

A CAS SCF study of reactive interactions between Be(3P) and H $_2$ ($^1\Sigma_g^+$)

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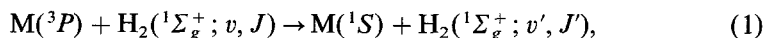
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Summary. The C_{2v} symmetry section of the Be(3P) + H $_2$ ($^1\Sigma_g^+$) adiabatic energy surface is investigated by using the CAS SCF method. The small active space CAS SCF calculations in the valence approximation are followed by a perturbation treatment of the dynamic, core, and core-valence contributions in the framework of the CASPT2 method. The possibility of the nonradiative chemical deactivation of the lowest triplet state of Be by the insertion mechanism is studied. The structure of the 3B_2 reaction intermediate BeH $_2$ is established. The calculations show that the symmetric dissociation of this intermediate into Be(1S) and 2H(2S) does not involve any barrier beyond the endothermicity of the corresponding reaction. The hydrogen abstraction mechanism via a linear configuration is shown to possess the activation barrier of about 25 mH.

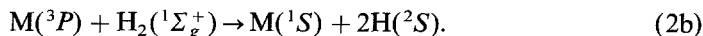
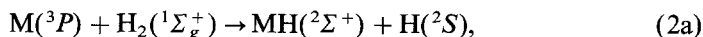
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1 Introduction

The quenching of the metastable (ns^1np^1 ; 3P) excited state of the group IIa and IIb atoms in collisions with molecules has been given a great deal of attention [1, 2]. Of particular interest, both experimentally and theoretically, is the quenching mechanism in collisions with H $_2$ molecules [1–6]. The quenching of the metal atom (M) excited state may proceed either via a pure energy transfer:



or may involve different chemical exit channels, e.g.:



The chemical processes of Eq. (2) are known to be the major exit channels in the collision quenching of the lowest triplet state of Zn, Cd, and Hg [1, 2]. The

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energy transfer and chemical mechanisms appear to compete with each other in the case of $\text{Mg}(^3P)$ [5, 6] while the chemical reaction of Eq. (2a) is expected to be [3] almost exclusively responsible for the quenching of $\text{Be}(^3P)$.

The main chemical processes underlying the quenching of the lowest triplet state of Be by collisions with H_2 have been studied by Poirier et al. [3]. They found that the reaction path of Eq. (2a) involves the formation of a relatively stable T-shaped BeH_2 complex dissociating asymmetrically into the final products BeH and H. The other exit channel of Eq. (2b) has not been investigated as being energetically unattractive. However, its importance in the quenching of $\text{Be}(^3P)$ may considerably increase for vibrationally excited states of H_2 and appears to be worth studying.

In this paper we report on accurate calculations of some selected portions of the adiabatic energy hypersurface for $\text{Be}(^3P) + \text{H}_2(^1\Sigma_g^+)$. The main attention is given to the so-called insertion mechanism leading to BeH_2 and to the energetics of its *symmetric* dissociation according to Eq. (2b). The C_{2v} symmetry structure of the ground state of BeH_2 is determined. The reaction between $\text{Be}(^3P)$ and $\text{H}_2(^1\Sigma_g^+)$, which results in the formation of $\text{BeH}_2(^3B_2)$, is shown to proceed without any activation barrier. Also the symmetric (C_{2v}) decay of BeH_2 according to Eq. (2b) does not seem to involve any barrier beyond the endothermicity of the corresponding chemical reaction. A limited study of the hydrogen abstraction mechanism of Eq. (2a) has been carried out as well and our results confirm the conclusions of Poirier et al. [3].

The methods employed in the present study and the pertinent computational details are surveyed in Sect. 2. The results are presented and discussed in Sect. 3. The main conclusions of our investigations are summarized in Sect. 4.

2 Methods and computational details

The main qualitative aspects of the potential energy surface for both the substrates and different products of the $\text{Be}(^3P)$ interaction with $\text{H}_2(^1\Sigma_g^+)$ are well accounted for by electronic configurations which can be generated from distributing 4 valence electrons among the valence orbitals. This makes the CAS SCF [7] method particularly suitable for the purpose of present calculations. However, the occupation number analysis for different choices of the active orbital subspace [7] indicates that for the majority of points on the energy surface the $2\sigma_g$ correlating orbital of H_2 is of considerable importance and needs to be included in the active orbital subspace.

The major part of CAS SCF calculations underlying the present study has been carried out with the active space built from $2s$ and $2p$ orbitals of Be and $1\sigma_g$, $1\sigma_u$, and $2\sigma_g$ orbitals of H_2 . This gives the appropriate qualitative description of the system at all geometries and a fair account of its energetics.

For the C_{2v} symmetry sections of the energy hypersurface, with the z axis of the coordinate system passing through Be and the bond midpoint of H_2 , the corresponding active space is referred to as (4120), where the numerical entries give the number of active orbitals per irreducible representation of the C_{2v} group. For linear arrangements this active orbital space becomes ($5\sigma 1\pi$).

The dynamic correlation contributions have been investigated only for selected geometries of the system and the corresponding calculations have been carried out within the framework of the recently developed single-state multi-reference CAS SCF perturbation approach (CASPT2) [8]. In contrast to different

limited configuration interaction (CI) methods, the perturbation approach with CAS SCF reference functions is explicitly size-consistent and avoids the use of approximate corrections for unlinked contributions [3]. The same approach offers also a possibility of the explicit evaluation of core and core-valence contributions to the interaction energy.

To avoid the discussion of the basis set truncation errors and related accuracy problems we have carried out our calculations by using the recently developed ANO [9] basis sets of Widmark et al. [10]. For Be the selected ANO basis set is of the form $[14s9p4d3f/5s4p2d1f]$ and is capable of giving an accurate description of $\text{Be}(^1S)$ and $\text{Be}(^3P)$ at both the SCF and correlated levels of approximation. The valence CAS SCF excitation energy of the $^1S \leftarrow ^3P$ transition in Be calculated with the present ANO basis set is 2.804 eV and compares well with the experimental value of 2.725 eV. A further improvement (2.762 eV) is obtained at the level of the CASPT2 treatment. An ANO basis set of a comparable quality ($[8s4p3d/4s3p1d]$) [10] has been used for H. The use of those large, general purpose ANO basis sets makes the present study distinctively more accurate than the earlier calculations of Poirier et al. [3]. Several subtleties of the potential energy surface for the system studied in this paper may considerably depend on the basis set choice.

All calculations have been performed by using the MOLCAS system of quantum chemistry programs [11, 12] developed in this laboratory. Among several other features of this system one should mention an efficient handling of the Raffanetti-type contractions in ANO basis sets [10–12].

3 Results and discussion

To avoid the presentation of the extensive numerical data most of the results calculated in this study will be presented in a graphical form. The numerical energy values for different molecular geometries can be obtained from the authors upon request.

The major part of the present study is concerned with the investigation of the C_{2v} section of the adiabatic energy surface for the lowest triplet state of the $\text{Be} + \text{H}_2$ system. This 3B_2 surface, which corresponds to the insertion mechanism of the $\text{Be}(^3P) + \text{H}_2(^1\Sigma_g^+)$ reaction, has been obtained from the (4120) CAS SCF calculations and is shown in Fig. 1. The substrate channel lies far to the right at the bottom of this plot, while the $\text{Be}(^1S) + 2\text{H}(^2S)$ exit channel constitutes its upper left hand side. The reaction is seen to proceed smoothly, i.e., without any activation barrier, to a stable intermediate $\text{Be} \cdot \cdot \text{H}_2$. Also no barrier, beyond the endothermicity of the corresponding dissociation reaction, is observed for the exit channel.

The lowest triplet state surface is, as a matter of fact, a result of the avoided crossing between the $\text{Be}(^3P) + \text{H}_2(^1\Sigma_g^+)$ and $\text{Be}(^1S) + \text{H}_2(^3\Sigma_u^+)$ diabatic surfaces. The avoided crossing region is shown separately in Fig. 2 for a series of different distances between the Be atom and the H_2 bond midpoint. The approaching $\text{Be}(^3P)$ atom can be also considered as a perturber affecting the vibrations of the H_2 molecule. The vibrational frequency data as function of the $\text{Be} \cdot \cdot \text{H}_2$ distance are shown in Table 1. By combining those data with the graphical information provided in Fig. 2 one can conclude that the $v = 3, 4$ vibrational excitations of H_2 might be sufficient for promoting its predissociation due to long range interactions with the perturber. The endothermicity of this reaction is equal to

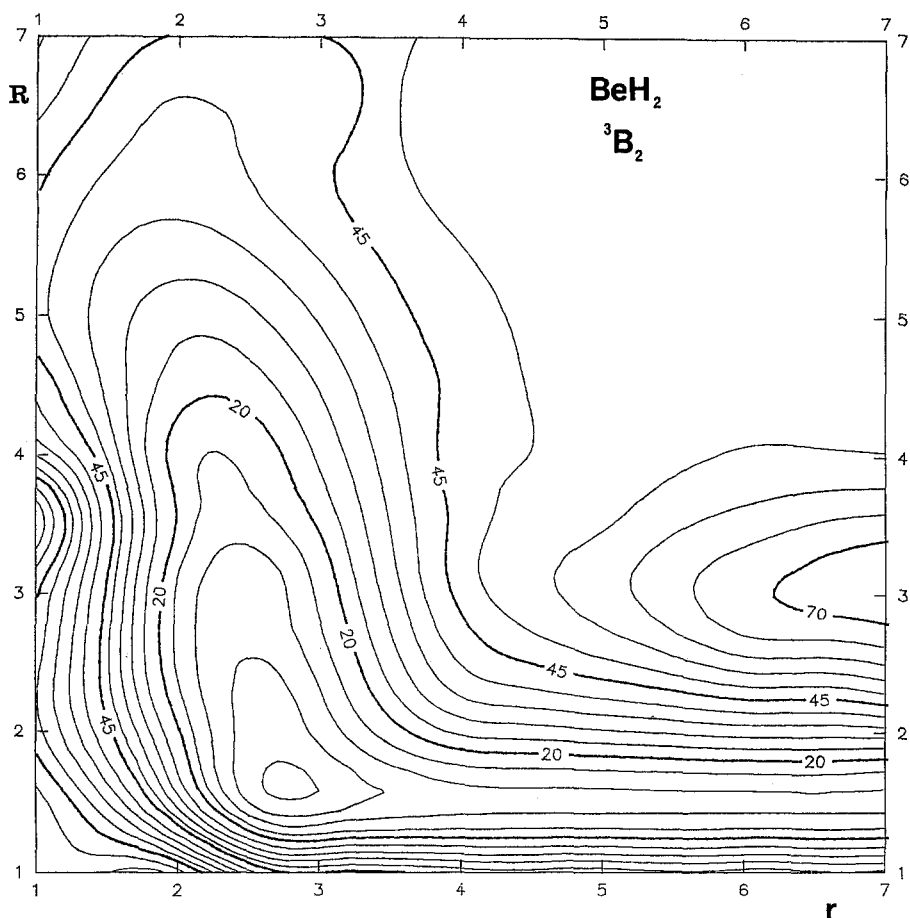


Fig. 1. The 3B_2 CAS SCF energy surface of the $\text{Be} \cdot + \text{H}_2$ system: r is the distance (in a.u.) between Be and the H_2 bond midpoint, R denotes the H–H distance (in a.u.). The isoenergetic curves are spaced by 5 mH and their labels correspond to the energy values (in mH) relative to the minimum for the BeH_2 complex

the difference between the $v=0, J=0$ level dissociation energy of $\text{H}_2({}^1\Sigma_g^+)$ (4.478 eV [13]) and the excitation energy of the 3P state of Be (2.725 eV [14]), i.e., amounts to 1.753 eV as compared to the value of 1.483 eV obtained in CAS SCF calculations with the (4120) active orbitals space. The CASPT2 approach, including the core and core-valence excitations, gives the value of 1.683 eV which compares very well with the experimental result. The barrier for the C_{2v} dissociation of H_2 ranges from about 0.52 eV at long separations between Be and H_2 down to zero at the mutual distances shorter than about 4 a.u.

The minimum on the 3B_2 surface which corresponds to the formation of a relatively stable species BeH_2 has been investigated by Poirier et al. [3] at the level of the SCF HF approximation. The subsequent SD–CI results reported by those authors correspond to the SCF HF geometry of the complex. In the present paper we have carried out an extensive study of the minimum region at the level of the (4120) CAS SCF and CASPT2 approximations. Both the valence

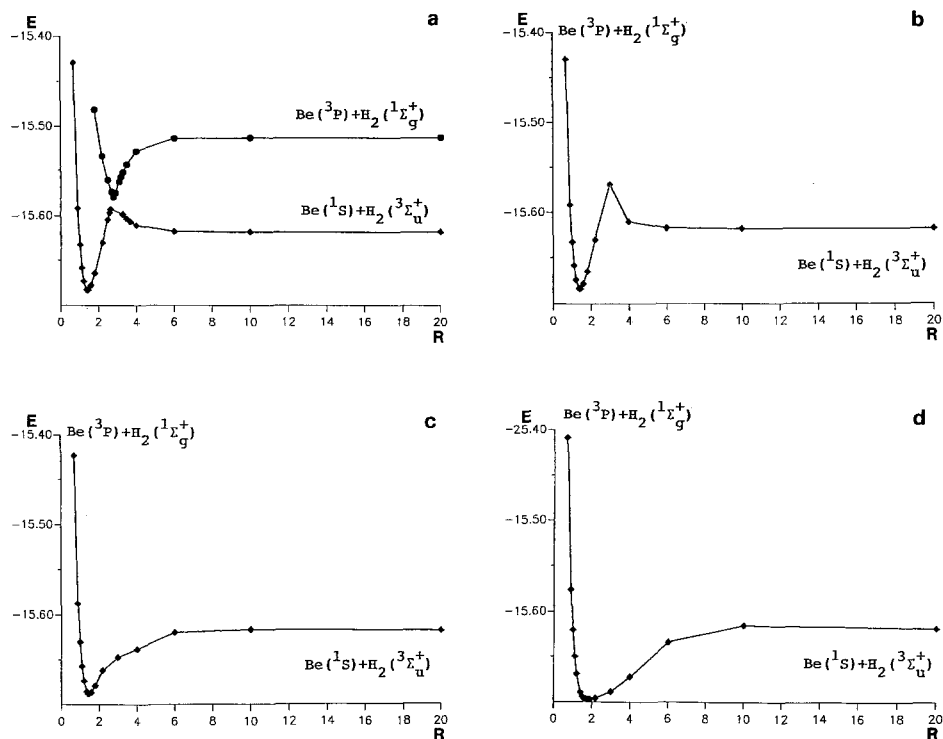


Fig. 2a–d. The CAS SCF energy (E , in a.u.) of the H $_2$ + Be system as a function of the H–H bond distance (R , in a.u.) for different distances r between the Be atom and the H $_2$ bond midpoint: (a) $r = 20.0$ a.u., both the lower and upper 3B_2 states are shown to illustrate the avoided crossing, (b) $r = 8.0$ a.u., the lowest 3B_2 state, (c) $r = 3.5$ a.u., the lowest 3B_2 state, (d) $r = 2.5$ a.u., the lowest 3B_2 state

Table 1. The equilibrium bond distance (R_e) and the bond stretching frequency (ω_e) of H $_2$ interacting with Be on the 3B_2 surface as a function of the distance (r) between Be and the bond midpoint of H $_2$

r (in a.u.)	R_e (Å)	ω_e (cm $^{-1}$)
2.00	1.7987	2153.9
2.50	1.0684	1470.1
2.75	0.8654	2532.2
3.00	0.8261	3012.7
3.50	0.7808	3949.3
4.00	0.7602	4078.1
8.00	0.7440	4396.5
20.00	0.7438	4399.5
Exptl. [13] ^a	0.7414	4401.2

^a Experimental data for the isolated H $_2$ molecule

and valence + core correlation effects have been investigated in the framework of the perturbation method [8]. It has been found that both the energy and the equilibrium geometry of the BeH_2 complex strongly depend on the core and core-valence correlation effects. This is illustrated by the data of Table 2.

The present energy and geometry data for the $\text{BeH}_2(^3B_2)$ system are very close to those obtained in SCF HF calculations by Poirier et al. [3]. The valence CASPT2 results show that the dynamic correlation effects lead to the opening of the H–Be–H angle. This effect is considerably enhanced by including the excitations from the $1s$ core of Be and leads to a further stabilization of the $\text{Be} \cdot \cdot \text{H}_2$ complex. This shows that the assumption of the unmodified SCF geometry used in SD–CI calculations of Poirier et al. [3] has no support in the geometry optimization results which have been carried out in the present paper at the level of correlating all 6 electrons of the system. The theoretical CASPT2 structure of the 3B_2 state of BeH_2 corresponds to the H–Be–H angle of 45.8° while the SCF value of Poirier et al. amounts to only 34.6° for the largest basis set used in their calculations. This observation makes rather doubtful their results for other critical points of the potential energy surface.

Adams et al. [4] have carried out a study of the 3B_2 energy surface for the C_{2v} symmetry approach of $\text{Mg}(^3P)$ to $\text{H}_2(^1\Sigma_g^+)$. Several aspects of their investigations are similar to the present ones. The major difference, however, follows from the fact that the entrance channel of the respective reaction is all the way repulsive; the $\text{Mg} \cdot \cdot \text{H}_2(^3B_2)$ system does not correspond to a minimum on the reaction surface. The approach of Mg to H_2 causes only a small change of the R_e value for H_2 [4] as compared to considerable modifications of the R_e value observed in the present case (see Table 1). The SCF C_{2v} surface for the $\text{Mg} \cdot \cdot \text{H}_2$ system calculated by Adams et al. [4] appears to exhibit more complex topology than the potential energy surface investigated in this paper. Since the electron correlation effects have been considered by Adams et al. only in a very limited way, one may wonder how strong is the dependence of their conclusions on both the dynamic and core correlation contributions.

Table 2. The energy and geometry of the T-shaped $\text{Be} \cdot \cdot \text{H}_2$ complex in the 3B_2 electronic state

	This work			Ref. [3]	
	CAS SCF (4120) ^a	CASPT2 ^b	CASPT2 ^c	SCF	SD–CI ^d
Energy ^e	–15.00	–28.67	–33.85	–13.39	–28.60
R^f	1.66	1.77	1.93	1.658	(1.658)
r^g	2.67	2.59	2.48	2.658	(2.658)

^a See text

^b Valence electron approximation

^c Core electrons included

^d SD–CI results including the Davidson correction calculated at the optimized SCF geometry

^e Energy relative $\text{Be}(^3P) + \text{H}_2$ at infinite mutual separation. The vibrational correction, which can be obtained from the data of Table 1, is not included in the H_2 reference energy. The relative energy values are given in mH

^f The H–H bond distance (in a.u.)

^g The distance between the Be atom and the H_2 bond midpoint (in a.u.)

In due course of our investigations we have also examined the hydrogen abstraction surface in the $C_{\infty v}$ symmetry of reactants. The major part of the corresponding calculations has been carried out at the level of the valence CAS SCF approximation with the ($5\sigma 1\pi$) active orbital space. The computed surface for the $^3\Sigma^+$ state confirms the earlier conclusions of Poirier et al. [3] and is virtually analogous to the $C_{\infty v}$ surface calculated by Adams et al. [4] for the Mg(3P) + H $_2$ ($^1\Sigma_g^+$) system. The exit channel which corresponds to MgH($^2\Sigma^+$) + H(2S) is separated from the entrance channel by a barrier. Its value, as obtained from the present CAS SCF calculations, amounts to about 25 mH above the endothermicity barrier. The latter one is found to be about 68.6 mH (with respect to pure electronic energies of BeH($^2\Sigma^+$) and H(2S)). A comparison of the total electronic energies corresponding to the substrates and products shows that the CAS SCF energy minimum for substrates lies about 3.4 mH above that for the reaction products. This difference is further increased by taking into account the zero-level vibrational energies of H $_2$ and BeH [13].

The results obtained for the linear arrangement of the reactants clearly indicate the preference of the insertion mechanism. The dominant route of the insertion reaction will obviously be the asymmetric dissociation of the 3B_2 BeH $_2$ complex followed by the vibrational and rotational excitation of BeH($^2\Sigma^+$). The yield of the symmetric dissociation, leading to the non-radiative deactivation of the 3P state of Be and the production of H(2S) will, however, increase in the range of higher energies by the translation-to-electronic energy transfer.

4 Conclusions

The symmetric C_{2v} portion of the reaction surface for the Be(3P) + H $_2$ ($^1\Sigma_g^+$) system has been studied by using the CAS SCF method with the (4120) active orbital space. The dynamic and core correlation contributions have been accounted for by using the perturbation approach developed recently for general CAS SCF reference functions [8]. The investigated 3B_2 surface is found to have a single local minimum which corresponds to a BeH $_2$ complex. The symmetric dissociation of this complex according to the reaction of Eq. (2b) has been found to have no barrier beyond the endothermicity of 1.683 eV.

The structure of the BeH $_2$ complex is shown to strongly depend on the core and core-valence contributions. The corresponding effects can be expected to be also important in the case of related calculations on interactions between Mg($^1,^3P$) with quenching molecules [15].

The present study confirms also the earlier conclusions concerning the predominance of the insertion mechanism of Eq. (2a) in the chemical quenching of the lowest triplet state of Be. However, at higher relative velocities the other exit channel of Eq. (2b) will gain some importance. The corresponding quenching mechanism can be then interpreted as the vibrational excitation of H $_2$ leading to its dissociation or predissociation.

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