First electronically excited state of the water-argon complex: An analytical fit to the CASPT2 potential

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Abstract

An analytical force field for the study of water photolysis and the cage effect in argon environment is constructed. A set of more than 200 *ab initio* CASPT2 points mapping important regions on the first exited potential energy surface of the H_2O-Ar cluster is fitted to a physically justified empirical model and the quality of the fit is discussed.

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I. INTRODUCTION

Cryogenic heterogeneous clusters consisting of a small hydrogen containing molecule and one or more rare gas atoms have unique properties both in their ground and excited electronic states. In the ground electronic state the light and cold hydrogen atom in a shallow intermolecular potential behaves as a strongly delocalized quantum particle. As a result, large amplitude bending motions are observed for clusters such as Rg...HX, where X represents a halogen and Rg a rare gas atom [1-3]. In cases, when the host molecule is embedded in large inert clusters or matrices this motion is even more delocalized and the molecule almost freely rotates [4-5].

This delocalization has a strong effect on the processes of photodissociation and caging initiated by photoexcitation of the hydrogen containing molecule into the first dissociative continuum. For example, in the Ar...HCl complex the delocalization in the bending modes strongly diminishes caging by the single solvent atom, which one would naively expect to be strong for an optimal collinear geometry [2-3]. For an HCl molecule in the first solvation shell of argon atoms it has among others been predicted that the relative yields of direct photodissociation and caging can be efficiently controlled by a preexcitation of the host into specific low-lying rotational states [5].

Among complexes containing triatomic molecules, geometry and vibrational structure of the H_2O-Ar cluster prepared by a supersonic jet expansion has been studied in most detail, primarily by means of high resolution IR and microwave gas phase spectroscopy [6-9]. In a complementary theoretical work, the ground electronic state potential energy surface of this cluster has been mapped at a high quality *ab initio* level [10]. While the photolysis of an isolated water molecule in the first excited continuum has been very well understood for some time [11], first information concerning this process in argon environment (so far only for a single solvent atom) has been gained only recently. A spectroscopic study of water photolysis in the H_2O-Ar complex [12] as well as a quasiclassical simulation using a semiempirical excited electronic state intermolecular potential [13] have demonstrated a significant effect of the single solvent atom on the photodissociation process.

For a quantitative modeling of water photolysis in argon clusters there is a clear need for an accurate description of the first excited state of these complexes. In our previous study, we have shown that the multiconfigurational self-consistent field method with a second order perturbation correction (CASPT2) [14-15] employing a sufficiently flexible basis set provides a reliable description of the excited state $H_2O(\tilde{A})$-Ar potential energy surface, and we have generated a limited number of *ab initio* points for geometries relevant for the photodissociation process [16]. Here, we complete the mapping of this potential surface and mainly present an accurate and physically justified analytical fit to the CASPT2 data. Given the computational complexity of the required *ab initio* calculations, a simple potential fit is an essential ingredient of any future classical or quantum molecular dynamics studies, especially for clusters with more than one solvent atom.

The paper is organized as follows. In Section II we introduce the system under study. The *ab initio* calculations are summarized in Section III and the fitting procedure is described in Section IV. Results and discussion are presented in Section V and Section VI contains the concluding remark.

II. SYSTEM

The geometry of the system under study is depicted in Fig. 1. The internal coordinates of the H_2O-Ar complex used for the *ab initio* mapping of the excited state surface are the two O-H distances r_1 and r_2, the H-O-H angle α, the O-Ar distance R, the in-plane angle θ, and the out-of-plane angle λ. The angles θ and λ define the O-Ar axis with respect to a line bisecting the water angle α. The angle $\lambda = 0^o$ corresponds to planar structures of the water-argon cluster possessing the C_s symmetry, while structures with a non-zero value of this angle are generally of the C_1 symmetry.

For an analytical fit which is constructed using functions depending on atom-atom distances we introduce also the two argon-hydrogen distances ρ_1 and ρ_2. Finally, since the first excited state of the water molecule corresponds to dissociation into the H and OH fragments we assume without any loss of generality the coordinate r_2 to be dissociative and the coordinate r_1 to be that of the nascent OH species.

III. *AB INITIO* COMPUTATIONS

As in our preliminary study [16] the CASPT2 method [14-15], which accounts for both dynamical and non-dynamical correlation effects, has been employed. Within this approach, CASSCF calculations are carried out for the (ground or excited) state of interest with a subsequent second order perturbation correction to the energy. Calculations reported here have been performed using the Dunning correlation-consistent polarized valence double zeta augmented basis set which has the form (13s9p2d)/[5s4p2d] for argon, (10s5p2d)/[4s3p2d] for oxygen, and (5s2p)/[3s2p] for hydrogen [17-18]. An oxygen diffuse s function (exponent 0.032) is added for correct description of Rydberg states of water. Such a basis set is suitable both for the description of excited states of water and for modeling of the repulsive part of the H_2O-Ar interaction.

A strong valence-Rydberg mixing has been observed for the first excited $^1B_1(\tilde{A})$ state of water [19]. In order to describe this mixing correctly a sufficiently large and flexible active space must be considered. Urban and Sadlej have included eight electrons in the active space for the description of low lying excited states of the water molecule [20]. Their CASSCF electronic excitation energies of the first excited singlet state are 7.76 and 7.31 eV for two different choices of the active space. Applying an analogous approach to the construction of the active space for the H_2O-Ar complex is computationally infeasible for an extended scan of the potential energy surface. Therefore, the possibility of using a smaller active space including four electrons has been considered.

In all calculations, the 1s core orbital of the oxygen atom has been kept frozen. Employing the C_{2v} symmetry, the active space has been constructed by including five orbitals of a_1 and two orbitals of b_1 symmetry containing four electrons. In the C_s symmetry (which is that of the planar H_2O-Ar complex) the water active space consists of six orbitals of A' symmetry occupied) and two orbitals of A" symmetry with four electrons. With these active spaces, the excitation energies to the first excited singlet state have been calculated as 7.48 and 7.49 eV for the C_{2v} and C_s symmetries, respectively. This is in an excellent agreement with the corresponding experimental value of 7.42 eV [21].

For the H_2O-Ar complex, the active space is expanded to seven orbitals of A' symmetry and three orbitals of A" symmetry. Further expansion of this active space has no effect on the excitation energy. When the C_1 symmetric non-planar H_2O-Ar geometries are considered, ten orbitals in the active space are used. This choice provides a smooth transition from C_s to C_1 structures with no artificial jump in energy.

IV. ANALYTICAL FIT

In order to enable dynamical simulations of photodissociation in water-argon and especially in larger H_2O-Ar_n complexes it is computationally inevitable to construct a simpler potential model than the elaborate *ab initio* calculations described above. Our strategy is to develop an accurate, physically meaningful, analytical, and in terms of the solvent pairwise potential. The potential parameters are optimized by fitting to CASPT2 points for the smallest H_2O-Ar cluster, and the potential can be then directly used for modeling of photolysis of water surrounded by an arbitrary number of argons.

The total energy of the excited $H_2O(\tilde{A})$-Ar_n complex is expressed as:

$$V_{H_2O(\tilde{A})-Ar_n} = V_{H_2O(\tilde{A})} + nV_{Ar} + \sum_{i}^{n} V_{int}^{i} + \sum_{i>j}^{n} V_{Ar-Ar}^{ij} \tag{1}$$

where n is the number of argon atoms, $V_{H_2O(\tilde{A})}$ is the electronic energy of water in the first excited state Ã, V_{Ar} is the electronic energy of an isolated argon atom, and the term V_{int}^{i}

represents the interaction energy between the water molecule and a single argon atom i. V^{ij}_{Ar-Ar} is the pair interaction between argon atoms i and j [22]. For the purpose of fitting to *ab initio* points, Eq. 1 with $n = 1$ serves as a definition equation for the interaction term V_{int}.

V_{Ar} is a number independent on any geometrical parameters, which for the method and basis used equals to -526.95529 au. The $V_{H_2O(\tilde{A})}$ term is a function of internal coordinates of the water molecule r_1, r_2, α (see Fig. 1). For its functional form we have directly adopted a highly accurate and elaborate excited state water potential from Ref. 11. Consistency of this step is given by the fact that this potential has been obtained by fitting to *ab initio* calculations of a quality comparable to those presented here. To match our definition of zero energy, the potential from Ref. 11 has been shifted by -75.89908 au.

The term V_{int} is generally a function of all six internal coordinates $r_1, r_2, \alpha, R, \rho_1, \rho_2$ of the water-argon complex (see Fig. 1). However, some simplifications can be done, since in the first excited state water dissociates to H+OH, and since we are only interested in the part of the potential energy surface which is relevant for the photolysis. Due to the fact that the particular choice of one of the two equivalent H + OH photodissociation channels is accomplished well before the collision with the solvent, we can construct the interaction with the argons for the dissociating and non-dissociating hydrogen separately. We neglect the r_1-dependence of the energy V_{int}, because the length of the non-dissociating O-H bond changes only slightly during the photodissociation, especially for low energies of the exciting photon [11]. The distance r_1=0.957 Å becomes then simply a constant in our fit. Another parameter the interaction potential V_{int} is only weakly dependent on, is the H-O-H angle α. This is especially true for the early stages of the photodissociation process where the angle α hardly changes from the water equilibrium value of 104.52^o [11]. Switching to atom-atom distances we then express the interaction term V_{int} as a function of only four coordinates r_2, R, ρ_1, ρ_2 (see Fig. 1). As is shown in the next section, such a choice is flexible enough to provide an accurate fit even for coordinates r_1 or α off their ground state equilibrium values.

The interaction potential acquires the following form

$$V_{int}(r_1, R, \rho_1, \rho_2) = V_o(R) + V_1(\rho_1, r_2) + V_2(\rho_2, r_2) \tag{2}$$

Here, V_o describes the oxygen-argon interaction, V_1 is the interaction between the argon and the non-dissociating hydrogen, and V_2 is the interaction between the argon and the dissociating hydrogen. Depending simultaneously on two atom-atom distances, both V_1 and V_2 potentials represent non-pairwise terms and can, therefore, account for the observed coupling between argon-hydrogen and oxygen-hydrogen interactions.

Simple analytical forms of V_o and V_1 potentials which lead to a good fit are as follows

$$V_o(R) = a_1 e^{-a_2 R} \tag{3}$$

and

$$V_1(\rho_1, r_2) = (b_1 - \frac{b_2}{r_2}) e^{-b_3 \rho_1} \tag{4}$$

where a_1, a_2, b_1, b_2, and b_3 are fitting parameters. The term V_2 which accounts for the coupling between the argon, oxygen, and photodissociating hydrogen acquires a more complicated form with a switch between an H_2O character for small values of r_2 and H+OH character for large r_2 values. Namely,

$$V_2(\rho_2, r_2) = V_s(\rho_2, r_2), r_2 < r_{2a} \tag{5}$$

$$V_2(\rho_2, r_2) = V_s(\rho_2, r_2) S(r_2, r_{2a}, r_{2b}) + V_l(\rho_2, r_2)[1 - S(r_2, r_{2a}, r_{2b})], r_{2a} < r_2 < r_{2b} \tag{6}$$

$$V_2(\rho_2, r_2) = V_l(\rho_2, r_2), r_2 > r_{2b} \tag{7}$$

Here, S is a switching function between functions V_s and V_l, relevant for small and large r_2 values, respectively. The following simple switching function has been found to work satisfactorily

$$\chi(r_2, r_{2a}, r_{2b}) = \frac{1}{2}(cos\frac{\pi(r_2 - r_{2a})}{(r_{2b} - r_{2a})} + 1) \tag{8}$$

with r_{2a}=1.25Å and r_{2b}=1.35Å. In this way, the argon-water character of the interaction V_2 is smoothly converted into an interaction between argon and a free hydrogen atom upon enlarging the hydrogen-oxygen separation during the photodissociation.

The term V_s, corresponding to small values of r_2 has a functional form

$$V_s(\rho_2, r_2) = (c_1 - c_2 r_2 + c_3 r_2^2) e^{-(c_4 + c_5 r_2)\rho_2} \tag{9}$$

This expression which couples the r_2 and ρ_2 distances via a low order Taylor expansion in r_2 both in the exponent and the pre-exponential factor turns out to be flexible enough for an accurate fit. For the term V_l which corresponds to large O-H separations the following expression has been found to work well

$$V_l(\rho_2, r_2) = (2.6456 - \frac{c_6}{r_2}) e^{-(2.2435 - \frac{c_7}{r_2})\rho_2 - (0.14592 + \frac{c_8}{r_2} - \frac{c_9}{r_2^2})\rho_2^2} \tag{10}$$

The three constants (in au, Å^{-1}, and Å^{-2}) in the above expression together with the expansion of the pre-exponential term and the exponent in terms of $\frac{1}{r_2}$ ensure correct asymptotic behavior at large O-H separations. Namely, for $r_2 \to \infty$ the V_l converges to an accurate fit to the repulsive part of the Ar-H potential obtained recently by fitting high quality *ab initio* CCSD(T)/aug-cc-pVQZ data [5]. At the same time, for large values of r_2 the interaction term V_{int} correlates well with the Ar...OH potential [23].

All the fourteen fitting parameters have been optimized by minimizing the sum of squares of differences between the analytical potential and corresponding *ab initio* excited energy values for more than 180 point relevant for the photodissociation process. The fitting procedure has been accomplished using a standard Levenberg-Marquardt method [24].

V. RESULTS AND DISCUSSION

This Letter reports on first results of an ongoing project directed towards modeling of the cage effect [25] in $H_2O(\tilde{A})$-Ar_n clusters. The long term goal is to understand the mechanism of hindering the motion of the photodissociating hydrogen by rare gas atoms, and possibly influence this process by a rotational excitation of the water molecule prior to photolysis. In this context, we are preferentially interested in the so called "cage effect cone" [16], i.e. in the part of the multidimensional potential energy surface where the argon atom is playing an active role in hindering the photodissociating hydrogen atom. Most of the generated geometries correspond, therefore, to the $H_2O(\tilde{A}) \rightarrow H + OH$ photodissociation pathway with the argon atom being close to its optimal ground state position.

CASPT2 energies for more than 200 different geometries of the excited $H_2O(\tilde{A})$-Ar cluster have been evaluated. In most cases, the length r_1 of the non-dissociating O-H bond and the H-O-H angle α have been fixed to their equilibrium values of 0.957 Å and 104.52^o, respectively. Several points have been, however, generated also for geometries with non-equilibrium values of the H-O-H angle or the non-dissociating O-H bond. These points have not been included into the fitting procedure, but rather have been used for testing the quality of the fit (see below). The length r_2 of the dissociating O-H bond has been varied from its ground state value of 0.957 Å to 2.4 Å. For most of the points, the argon-oxygen distance R has been kept at the ground state optimal value of 3.75 Å. At this distance the ground electronic potential surface is practically isotropic with respect to a particular water-argon orientation. The in-plane angle θ (see Fig. 1) has, therefore, been sampled in to whole range $(0, 360^o)$. Most of these points correspond to planar C_s geometries which grossly simplifies the *ab initio* calculation. However, we have also generated a set of non-planar structures to verify that no new physical effects arise that could not be extracted from calculations for planar geometries.

The effect of the basis set superposition error (BSSE) has been found to be negligible [16]. This is connected with the fact that we are primarily interested in repulsive parts of the excited state potential corresponding to photodissociation and caging processes. Note, that due to the excess energy of the photodissociating hydrogen of more than 2 eV [11] the system is highly energetic. Therefore, the dynamics is insensitive to the exact shape of the Van der Waals regions of the potential surface with a very weak binding of a few meV, which may be more influenced by the BSSE.

The way we have undergone to make the *ab initio* results practical for future dynamical simulations has been a construction of a relatively simple analytical potential model by a least-square fit to the calculated energies. The optimized values of the fourteen fitting parameters are listed in Table I. Atomic units (Hartree) are used as energetic units and Angströms as distance units. A general rule of thumb that the number of points should exceed ten times the number of parameters has been well fulfilled. The mean deviation of the fit from the *ab initio* data is 85 meV which is very satisfactory, especially if compared to the excess energy of 2 eV available in the photoexcited complex. Finally, all the parameters acquire physically meaningful values.

Cuts of the most relevant parts of the generated $H_2O(\tilde{A})$-Ar potential energy surface are shown in a composite Fig. 2. Each of the insert figures depicts a particular dissociation curve, i.e. the dependence of the first excited state energy on the dissociative O-H coordinate r_2. Each curve corresponds to a certain orientation of the argon atom with respect to the water molecule for planar cluster geometries with the argon-oxygen distance R=3.75 Å. Both the CASPT2 energies and the results of the analytical fit are presented. Fig. 2a shows a cut of the potential surface outside the "cage effect cone" where the dissociating hydrogen does not collide with the argon atom. This curve is, therefore, purely repulsive and corresponds to the dissociation of an isolated water molecule in the first dissociative continuum. The accuracy of the fit in this region is solely due to the high quality of the excited water potential taken from Ref. 11. On the other hand, Figs. 2b, 2c, and 2d depict three different cuts through the "cage effect cone". These cuts correspond to collinear and near-collinear O-H-Ar geometries, where the interaction between the photodissociating hydrogen and the argon atom is strong and results in a repulsive collision. As a consequence of simultaneous repulsive hydrogen-oxygen and hydrogen-argon interactions a potential well is formed on these curves at intermediate values of the O-H separation r_2. Note also a slight change of the curvature of all the potentials at small values of r_2 which is solely due to character of the excited water potential itself [11]. It can be seen that for small O-H separations as well as in the region of strong argon-photodissociating water interaction the analytical fit is in an excellent agreement with the *ab initio* points.

The quality of the analytical fit has been also tested for geometries, which have not been included into the fitting procedure, but which are nevertheless relevant for the photodissociation process. In particular, we have constructed dissociation curves in the "cage effect cone" with the H-O-H angle α or the O-H distance r_1 shifted from its equilibrium value. Fig. 3a,b depict the dependence of the CASPT2 and fitted $H_2O(\tilde{A})$-Ar energies on the dissociative r_2 coordinate for the H-O-H angle equal to $\alpha = 94.52^o$ and $\alpha = 114.52^o$. Analogous potential curves, corresponding to changing the non-dissociating O-H distance to $r_1 = 0.907$ Å and $r_1 = 1.007$ Å are shown in Fig. 3c,d. As can be seen, a quantitative agreement between *ab initio* values the analytical fit is obtained in both cases and the fit can, therefore, be used for a wide range of geometries important for the photodissociation dynamics.

VI. CONCLUSIONS

Water photolysis in the $H_2O(\tilde{A})$-Ar cluster has been studied using a high quality *ab initio* CASPT2 method with a sufficiently flexible basis set. Special emphasis has been paid to the so called "cage effect cone" where the argon atom hinders the motion of the dissociating hydrogen. Based on the *ab initio* calculations an accurate, analytical, and physically justified force field suitable for dynamical calculations of $H_2O(\tilde{A})$-Ar_n complexes has been constructed.

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Table 1

Optimized values of fitting parameters

a_1	122.34 au
a_2	3.61 Å^{-1}
b_1	12.76 au
b_2	2.35 au Å
b_3	3.89 Å^{-1}
c_1	5.67 au
c_2	11.22 au Å^{-1}
c_3	6.10 au Å^{-2}
c_4	0.980 Å^{-1}
c_5	0.771 Å^{-2}
c_6	3.04 au Å
c_7	2.28
c_8	1.11 Å^{-1}
c_9	1.09

FIGURES

FIG. 1. Definition of internal degrees of freedom of the H_2O-Ar complex. r_1 and r_2 are the non-dissociating and dissociating OH bonds, α is the H-O-H angle, θ is the angle between the water C_2 axis and the O-Ar line, λ is the Ar-O-H-H torsion angle, R is the O-Ar distance, and ρ_1 and ρ_2 are the two H-Ar distances.

FIG. 2. Comparison between *ab initio* and fitted dissociation curves corresponding to a planar H_2O-Ar complex with different values of the angle θ (see Fig. 1): a) θ=90^o, b) θ=143^o, c) θ=118^o, and d) θ=127.74^o (collinear O-H-Ar arrangement).

FIG. 3. Comparison between *ab initio* and fitted dissociation curves corresponding to a planar H_2O-Ar complex with non-equilibrium values of the H-O-H angle α: a) α=94.52^o, and b) α=114.52^o, or non-equilibrium values of the non-dissociating O-H distance r_1: c) r_1=0.907 Å, and d) r_1=1.007 Å. The O, (dissociating) H, and Ar atoms are collinear.

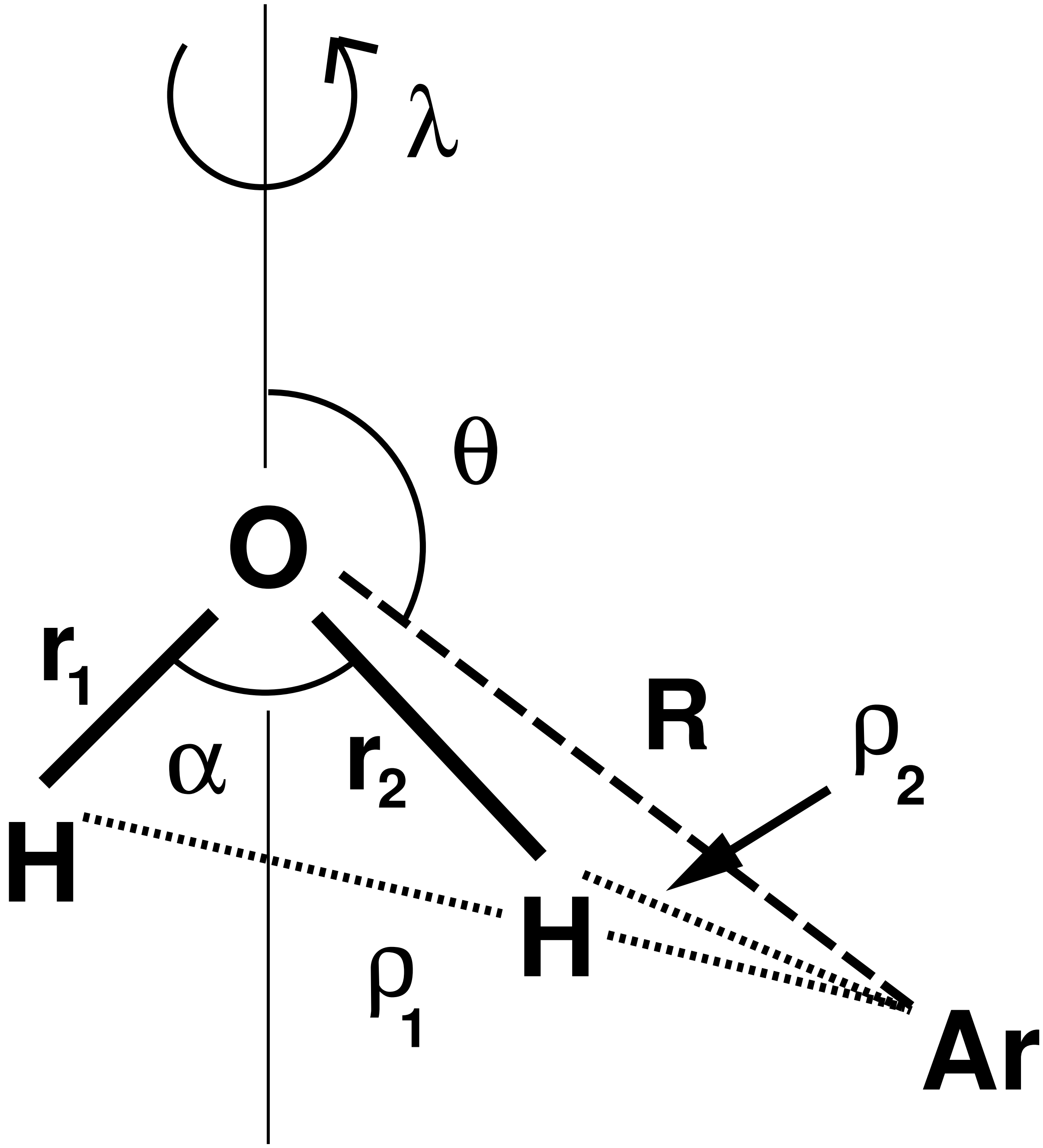

Figure 1 (Slavicek, Nachtigallova, Jungwirth)

Figure 2 (Slavicek, Nachtigallova, Jungwirth)

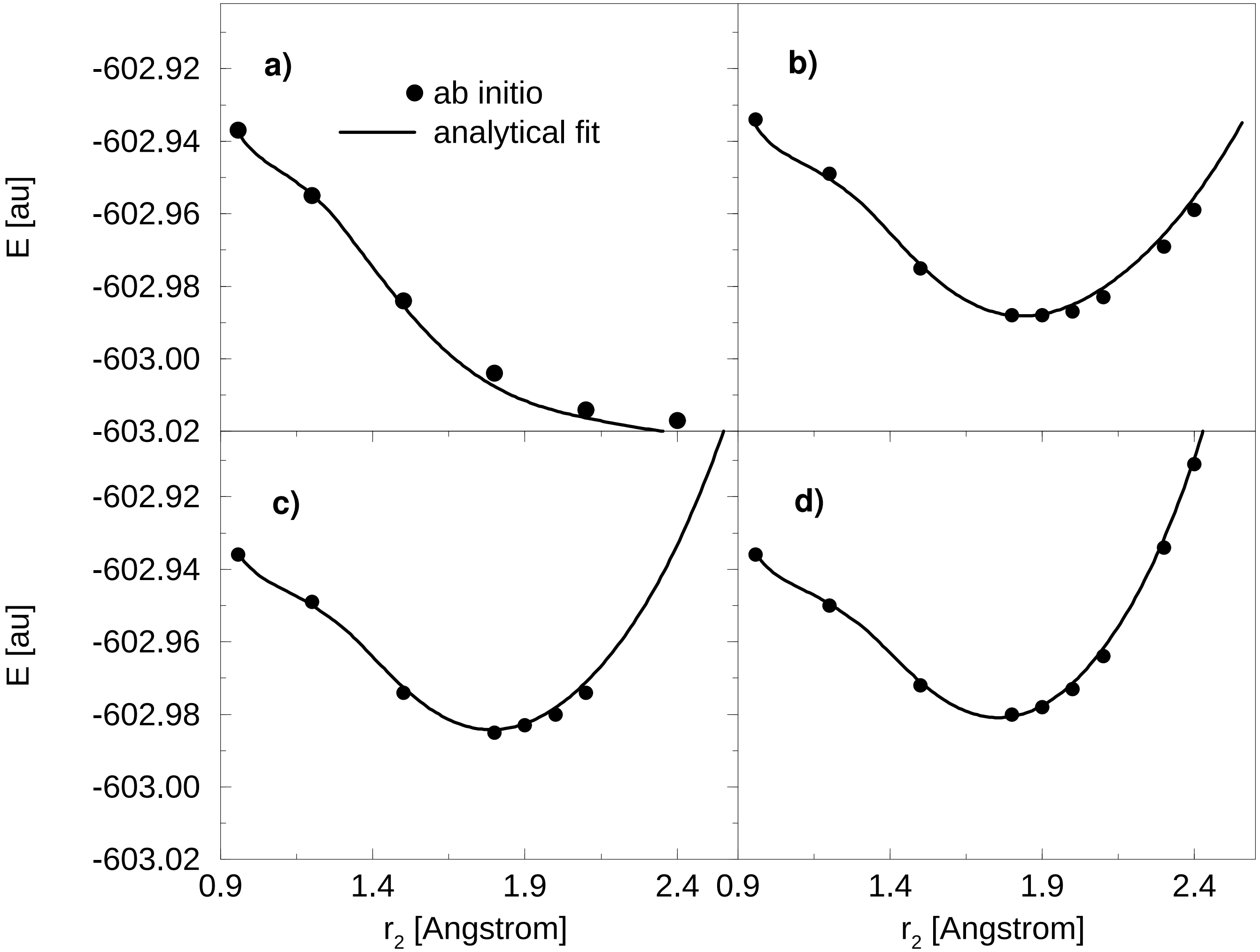

Figure 3 (Slavicek, Nachtigallova, Jungwirth)