ have been identified in the interstellar media, and many experimental as well as theoretical studies have been focussed on the characterization of the bound states of these ions. For relevant information see ref. 10 and references

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therein. In recent years, high level *ab initio* computations have become available characterizing the interaction well. Puzzarini *et al*⁸ computed the GS PES of HCO⁺ ion near its equilibrium geometry (collinear) and predicted the vibrational and rotational frequencies of the HCO⁺ ion using variational calculations at the CASSCF-MRCI/*cc-pVQZ* level of theory. Mladenovic and Schmatz⁹ computed the three-dimensional ground state PES for the HCO⁺ and HOC⁺ ions using the CCSD(T) method employing the *cc-pVTZ* basis set of Dunning,¹¹ and predicted the rovibrational spectrum along with the number and densities of bound vibrational states.⁹ Just recently, a new full three-dimensional *ab initio* GS PES in the Jacobi coordinates was obtained by our group¹⁰ to study the time-independent quantum dynamics of vibrational excitations in the system in the framework of VCC-RIOSAs scheme on the GS PES. Overall, computed collision attributes were found to be in good agreement with the experiments.²

Although accurate description of the GS PES for the title system has become available there is a lack of understanding on the characteristics of the ES PES and on the coupling between the two. In our previous study,⁷ we had studied the non-adiabatic interactions between the GS and several low lying excited states of the system only as a function of R and obtained the corresponding potential energy curves using the *ab initio* MRCI computations. We extend our study to compute the GS and the first ES PESs and their non-adiabatic coupling elements which would be helpful for the quantum dynamical study.

The paper is organized as follows. In §2 the details of computational methodology have been given. In the sub-sections of 2, the details about non-adiabatic coupling elements, mixing angle and diabatic potential energy surfaces have been given, along with

results and discussion, followed by a summary in §3.

2. Computational methodology

2.1 Diabatic potential energy surface (DPES)

Ab initio calculations have been carried out in two different molecular orientations in the Jacobi coordinates (shown in figure 1) where r is the inter-nuclear distance of CO, R is the distance of the proton from the center of mass (CM) of CO molecule and γ is the angle, $\cos^{-1}(R.r)$. $\gamma=0^\circ$ defines the collinear approach of proton towards O-atom while $\gamma=90^\circ$ defines the perpendicular approach towards the CM of CO. The computations have been performed in C_{2v} and C_s point groups for the collinear and off-collinear geometries. The PESs have been obtained by multi-reference configuration (MRCI) method using the MOLPRO suite of programs.¹² We have used Dunning's *cc-pVTZ* (correlation consistent polarized Valence Triple Zeta) basis sets for H, C and O atoms.¹¹ The computations have been performed in the collinear and off-collinear geometries for the following set of grid points. For $\gamma=0^\circ$, $R=1.4-2.0$ (0.2), 2.1-4.2 (0.1), 4.4-6.0 (0.2), 7.0-10.0 (1.0), 12.0-20.0 (2.0); $r=1.5-3.2$ (0.1) and for $\gamma=90^\circ$, $R=0.6-2.0$ (0.2), 2.1-4.2 (0.1), 4.4-6.0 (0.2), 7.0-10.0 (1.0), 12.0-20.0 (2.0); $r=1.6-3.2$ (0.1). The number in the parenthesis indicates the increments in the stated intervals. We use atomic units throughout unless it is stated otherwise. The spectroscopic designations of the ground and the first excited states for $\gamma=0^\circ$ are $1^1\Sigma^+$ and $2^1\Sigma^+$ and for $\gamma=90^\circ$ are $1^1A'$ and $2^1A'$. $1^1\Sigma^+$ state corresponds to the asymptotic entrance channel, $H^+ + CO(1^1\Sigma^+)$, whereas $2^1\Sigma^+$ corresponds to the asymptotic CT channel, $H(2S) + CO^+(2^2\Sigma^+)$. The computed energy difference between these asymptotic channels is found to be 0.39 eV as compared to the reported experimental value of 0.42 eV.² The adiabatic GS and ES PESs are shown in figure 2a for $\gamma=0^\circ$ and $\gamma=90^\circ$. These PESs become very close energetically in the asymptotic regions ($R > 8a_0$) and run parallel exhibiting a typical Rosen-Zener-Demkov type of coupling.^{6,13,14} Contour plots of these PESs have also been shown in figure 3a. The GS PES exhibits an interaction well in both the orientations; the well in the collinear geometry is relatively deeper and located slightly inward. In contrast, the ES PESs are purely repulsive, and one sees a hump which originates from the avoided crossing with the next higher excited state ($3^1\Sigma^+$) (see figure 2 of ref. 7)

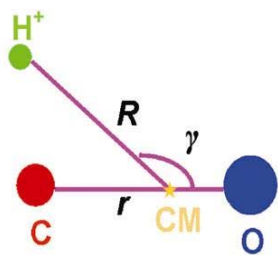


Figure 1. Jacobi Coordinates: R is the distance of H^+ from center of mass (CM) of CO and r is internuclear distance of CO and $\gamma = \cos^{-1}(R.r)$.

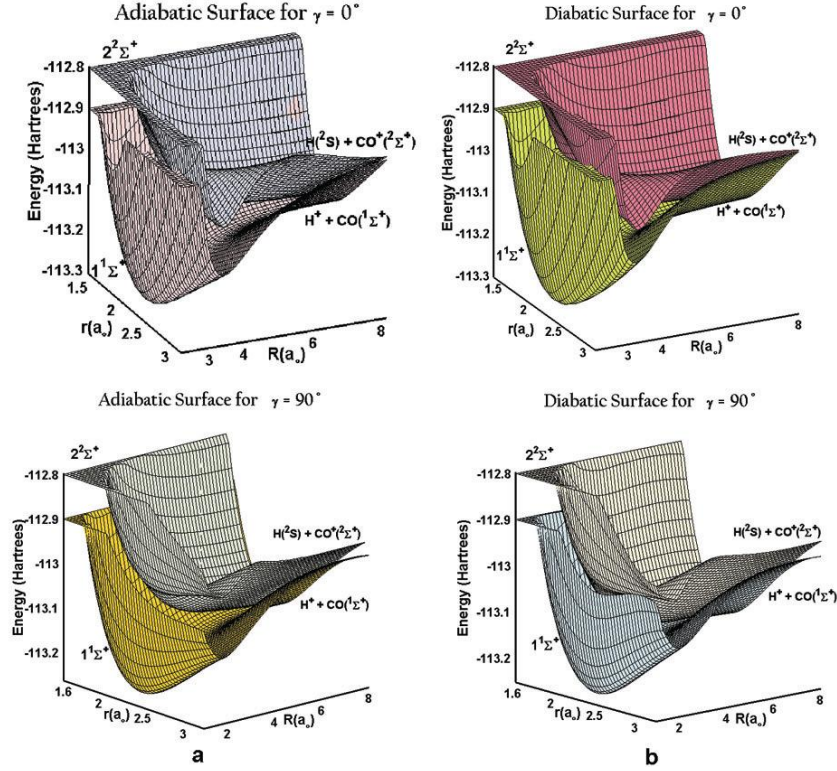


Figure 2. The GS and the ES PESs for $\gamma=0^\circ$ and $\gamma=90^\circ$ (a) adiabatic PESs; (b) the corresponding diabatic PESs.

2.2 Non-adiabatic coupling matrix element (NACME)

The dynamical calculations in the adiabatic representation requires a knowledge of the kinetic coupling elements of the form

$$\tau = \left\langle \psi_1^a \left| \frac{\partial^n}{\partial R^n} \right| \psi_2^a \right\rangle, \quad (1)$$

where $n = 1$ or $n = 2$. The terms with $n = 2$ are generally neglected since they are generally small in magnitude.¹⁵ The kets ψ_1^a and ψ_2^a represent the electronic wavefunctions of the two adiabatic states and R stands for radial nuclear coordinate. Non-adiabatic coupling matrix elements (NACME) have been computed between the GS and the first excited states by numerical differentiation using finited difference method,¹⁶

$$\left\langle \psi_1^a \left| \frac{\partial^n}{\partial R^n} \right| \psi_2^a \right\rangle_{R_0} = \frac{1}{2\Delta R} \langle \psi_1^a(R_0 + \Delta R) | \psi_2^a(R_0 - \Delta R) \rangle, \quad (2)$$

where ΔR is the small increment. We have used the MOLPRO code¹² to compute the NACME values. In this procedure, first the orbitals are determined at a reference geometry, then the calculations are performed at displaced geometries. The NACME values have been obtained using the MRCI method by computing the finite-differences of configuration interaction (CI) wavefunctions with $\Delta R = 0.0002a_0$. Additional calculations were also performed for a few data points with $\Delta R = 0.002a_0$ and the obtained values were identical with the values obtained with $\Delta R = 0.0002a_0$. In earlier non-adiabatic studies NACME values were also computed using MOLPRO for He-CN collisions¹⁷ and for H_2S photodissociation.^{18,19}

Kimura *et al*²⁰ had computed the NACME values for this system (as a function of R only) and our previous results⁷ compare well with their data. Generally, for the two orientations, couplings show similarities in both shape and magnitude. At large R , NACME value becomes very small (almost zero) and for smaller R it goes up through a positive maximum and then through a negative maximum (figure 4 of ref. 7).

2.3 Diabatization and mixing angle

In the adiabatic representation, the non-adiabatic coupling originates in the kinetic energy terms. The singularities of the NACMEs and their abrupt changes within certain ranges of configuration space make the computational task very difficult. Such a situation can be avoided if one transforms the wavefunction using an orthogonal transform into another set of wavefunction in which the NACME values become (zero or) vanishing small. In this (diabatic) representation the non-adiabatic coupling originates into the potential energy terms which are convenient to handle computationally. It is not always possible to make the non-adiabatic coupling terms exactly zero. But in the diabatic representations they can be made vanishingly small in the kinetic energy terms and thus one obtains a quasi-diabatization of the coupling.

For the computational convenience, we treat the coupling between the two electronic states in a diabatic representation. The diabaticization procedures, their exactness and their associated advantages for numerical computations have been discussed and documented in the literature in detail.^{21–27} A general discussion on it has also been recently published.²⁸ For convenience and familiarity of terms, we summarize the essential detail below.

For a two state coupling the transformation from the adiabatic representation to the diabatic representation is achieved by the following unitary transformation

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

where $\psi_{1,2}^a$ and $\psi_{1,2}^d$ are the adiabatic and diabatic electronic wave function, respectively. α is the mixing angle between the two adiabatic electronic states and it is a function of R and r for fixed value of γ . Since $\langle \psi_1^d | \partial / \partial R | \psi_2^d \rangle \approx 0$, the mixing angle α can be obtained by integration of NACME.^{16,17,19,22,24,25} However, computation of α through this route may become quite cumbersome with increase of dimensionality of a problem.

Using (3), the matrix elements of \hat{H}_e are given by

$$V_{11}^d = \langle \psi_1^d | \hat{H}_e | \psi_1^d \rangle = V_1^a \cos^2 \alpha + V_2^a \sin^2 \alpha, \quad (4)$$

$$V_{22}^d = \langle \psi_2^d | \hat{H}_e | \psi_2^d \rangle = V_1^a \sin^2 \alpha + V_2^a \cos^2 \alpha, \quad (5)$$

$$V_{12}^d = \langle \psi_1^d | \hat{H}_e | \psi_2^d \rangle = (V_1^a - V_2^a) \cos \alpha \sin \alpha, \quad (6)$$

and $V_{12}^d = V_{21}^d$. The $V_{1,2}^a$ are the potential energies in the adiabatic representation. V_1^d and V_2^d are the corresponding potentials energies in the diabatic representation and V_{12}^d is the coupling potential between the two states.

Several authors have also proposed schemes to derive α from the knowledge of NACME obtained from the solution of electronic Schrödinger equation.^{29,30} Other approximate methods^{16,17,31–33} have also been suggested which avoid the direct computation of NACME and α is obtained from the CI coefficients of the electronic wave functions.

In the present study, we have used the MOLPRO code to obtain quasi-diabatic states directly wherein the diabaticization is achieved by determining the diabatic wave functions and the corresponding CI vectors which vary as little as possible as a function of geometry.^{16,17,32} This condition is met by using the invariance of the MRCI energies with respect to unitary transformations among the active orbitals so that the geometry dependence of the orbitals is minimized. This is accomplished by maximizing the overlap for all the pairs of the active orbitals at R_{ref} ($R = 16a_0$, $r = r_{\text{eq}} = 2.1322a_0$) with those at a neighbourhood geometry R' using the Jacobi rotation technique. The description and application of the procedure for a general case is described in detail in (ref. 19).

The obtained mixing angle α has been plotted as a function of R and r for $\gamma = 0^\circ$ and $\gamma = 90^\circ$ in figure 4. It can be seen that α goes to zero for $R \geq 16a_0$ where both the adiabatic and diabatic potentials become identical. In figure 5 diabatic coupling potential $V_{12}^d (= V_{21}^d)$ are shown as a function of R and r for both orientations. The magnitude of the coupling potential is relatively low and it shows its strength for $R < 6a_0$. The computed diabatic PESs for $\gamma = 0^\circ$ and $\gamma = 90^\circ$ are shown in figure 2b and their contour plots are shown in figure 3b. Interestingly, these PESs appear similar to the corresponding adiabatic PESs and they do not show any crossings contrary to general expectations. As pointed out above, the adiabatic PESs show Rosen–Zener–Demkov type of coupling^{6,13,14} exhibiting wide regions of weakly coupled and nearly parallel adiabatic PESs. In such situations, the diabatic PESs may not cross because of weak coupling. It is worthwhile to point out here that similar observations have also been found for other model systems exhibiting this type of weak

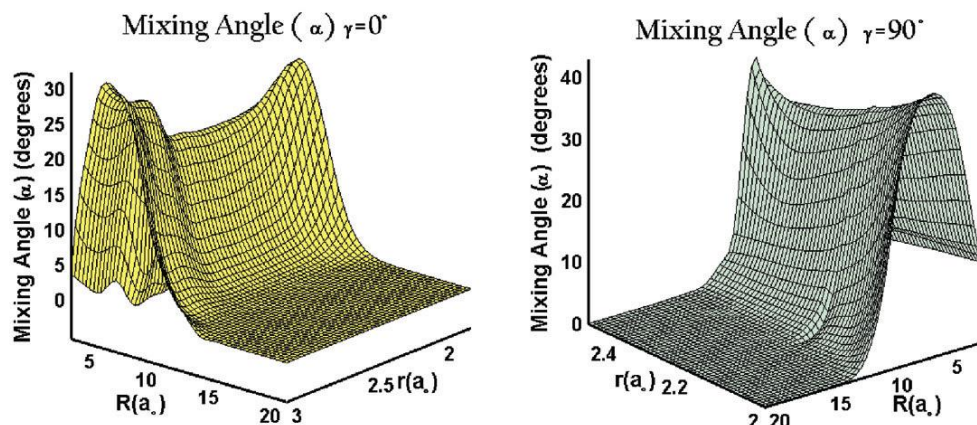


Figure 4. Mixing Angle for $\gamma = 0^\circ$ and $\gamma = 90^\circ$.

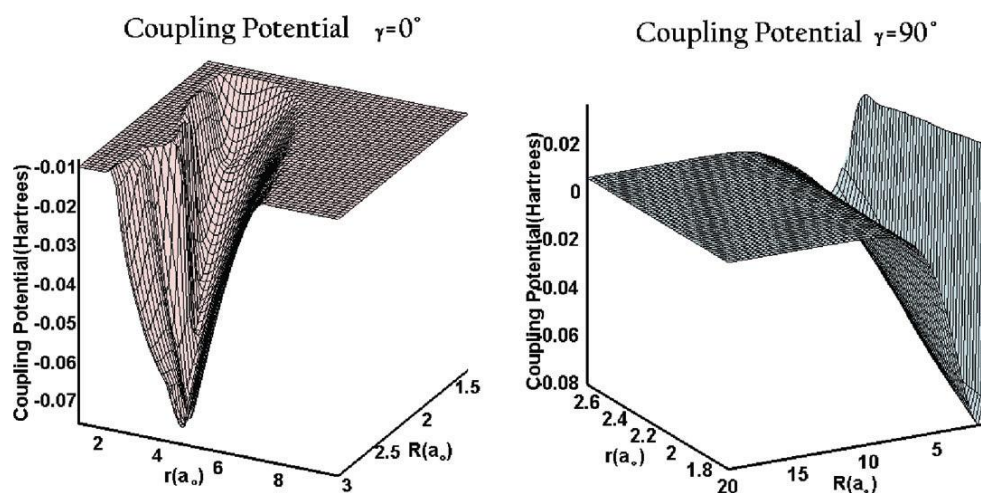


Figure 5. Diabatic coupling potential V_{12}^d for $\gamma = 0^\circ$ and $\gamma = 90^\circ$.

coupling.³⁴ It is that for the low strength of V_{12}^d that the probability of the CT processes would be low as hinted by experiments.² It would be worthwhile to obtain the diabatic PESs in full dimensionality (as a function of R , r , and γ) in order to carry out quantum dynamics study and compare the collision attributes which have been obtained from experiments.

3. Summary

In the present study the GS ($1^1\Sigma^+$, asymptotically correlating to $\text{H}^+ + \text{CO}(1^1\Sigma^+)$) and the ES ($2^1\Sigma^+$, asymptotically correlating to $(\text{H}(^2\text{S}) + \text{CO}^+(1^2\Sigma^+))$) of the $\text{H}^+ + \text{CO}$ system have been obtained from *ab initio* computations using the MRCI method and Dunning's

cc-pVTZ basis set. The corresponding quasi-diabatic PESs and the non-adiabatic coupling expressed in terms of diabatic coupling potential have also been obtained using the diabatisation procedure recently proposed in the literature based on the quasi-diabatic electronic wavefunctions and their CI coefficients. To the best of our knowledge perhaps this is the first attempt to construct the diabatic PESs for the title system.

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