Water photolysis in rare gas environment: The CASPT2 excited state $H_2O(\tilde{A})$-Ar potential

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Abstract

The potential energy surface of the first excited state of the water-argon complex is explored at a multireference perturbation theory level as an initial step of the project aimed at the study and control of photodissociation in H_2O-Ar_n ($n = 1, 2, ..., 12$) clusters. *Ab initio* calculations, which will serve as a basis for the construction of an analytical force field for dynamical simulations, reveal the anisotropy of the excited state surface and weak potential coupling between intermolecular and intramolecular degrees of freedom. The importance of the "cage effect" is demonstrated.

This paper is dedicated to Professor Rudolf Zahradník on the occasion of his 70th birthday.

I. INTRODUCTION

The *ab initio* description of weakly bound intermolecular complexes in the electronic ground state was pioneered by Zahradník and collaborators more than 20 years ago.[1] A major breakthrough in quantitative description of weak interactions was enabled by a strict application of non-empirical methods accounting for a large portion of the correlation energy via post-Hartree-Fock treatments using extended basis sets. Only recently, electronically excited intermolecular complexes have been considered theoretically[2–4] in connection with the high resolution crossed molecular beam measurements,[5] fluorescence excitation spectroscopy[6–7] and pump-probe spectroscopy.[8] It is generally recognized, that due to the limitations of single-reference methods for the study of excited states, their description is more difficult than that of the ground state. A practical and usually sufficiently accurate quantum chemical tool for calculations of excited states of medium size molecules and complexes is the complete active space multiconfigurational self-consistent field method with second order perturbation corrections (CASPT2) which includes dominant parts of both static and dynamic correlation energies.[9]

In recent years, a considerable attention has been directed towards studies of photodissociation of molecules weakly bound to one or more rare gas atoms.[10] A generic case for the triatomic molecule-rare gas atom systems is represented by the water-argon van der Waals complex. In its ground electronic state, the H_2O-Ar species has been thoroughly investigated experimentally[11–14] and a reliable *ab initio* intermolecular potential has been developed.[15] Only very recently, photodissociation of the water-argon complex in the first excited continuum has also attracted a considerable attention. High resolution spectroscopic experiments revealed quantitative difference between the complexed and bare water photolysis[16] and a quasiclassical trajectory study using an approximate semiempirical excited state intermolecular potential has been performed.[17] While no excited state studies have been reported for clusters with more than one argon atom, it is worth mentioning that complementary experiments in cryogenic rare gas matrices have been completed nearly a decade ago.[18–20]

It is our long-term goal to study and control the photodissociation dynamics of molecules embedded in inert clusters. In particular, the cage effect[21–22] and its dependence on the number of rare gas atoms (from a single solvent atom to first few solvation shells with the limit of bulk solvation) is studied.[23–25] At the same time, investigations are directed towards influencing the photodissociation quantum yield by preparation of the chromophore in a specific vibrational and rotational state prior to photolysis.[26] Vibrational control of the products of photolysis in the bare H_2O molecule and its deuterated analogues has been successfully carried out experimentally[27–31] and a detailed quantum dynamical study of water photodissociation using a sophisticated potential fitted to *ab initio* data has been completed.[32–34] Our plan is to investigate the solvent effect on the vibrational/rotational control mechanism in H_2O-Ar_n $(n = 1, 2, ..., 12)$ clusters where the largest cluster represents a complete first solvation shell. The lack of an accurate intermolecular potential surface on which the photodissociation dynamics takes place is currently the major limitation for such a study. The potential energy surface of the first electronically excited state of the H_2O-Ar complex presented in this paper is the first step on the way towards the sophisticated theoretical description of photodissociation dynamics in H_2O-Ar_n clusters.

The paper is organized as follows. In Section II we briefly describe the CASPT2 methods and its application to the system under study. In Section III we show and discuss the results, and a brief summary is presented in Section IV.

II. COMPUTATIONAL METHOD

The CASPT2 method was used for all the calculations. This method accounts for both dynamical and non-dynamical correlation effects. In this method, CASSCF calculations are carried out for the state of interest and resulting wave functions and orbitals are used for subsequent multi-reference CASPT2 calculations. The calculations were performed using the Dunning's correlation-consistent polarized valence double zeta augmented basis set which has the form (13s9p2d)/[5s4p2d] for Ar, (10s5p2d)/[4s3p2d] for O, and (5s2p)/[3s2p] for H.[35] A diffuse s function (exponent 0.032) was added for description of Rydberg states of water. This basis set is suitable for describtion of both the excited states of water and the weak Ar-H_2O interaction.

In the first excited state of water ($^1B_1$ state for the molecular orientation used in this study), a strong valence-Rydberg mixing has been observed.[36] In order to describe this mixing correctly a sufficiently large and flexible active space needs to be considered. Urban and Sadlej have included eight electrons in the active space for description of low lying excited states of the water molecule.[37] Their electronic excitation energies of the first singlet excited state, calculated at the CASSCF level, were 7.76 and 7.31 eV for two different choices of the active space. Applying the same approach to the construction of the active space for the H_2O-Ar complex is not computationally feasible for an extended scan of the potential energy surface. Therefore, we tested the reliability of CASPT2 calculations employing a smaller active space including four electrons.

For the construction of the CASSCF wavefunction we first calculated the first singlet excited state ($^1B_1$) of water assuming the C_{2v} symmetry. In all these calculations, the 1s core orbital of the oxygen atom was kept frozen. One orbital of a_1 and one orbital of b_2 symmetries were inactive. The active space was constructed of one a_1 and one b_1 occupied orbitals and four a_1 and one b_1 virtual orbitals. With this active space, the CASPT2 water excitation energy of 7.48 eV was obtained, which is in excellent agreement with the experimentally measured value of 7.42 eV.[38] In the C_s symmetry (which is that of the planar H_2O-Ar complex) the water active space consisted of six orbitals of A' symmetry (one occupied) and two orbitals of A" symmetry (one occupied). With this active space, the first excitation energy of water is 7.49 eV which quantitatively agrees with the corresponding calculation in the C_{2v} symmetry.

For the Ar-H_2O planar structures, the active space was expanded to seven orbitals of A' symmetry and three orbitals of A" symmetry. Further expansion of this active space had no effect on the excitation energies of the A" state. When the C_1 symmetry of (non-planar)

Ar-H_2O geometries was considered ten orbitals in the active space were used. This choice provides a smooth transition from C_s to C_1 structures.

III. RESULTS AND DISCUSSION

A complete description of the $H_2O(\tilde{A})$-Ar multidimensional potential energy surface covering extended motions along all six internal degrees of freedom of the sytem would require an immense computational effort. On the other hand, from the point of view of future dynamical studies, we are interested only in a small portion of the surface. Namely, argon geometries around the solvent equilibrium positions in the ground state H_2O-Ar_n clusters and geometries along the $H_2O \rightarrow H + OH$ photodissociation path in the excited state are of a particular relevance.

The geometry of the H_2O-Ar complex is depicted in Fig. 1 together with the definition of internal degrees of freedom. While the planar arrangements ($\lambda = 0^o$) possess the C_s symmetry, non-planar structures do not have any element of symmetry (C_1). In the electronic ground state the weakly bound complex is nearly isotropic in angles θ and λ (for definition see Fig. 1) with an optimal O-Ar distance of approximately 3.75 Å.[15] In this study, the following set of the H_2O-Ar cluster geometries is sampled. The non-dissociating OH bond is fixed at its equilibrium distance $r_1 = 0.957$Å and the H-O-H angle is kept at its equilibrium value $\theta = 104.52^o$. The length of the dissociating OH bond r_2 is varied from 0.957 to 2.4 Å. From the intermolecular degrees of freedom the O-Ar distance is kept at its ground state optimal value $R = 3.75$Å and the "in-plane" angle θ (see Fig. 1) is varied in the whole range $0 - 360^o$ (due to the reduced symmetry of the photodissociating water molecule angles beyond 180^o have to be sampled, too). Most of the generated points on the excited state potential energy surface correspond to planar geometries of the system ($\lambda = 0^o$), however, representative non-planar geometries ($\lambda = 15^o$) have also been considered.

Figures 2 and 3 depict the dependence of the CASPT2 energy on the length of the dissociating OH bond for different values of the angle θ. Energies of planar geometries corresponding to the argon atom in the vicinity of the photodissociating hydrogen atom ($90^o < \theta < 180^o$) are shown in Fig. 2. For OH separations smaller than 1.5 Å, all the curves are strongly repulsive which reflects the character of the first excited state of the water molecule. However, for angles corresponding to collinear ($\theta = 128^o$) or near-collinear O-H-Ar arrangements a strong cage effect is observed at larger OH distances, which can be attributed to the repulsion between the approaching H and Ar atoms. This is in sharp contrast with the purely repulsive character of curves outside the "cage effect cone" e.g., those with the angle θ equal to 90 and 180^o (see Fig. 2). The existence of this potential well can result in a temporary trapping of the photodissociating hydrogen atom, especially if several argon atoms form the cage. This leads to effects like delayed cage exit or even recombination, as observed in a similar photolyzed $HClAr_{12}$ system.[26,39]

Fig. 3 depicts potential curves for planar geometries with θ equal to 0 and 232^o (argon atom against the non-dissociating hydrogen) and for a representative non-planar set with $\lambda = 15^o$ and $\theta = 232^o$. All these curves are outside the "cage effect cone" and, therefore, repulsive. The mutual similarity of these curves indicates that the angular anisotropy of the excited state potential concerns practically only the "cage effect cone" region.

Another way of visualizing the calculated part of the potential energy surface, which is well suited for quantitative evaluation of the anisotropy of the excited state potential, is to plot the angular θ-dependence of the (planar) complex energy for different values of the photodissociating OH bond length r_2. Fig. 4 shows θ-dependent energy curves for $r_2 = 0.957, 1.5, 1.8, 2.1, 2.2,$ and 2.4 Å. One can see that for the ground state equilibrium water geometry with $r_2 = 0.957$Å the angular anisotropy is very weak. However, upon prolonging the OH bond during photodissociation the potential in the "cage effect cone" characterized roughly by $100^o < \theta < 160^o$ becomes strongly anisotropic. The shape of these curves provides guidance for future construction of an analytical fit to the potential energy surface.

Finally, Fig. 5 demonstrates the minor effect of the basis set superposition error (BSSE) on the results at the given theoretical level. We present here a set of geometries where the BSSE was found to be the most significant. Namely, the r_2-dependent potential curve for a planar complex with a collinear O-H-Ar arrangement ($\theta = 128^o$) with and without BSSE is shown. The two curves are very close and nearly parallel to each other with differences being within the limit of the error of the CASPT2 method. It should be stressed at this point that the dynamics of the photolysis and the cage effect is governed by the repulsive parts of the O-H and Ar-H interactions while the weak attractive parts where the BSSE would be relatively more significant are quite unimportant for the excited state processes.

IV. CONCLUSIONS

We have presented in this paper a CASPT2 study of a part of the first excited state potential energy surface of the water-argon complex, relevant for the photodissociation dynamics in H_2O-Ar_n ($n = 1, 2, ..., 12$) clusters. It has been demonstrated that the anisotropy of the excited state potential is mostly due to the cage effect. The shape and anisotropy of the surface is discussed in view of a future analytical potential fit for dynamical simulations.

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FIGURES

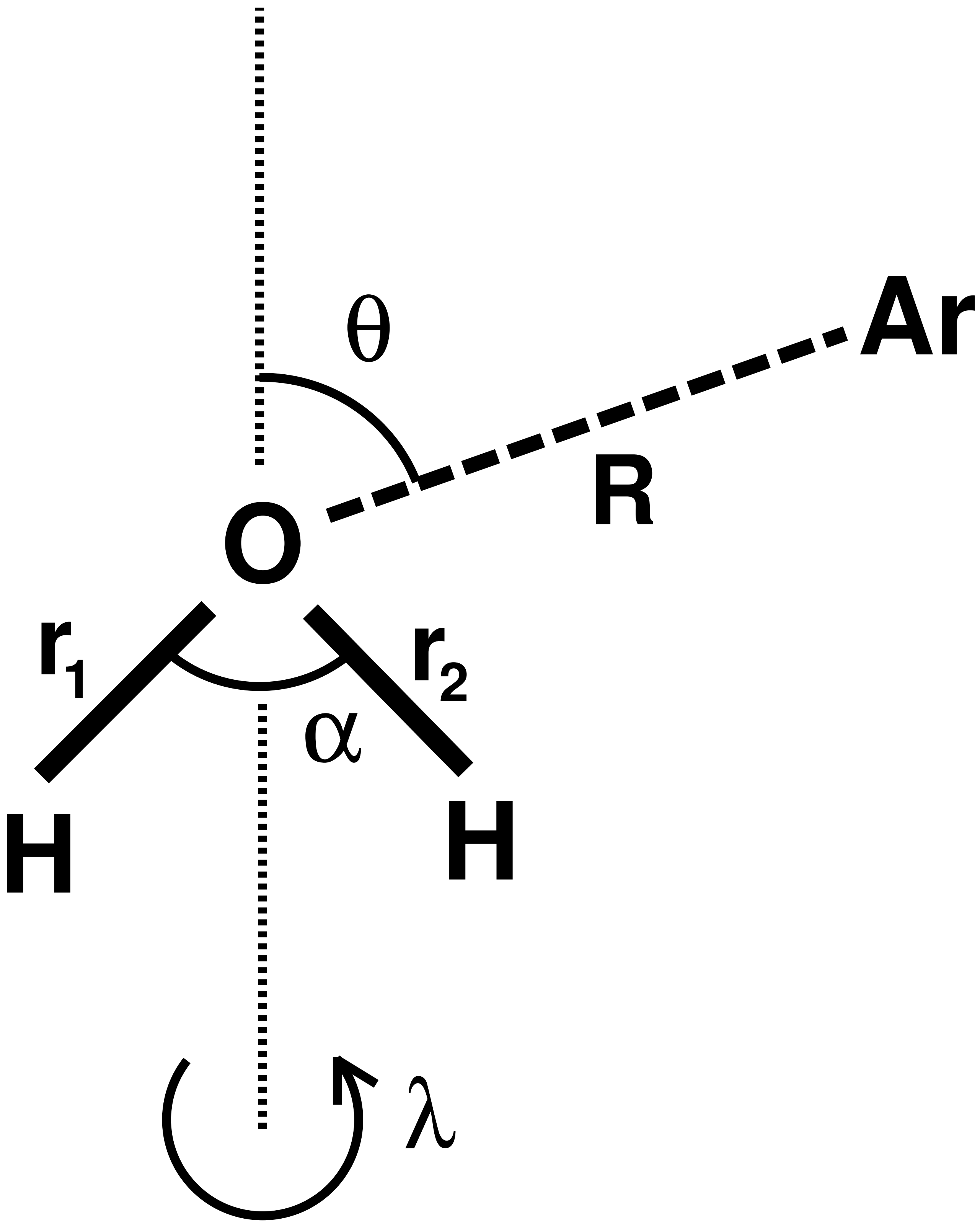
FIG. 1. The geometry of the H_2O-Ar complex with definitions of the internal degrees of freedom. r_1 and r_2 are the two OH bond lengths, α is the H-O-H angle, θ is the angle between the water C_2 axis and the O-Ar line, and λ is the Ar-O-H-H torsion angle.

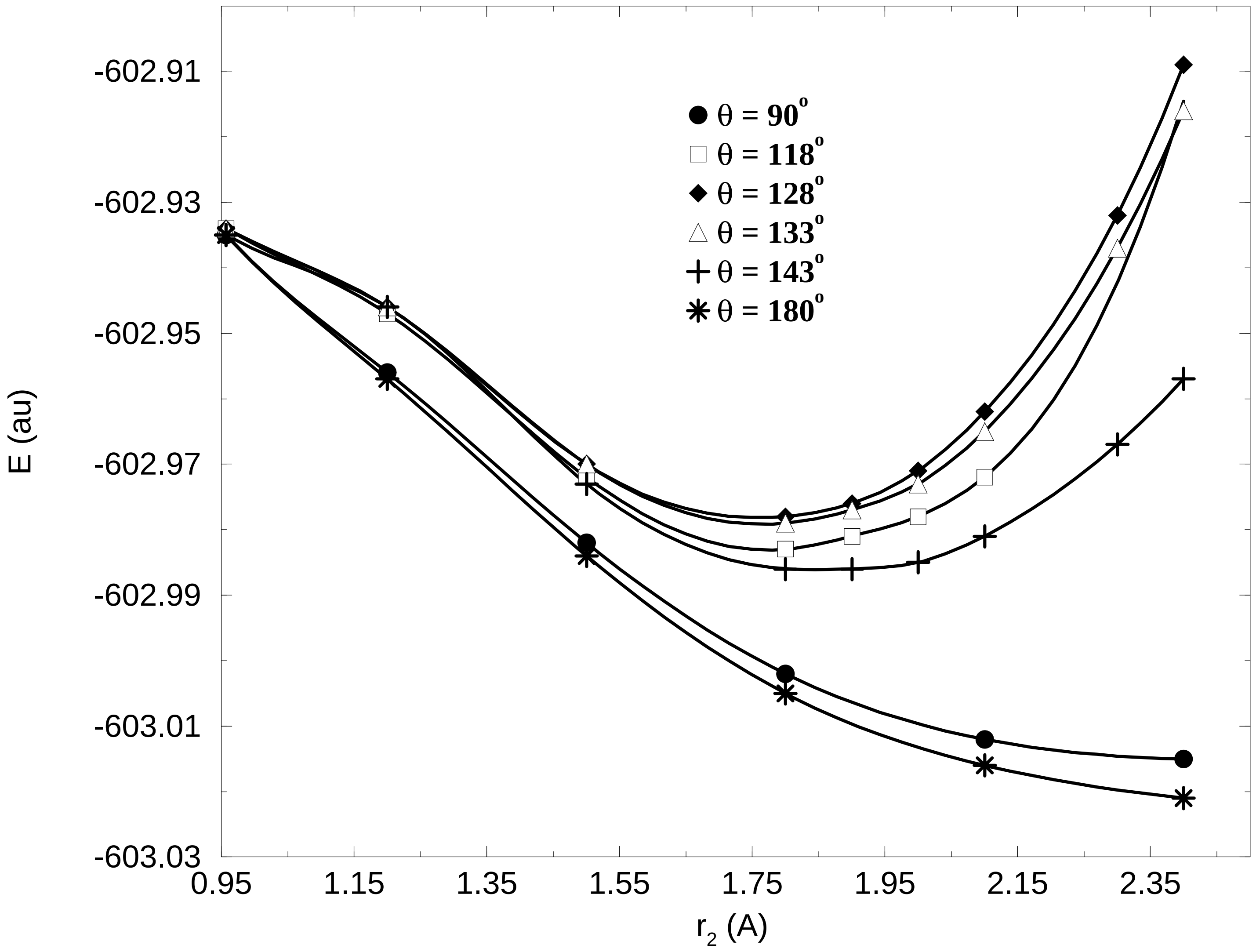
FIG. 2. The CASPT2 energy as a function of the photodissociating OH bond distance for planar geometries for $\theta = 90, 118, 128, 133, 143,$ and 180^o.

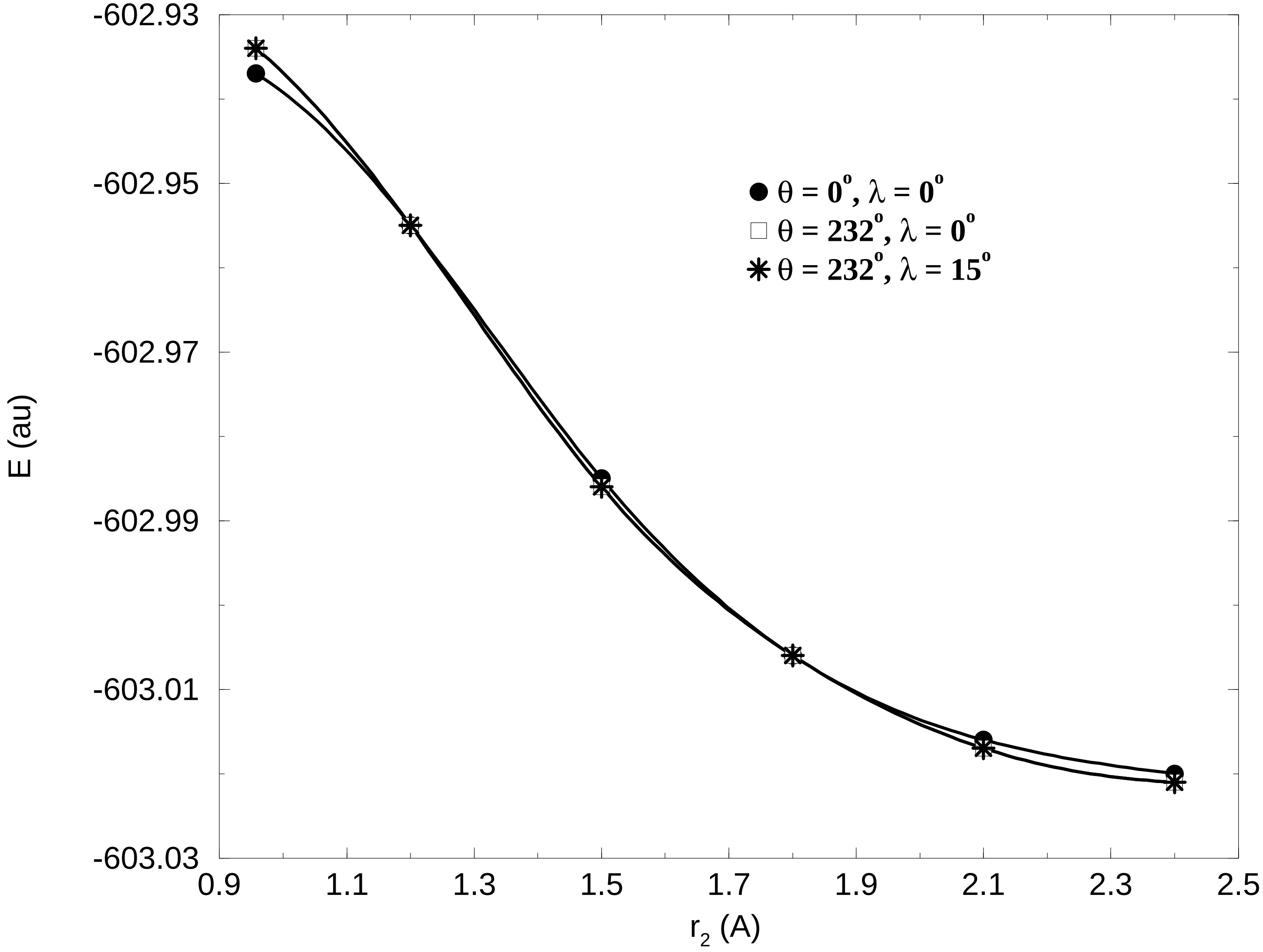
FIG. 3. The CASPT2 energy as a function of the photodissociating OH bond distance for planar geometries with $\theta = 0$ and 232^o and for non-planar geometries with $\lambda = 15^o$ and $\theta = 232^o$.

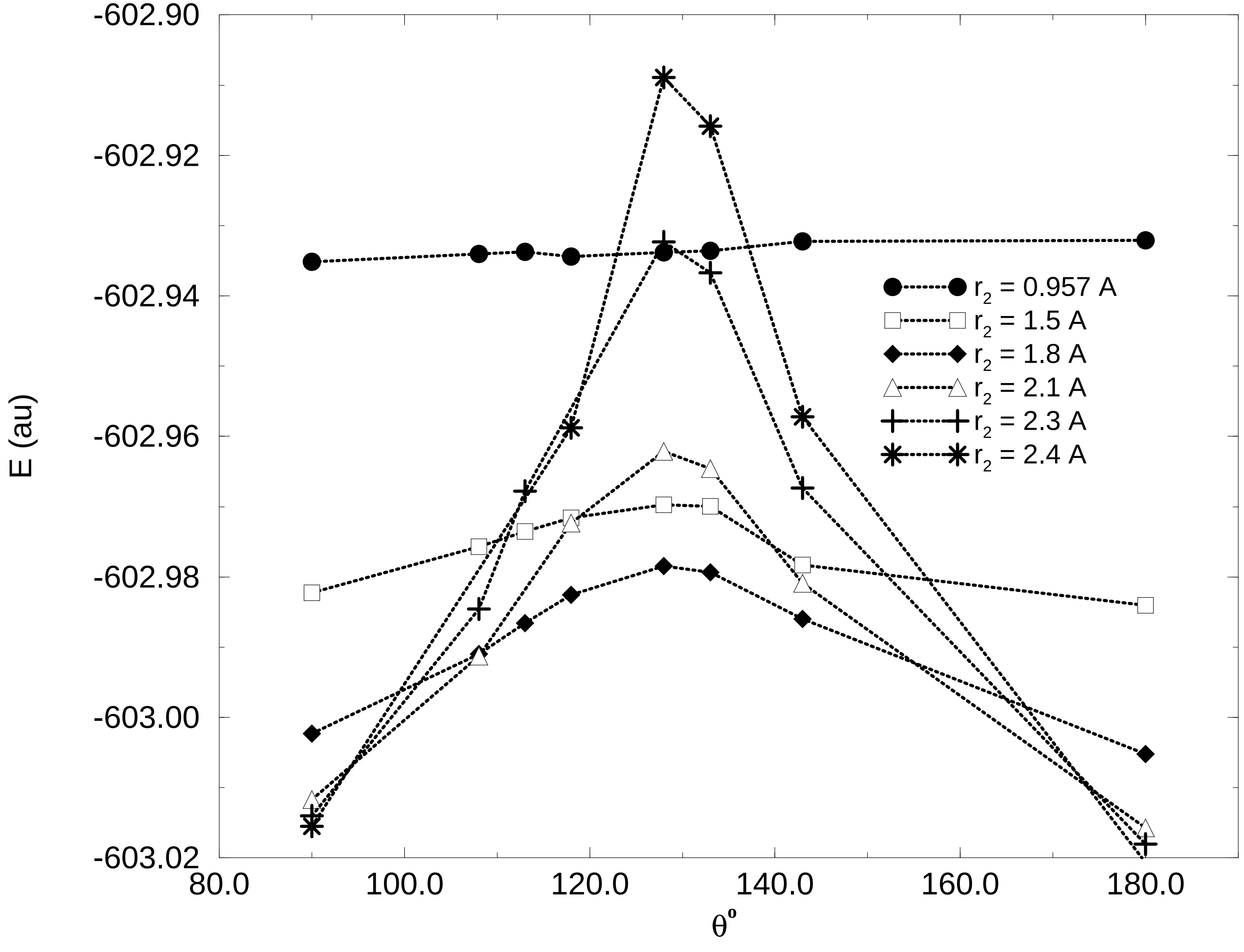
FIG. 4. The angular θ-dependence of the CASPT2 energy for different values of the photodissociating OH bond distance $r_2 = 0.957, 1.5, 1.8, 2.1, 2.3,$ and 2.4Å.

FIG. 5. The effect of the basis set superposition error on the photodissociating OH bond distance $r_1 = 0.957 - 2.4$ Åand $\theta = 128^o$ (collinear O-H-Ar arrangement).

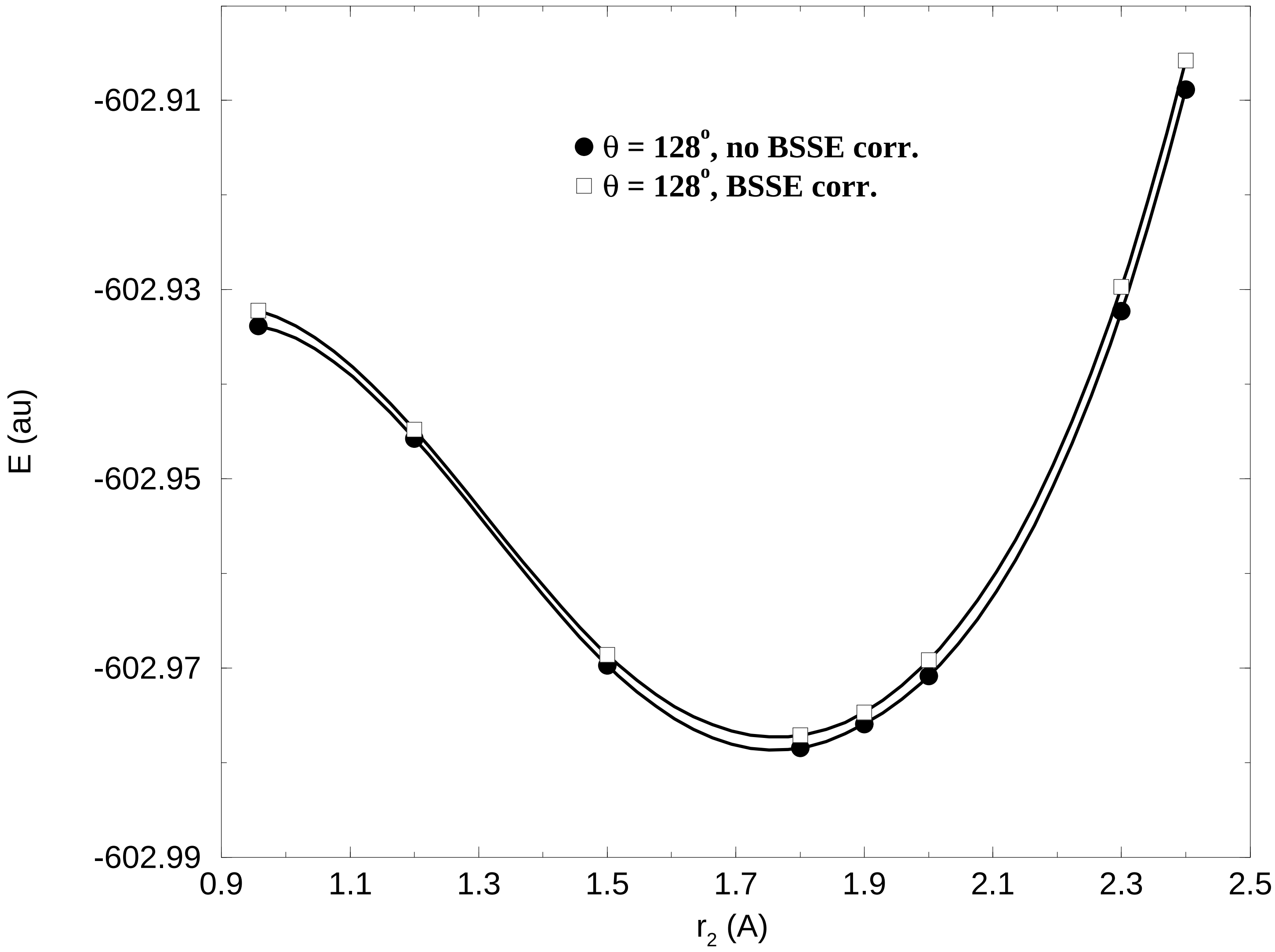

θ
Ar
R
O
r1
r2
α
H
H
λ


θ = 90°
θ = 118°
θ = 128°
θ = 133°
θ = 143°
θ = 180°
E (au)
-602.91
-602.93
-602.95
-602.97
-602.99
-603.01
-603.03
0.95
1.15
1.35
1.55
1.75
1.95
2.15
2.35
r2 (A)


-602.93
-602.95
-602.97
-602.99
-603.01
-603.03
E (au)
0.9
1.1
1.3
1.5
1.7
1.9
2.1
2.3
2.5
r_2 (A)
θ = 0°, λ = 0°
θ = 232°, λ = 0°
θ = 232°, λ = 15°



-602.90
-602.92
-602.94
-602.96
-602.98
-603.00
-603.02
E (au)
80.0
100.0
120.0
140.0
160.0
180.0
θ°
r2 = 0.957 A
r2 = 1.5 A
r2 = 1.8 A
r2 = 2.1 A
r2 = 2.3 A
r2 = 2.4 A


θ = 128°, no BSSE corr.
θ = 128°, BSSE corr.
E (au)
-602.91
-602.93
-602.95
-602.97
-602.99
0.9
1.1
1.3
1.5
1.7
1.9
2.1
2.3
2.5
r2 (A)