

Ab initio potential energy surfaces for $\text{Cd}(1\text{P})+\text{H}_2=\text{CdH}(\text{X } 2\Sigma^+)+\text{H}$, $\text{HCdH}(\text{X } 1\Sigma^+ \text{g})$, $\text{Cd}(3\text{P})+\text{H}_2$, and $\text{Cd}(1\text{S})+\text{H}+\text{H}$

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***Ab initio* potential-energy surfaces for $\text{Cd}(^1P) + \text{H}_2 \Rightarrow \text{CdH}(X^2\Sigma^+) + \text{H}$, $\text{HCdH}(X^1\Sigma_g^+)$, $\text{Cd}(^3P) + \text{H}_2$, and $\text{Cd}(^1S) + \text{H} + \text{H}$**

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The outcome of laser excitation of the van der Waals CdH_2 complex [which consists of a ground-state $\text{Cd}(^1S)$ atom bound to an H_2 molecule] to its lowest-energy singlet state(s), which connects with $\text{Cd}(^1P) + \text{H}_2$, is examined by calculating *ab initio* potential-energy surfaces for the above excited singlet states, the corresponding underlying triplet states [connecting to $\text{Cd}(^3P) + \text{H}_2$], and the singlet ground state. It is necessary to study such a multitude of states because energetically accessible reaction products such as $\text{Cd}(^3P) + \text{H}_2$, $\text{CdH}(X^2\Sigma^+) + \text{H}$, $\text{Cd} + \text{H} + \text{H}$, and $\text{HCdH}(X^1\Sigma_g^+)$ connect to various surfaces. In carrying out these calculations, the lowest-energy surface of 1A_1 symmetry was evaluated at nearly 1100 C_{2v} geometries using complete-active-space self-consistent-field wave functions with a valence double-zeta and a double-zeta-plus-polarization basis set on cadmium and hydrogen, respectively. The excited singlet and triplet surfaces that correlate with 1P_1 and 3P_1 levels of Cd plus ground-state H_2 were examined in detail along paths that flux prepared by laser excitation of the singlet surface(s) is most likely to follow. Among the photoexcited singlet states, the 1B_2 surface is found to provide the most energetically attractive approach path for the excited CdH_2 van der Waals complex to access geometries from which HCdH , $\text{Cd} + \text{H} + \text{H}$, and $\text{CdH} + \text{H}$ can be formed via intersection and coupling with the lowest 1A_1 surface. The 1B_1 surface is found to be weakly attractive, and the excited 1A_1 surface to be repulsive at geometries characteristic of the nascent photoexcited species. The underlying triplet surfaces are found to be repulsive (3A_1), weakly attractive (3B_1), and slightly more attractive (3B_2) at such geometries. The repulsive 3A_1 surface intersects the 1B_2 surface in the latter's entrance-channel "streambed"; the 3B_1 state intersects the 1B_2 surface closer to where the 1B_2 and lowest 1A_1 cross. The 3A_1 and 1B_1 surfaces also intersect in the entrance streambed of the latter. All such triplet-singlet crossings provide paths to $\text{Cd}(^3P) + \text{H}_2$.

I. INTRODUCTION

A. van der Waals "half-collision" experiments

The synthesis and excited-state chemistry of metal-rare-gas and similar metal-molecule van der Waals complexes have been topics of both experimental¹⁻¹² and theoretical¹³⁻¹⁹ studies for at least a decade. "Half-collision" experiments¹⁻⁹ in which a ground-state van der Waals complex is prepared and then promoted to an upper electronic state via photon excitation have yielded much structural, energetic, and reactivity information on low-lying excited-state potential-energy surfaces of several such molecules. For example, pump-and-probe laser experiments^{5,8,9} have detected the electronic quenching of excited singlet-state Cd-Q complexes (Q is a quenching moiety, such as Xe, H_2 , or CH_4) to produce triplet states that predissociate to yield 3P_J Cd atoms and ground-state Q species.

Of particular importance for interpreting the $\text{Cd} + \text{H}_2$ experiments treated here are (i) the ground-state potential surface for geometries ranging from the van der Waals complex to those characterizing any and all product species, (ii) the low-energy excited states of the same spin multiplicity as

the ground state over this same range of geometries, and (iii) the "close approach" or intersection of any underlying states of different spin multiplicity with any of these former states. For example, it is via such intersections that 3P_J Cd atoms are thought to form in the above illustration.

B. Using H_2 as a quencher for $\text{Cd}(^1P_1)$

Earlier "full-collision" experiments¹⁰⁻¹² in which 1P Cd or 3P_J Cd atoms are prepared and allowed to collide with quencher gas atoms or molecules provide data that supplements that obtained in the half-collision pump-and-probe experiments. When the hydrogen molecule is used as a potential quencher for 1P_1 Cd atoms in full-collision experiments, in addition to observing electronically deactivated 3P_J Cd atoms (presumably generated via the intersection of a repulsive triplet surface correlating with the 3P_J Cd atom + H_2 and one of the nascently excited singlet surfaces), the chemical reaction products $\text{CdH} + \text{H}$ and $\text{Cd} + \text{H} + \text{H}$ are also detected.¹⁰ When $\text{Cd}(^3P_1)$ collides with H_2 (or D_2 or HD), $\text{CdH}(X^2\Sigma^+)$ (or CdD) is observed.^{11,12} The rotational quantum state populations of the CdH (or CdD) are bimodal, and have been explained in terms of a small activation barrier on the triplet surface. The mechanisms by which all of the above reaction products are formed are the central focus of the work discussed here.

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C. The physical nature of the ground and lowest triplet and singlet-state surfaces of CdH_2 near the van der Waals complex geometry

1. The ground-state van der Waals complex geometry

The chemically reactive events in the laser-excited half-collision experiments are thought to begin via excitation of ground-state singlet CdH_2 at a geometry characteristic of this weakly bound van der Waals complex. The complex is undoubtedly quite "floppy" with regard to angular motion of the H_2 moiety, but is thought to have an equilibrium structure with an H–H distance r of ca. 0.76 Å and a Cd-to-center of H–H bond distance R of ca. 4 Å. It is quite likely that "bending" motion of the H_2 moiety permits this complex to access linear or nearly linear geometries, as well as C_{2v} or near C_{2v} symmetries.

Therefore, we are required to explore the outcomes of photoexcitation processes that place the CdH_2 species on excited electronic states at geometries ranging from linear to C_{2v} . As shown below, flux that begins near linear geometries is less likely to progress toward any of the reaction products studied here because all excited singlet surfaces are repulsive for near-linear geometries. On the other hand, flux placed on excited-state singlet surfaces near C_{2v} geometries (with R near 4 Å and r near 0.76 Å) is shown to experience attractive forces for the 1B_2 and 1B_1 states, which causes flux moving initially on these states to dominate the formation of the reaction products.

2. The lowest excited singlet states

The CdH_2 complex has three (1A_1 , 1B_1 , and 1B_2 in C_{2v} geometry or $^1\Sigma$ and $^1\Pi$ for linear geometry) excited singlet states that derive from 1P_1 excited Cd interacting with a

ground-state H_2 molecule. At the geometry of the ground-state van der Waals complex, these states lie ca. 125 kcal/mol above the ground state (our reference point of energy throughout this study). These singlet states have more than enough energy to produce $\text{Cd}(^3P) + \text{H}_2$ (which lies at 88 kcal/mol), HCdH (which lies at 24 kcal/mol), $\text{Cd}(^1S) + \text{H} + \text{H}$ (lying at 110 kcal/mol), or $\text{CdH}(X^2\Sigma^+) + \text{H}$ (at 92 kcal/mol). They do not have enough energy to generate excited $\text{CdH}(A^2\Pi) + \text{H}$ (at 157 kcal/mol) or $\text{CdH}(B^2\Sigma^+) + \text{H}$ (at 163 kcal/mol). These and other relevant energies are summarized in Table I; all such energies do not contain any zero-point corrections.

Near the geometry of the ground-state van der Waals complex, the three singlet states are expected to display quite different behaviors as functions of R , the distance from the Cd atom to the midpoint of the H–H bond. Our findings indeed detect such differences, and show that the most energetically favorable approach for nascently excited CdH_2 is along C_{2v} symmetry (or nearly so), with the 1B_2 surface being the most attractive, and the 1B_1 surface weakly attractive. Linear approaches or approach on the 1A_1 surface at near C_{2v} symmetry are not favorable in the van der Waals region.

3. The lowest excited triplet states

The CdH_2 complex has three (3A_1 , 3B_1 , and 3B_2 in C_{2v} geometry or $^3\Sigma$ and $^3\Pi$ for linear geometry) excited triplet states that derive from 3P_1 excited Cd interacting with a ground-state H_2 molecule. At the geometry of the ground-state van der Waals complex, these states lie ca. 88 kcal/mol above the ground state. The primary relevance of these triplet states to the present study is that they provide, by their inter-

TABLE I. Structures and relative energies of various states of CdH_2 , $\text{Cd} + \text{H}_2$, HCdH , and $\text{CdH} + \text{H}$.^a

Species	Geometry ^b (Å)	Calc. energy (kcal/mol) ^b	Expt. energy (kcal/mol)
$\text{Cd}(^1S) + \text{H}_2$	$R = \infty, r = 0.76$	0	0
$\text{Cd}(^3P) + \text{H}_2$	$R = \infty, r = 0.76$	78	88 ^c
$\text{Cd}(^1P) + \text{H}_2$	$R = \infty, r = 0.76$	126	125 ^c
$\text{Cd}(^1S) + \text{H} + \text{H}$	$R = \infty, r = \infty$	96	110 ^d
$\text{CdH}(X^2\Sigma^+) + \text{H}$	$R_{\text{CdH}} = 1.83$	85	92 ^d
$\text{CdH}(A^2\Pi) + \text{H}$	$R_{\text{CdH}} = 1.76$	148	157 ^d
$\text{CdH}(B^2\Sigma^+) + \text{H}$	$R_{\text{CdH}} = 2.51$	151	163 ^d
$\text{HCdH}(^1\Sigma_g^+)^e$	$R = 0.0, r = 3.48$	24	
$\text{CdH}_2(^1B_2)^e$	$R = 1.69, r = 1.92$	106	
$\text{CdH}_2(^3B_2)^e$	$R = 1.70, r = 2.12$	86	
$\text{CdH}_2(^1A_1)^f$	$R = 1.69, r = 1.92$	99	
$\text{CdHH}(^3\Sigma^+)^g$	$R = 2.56, r = 1.16$	106	
$\text{CdH}_2(^3B_2)^h$	$R = 1.84, r = 1.28$	92	

^a All energies in kcal/mol relative to $\text{Cd}(^1S) + \text{H}_2$; no zero-point corrections are included.

^b This work.

^c Reference 26.

^d Reference 27.

^e The energies and geometries reported correspond to the local equilibrium geometries of these species on the electronic state specified.

^f This energy belongs to the ground 1A_1 state at the geometry where the 1B_2 state has its minimum. The 99 and 106 kcal/mol demonstrate that the 1B_2 state lies above the 1A_1 state at this geometry.

^g This point is a transition state on the colinear $\text{Cd}(^3P) + \text{HH} \Rightarrow \text{CdH}(X^2\Sigma^+) + \text{H}$ surface.

^h This point is a transition state on the $\text{Cd}(^3P) + \text{H}_2 \Rightarrow \text{CdH}_2(^3B_2)$ surface.

section(s) with the laser-accessed singlet states, the primary route to $\text{Cd}(^3P_J) + \text{H}_2$ and one of two routes to $\text{CdH}(X^2\Sigma^+) + \text{H}$.

Near the geometry of the ground-state van der Waals complex, the three triplet states are also expected to display quite different behaviors as functions of R . Our findings detect such differences, and show that the most repulsive interaction arises from the 3A_1 surface. The 3B_1 and 3B_2 surfaces are weakly attractive at such geometries.

D. Why emphasis is placed on C_{2v} geometries

In attempting to address the fate of flux prepared via photon absorption on the three singlet excited surfaces, we can ignore flux that is prepared near linear geometries. At such geometries all three singlet states ($2^1\Sigma^+$ and $^1\Pi$) are either repulsive ($2^1\Sigma^+$) or not nearly as attractive ($^1\Pi$) as for C_{2v} geometries (see Sec. III B). Thus, flux prepared near linear geometries will either (i) move outward to larger R values ($2^1\Sigma^+$) or (ii) “wait” ($^1\Pi$) until bending motion causes the complex to access near- C_{2v} geometries at which time it will encounter strongly attractive forces that move it to smaller R .

For these reasons, the three singlet PESs (potential-energy surfaces) were examined by performing C_{2v} -symmetry calculations beginning near the ground-state van der Waals complex geometry $R = 4 \text{ \AA}$ and $r = 0.76 \text{ \AA}$. For these PESs, gradient information was employed to search for minima and transition states as well as to find and follow “streambeds” that connect such stationary points. The stabilities of C_{2v} geometries to asymmetric distortions of b_2 symmetry were tested at various points along the streambeds.

In addition to mapping out the most energetically favorable directions for flux to flow on the singlet PESs (in particular, the 1B_2 and 1A_1 surfaces), cognizance was taken of the locations of nearby triplet states as “streambeds” were followed on these *singlet* surfaces. Any intersections of the singlet-state surface being followed by underlying triplet surface(s) were noted; such intersections are of great importance because they provide access to $\text{Cd}(^3P) + \text{H}_2$ products.

E. The role of the underlying ground-state 1A_1 surface

1. The ground-state HCdH and $\text{Cd} + \text{H} + \text{H}$ species lie on the underlying 1A_1 surface

As reaction flux begins to evolve on the 1B_2 surface under the C_{2v} geometries characteristic of the “insertion” path described briefly above, strong forces arise that cause the CdH_2 nuclei to move to smaller R values and to somewhat larger H–H distances (r) while preserving C_{2v} symmetry. Eventually, the 1B_2 surface approaches and intersects the 1A_1 surface, whose energy rises along this path because of the Woodward–Hoffmann “forbidden” nature of the ground-state $\text{Cd} + \text{H}_2$ insertion reaction.^{15,17} Production of *ground-state* HCdH , which lies on the underlying 1A_1 PES, can thus occur if flux can evolve onto this 1A_1 surface from the 1B_2 surface. Possible mechanisms for such 1B_2 -to- 1A_1 surface

“hoppings” are therefore important topics that the present work needs to address.

It turns out that the 1B_1 surface does *not* approach the 1A_1 surface along a path that flux would follow if placed on it, so 1B_1 - 1A_1 PES “hoppings” do not provide an avenue to HCdH formation.

2. Intersections or nonadiabatic couplings between the 1B_2 and 1A_1 surfaces can open the $\text{HCdH}(X^1\Sigma^+)$ and $\text{Cd}(^1S) + \text{H} + \text{H}$ channels

As flux evolves on the 1B_2 surface along C_{2v} symmetry, geometries may be reached near which the 1B_2 and 1A_1 surfaces intersect. At such geometries, even slight asymmetric distortions of the CdH_2 framework can cause flux to be “funnelled” to the 1A_1 surface. Such distortions reduce the symmetry from C_{2v} to C_s under which the 1A_1 and 1B_2 surfaces both are of $^1A'$ symmetry and hence can couple.

Once on the 1A_1 surface, the HCdH and $\text{Cd} + \text{H} + \text{H}$ products may be formed since the energy of the initially excited 1B_2 state of CdH_2 makes both product channels accessible. Only the presence of a substantial activation barrier along the paths to these products would alter this conclusion.

3. Intersections and nonadiabatic couplings between the 1B_2 and 1A_1 surfaces can also lead to $\text{CdH}(X^2\Sigma^+) + \text{H}$

The above surface-intersection picture can also explain how the asymmetric reaction products $\text{CdH} + \text{H}$ can be formed. If C_{2v} symmetry were rigorously retained, $\text{CdH} + \text{H}$ could not be formed by flux that exists on either surface (1B_2 or 1A_1) even if the surfaces intersect. However, if distortions away from C_{2v} geometries occur (as they must because of the zero-point motion along the asymmetric b_2 vibration of CdH_2), flux can evolve from one surface to the other near their intersections. Once non- C_{2v} symmetry is reached, the path to $\text{CdH}(^2\Sigma^+) + \text{H}$ (lying at 92 kcal/mol) may be available. The $\text{CdH} + \text{H}$ path is likely to be followed unless strong restoring forces (i.e., large positive curvature) exist along the b_2 mode direction. For this reason, in the present work the curvature along the b_2 direction has been monitored for the 1B_2 and 1A_1 surfaces; in either case, the appearance of negative curvature provides a sign of geometrical instability that may lead to $\text{CdH} + \text{H}$.

In addition to the possibility that the surfaces intersect and thereby cause flux to move from the 1B_2 to the 1A_1 surface, there exists a mechanism that does not require surface intersection. Nonadiabatic coupling, induced by vibrational motion along the asymmetric b_2 vibration of CdH_2 , can also couple the 1B_2 and 1A_1 surfaces. Such couplings are known²⁰ to occur most strongly when the two surfaces involved approach closely in energy, but surface intersection is *not* necessary. To explore the role of this mechanism, it is again important to locate geometries at which the two states approach closely and to monitor the curvatures of the two PESs along the b_2 direction.

F. Asymmetric-mode instability is the key to forming $\text{CdH}(X^2\Sigma^+) + \text{H}$

Formation of the asymmetric reaction products $\text{CdH} + \text{H}$ requires that geometrical instability exist along the asymmetric distortion mode somewhere along the path taken by the reaction flux. Since the flux is assumed to begin on the 1B_2 surface, it is natural to first search for geometries at which instability along the b_2 distortion mode appears on this surface. If such geometries do not exist or are energetically inaccessible, the 1A_1 surface should be searched for such unstable geometries because flux can eventually move to this surface from the 1B_2 surface as discussed above. If such instability occurs while the flux is on the 1A_1 surface, this flux can move spontaneously away from C_{2v} symmetry and thus toward $\text{CdH} + \text{H}$; if instability occurs while on the 1B_2 surface, the flux can move toward $\text{CdH} + \text{H}$ while on this surface.

The strength of the factors that produce negative b_2 -mode curvature on, for example, the 1A_1 surface is governed by matrix elements of the form²⁰

$$\frac{|\langle ^1A_1 | \partial H / \partial Q_{b_2} | ^1B_2 \rangle|^2}{E(^1A_1) - E(^1B_2)},$$

where $\partial H / \partial Q_{b_2}$ represents the derivative of the electronic Hamiltonian with respect to distortion along the b_2 mode. The closer the 1B_2 state approaches the underlying 1A_1 state, the larger is the magnitude of this 1A_1 -state negative-curvature factor. Only at geometries where the 1B_2 state lies *above* the 1A_1 state will negative b_2 curvature likely to occur on the 1A_1 PES.

Alternatively, the 1B_2 state may develop negative b_2 curvature if the 1B_2 state intersects and moves below the 1A_1 state. In this case, the same factor displayed above, but with opposite sign, induces negative b_2 -mode curvature on the 1B_2 state. In either event, one of the two states (the *lower-energy PES* at any geometry) may possess instability along the asymmetric b_2 mode, and therefore provide an open channel to production of $\text{CdH} + \text{H}$ products. To explore these possibilities, one must search for geometries at which the two electronic states intersect or approach closely; clearly, this became one of the primary tasks of the present work.

G. Formation of $\text{Cd}(^3P) + \text{H}_2$ involves intersections by underlying triplet surfaces

As flux moves inward to smaller R values either on the (strongly attractive) 1B_2 surface or on the (weakly attractive) 1B_1 surface, repulsive triplet-state surfaces may approach and intersect the singlet surface from below. In this event, flux can "hop" (albeit, with spin-orbit coupling required) to the triplet surface, and subsequently lead to $\text{Cd}(^3P_J) + \text{H}_2$ products. Such intersections have indeed been found for both of the above singlet surfaces and are characterized in Sec. III C.

II. COMPUTATIONAL METHODS

A. Configuration space

In order to obtain a qualitatively accurate description of the global 1A_1 potential-energy surface for CdH_2 , complete-active-space self-consistent-field (CASSCF) wave functions were employed. The active space consisted of the two $5s$ electrons of Cd and the two σ_g electrons of H_2 distributed in all possible ways among the six valence orbitals. In the asymptotic region corresponding to $\text{Cd} + \text{H}_2$, these orbitals are the $5s$ and $5p$ orbitals of Cd and the σ_g and σ_u^* orbitals of H_2 . For C_{2v} geometries in which the Cd and H_2 moieties interact, they are three a_1 , one b_1 , and two b_2 orbitals. At linear geometries, using the C_{2v} symmetry limits of our computer codes, these are four a_1 (i.e., σ), one b_1 (i.e., π), and one b_2 (i.e., π) orbitals.

Preliminary calculations which included the outermost occupied d orbitals of Cd in the active space showed that they were of minor importance in describing the addition of H_2 to Cd on the 1A_1 PES. For example, the natural orbital occupation numbers of the d orbitals were consistently greater than 1.99 electrons; hence, they were excluded from the active space in the large number of calculations needed to describe the PES studied here.

This choice of active space yields 37 and 28 configuration state functions (CSFs) of 1A_1 and 1B_2 symmetry, respectively, and is sufficiently flexible to describe the asymptotic $\text{Cd} + \text{H}_2$, $\text{Cd} + \text{H} + \text{H}$, and linear $\text{H}-\text{Cd}-\text{H}$ regions of the potential-energy surface, the $\text{Cd}(^1S) + \text{H}_2$ and $\text{Cd}(^1P) + \text{H}_2$ linear species, as well as all intermediate points. While a more extensive treatment of correlation as well as consideration of spin-orbit coupling would be required to obtain quantitative accuracy in the surface, the present CASSCF treatment is sufficient for qualitative interpretations of the PES.

B. Atomic-orbital basis sets

The basis set used for cadmium consists of the Hay-Wadt effective core potential and the associated valence double-zeta basis set.²¹ In order to obtain a more accurate $^1S \rightarrow ^1P$ excitation energy for Cd, a set of diffuse s and p functions were added to the valence basis set, with exponents of 0.021 76 and 0.0162, respectively. The basis set for hydrogen was constructed by adding a set of p -type polarization functions (with an exponent of 1.1) to the Pople-21 G hydrogen basis.²²

All calculations were performed using GAMESS (Ref. 23) or the MESSKIT (Ref. 24) suite of computer programs. The 1A_1 PES was constructed by calculating a grid of approximately 1100 single-point energies, which were then fit using a two-dimensional cubic spline interpolation.

C. Geometrical curvature calculations

As explained in the Introduction, it is anticipated that some regions of the ground 1A_1 or excited 1B_2 PES will be energetically unstable with respect to distortions of b_2 symmetry (i.e., the asymmetric Cd-H stretch). In order to determine the regions of the surface in which this occurs, the matrix of energy second derivatives (i.e., the Hessian ma-

trix) was computed at selected points. Neither GAMESS nor our MESSKIT program can carry out such a second-derivative calculation analytically with the pseudopotentials employed for Cd, so finite-difference methods were used to compute the second energy derivative from the analytically calculated first derivatives. This was followed by application of the projection scheme of Miller, Handy, and Adams²⁵ (to project out the nonzero gradient vector) and diagonalization to determine if the b_2 mode has an imaginary frequency.

D. Geometries to explore

Points of the 1B_2 PES were computed (1) near the ground-state van der Waals complex geometry that characterizes the nascent photoexcited species of the half-collision experiments, (2) along a "streambed" path connecting this initially excited 1B_2 species with the 20 kcal/mol deep minimum on this same 1B_2 surface (this path is detailed later), (3) in regions where the ground 1A_1 surface displayed negative curvature along the asymmetric stretching mode of b_2 symmetry (such regions signal the close approach of the 1B_2 PES), (4) in regions where the 1B_2 and 1A_1 PESs intersect, and (5) along the above 1B_2 state's streambed where intersections with 3A_1 and 3B_1 PESs were detected.

Points on the ground 1A_1 surface were evaluated at a large number of R and r values to achieve a more global picture. Moreover, efforts were made to find and characterize geometries at which b_2 -mode instability is present on the 1A_1 surface as well as geometries where the 1B_2 surface intersects this 1A_1 surface.

The 1B_1 PES was examined (1) near the ground-state van der Waals complex geometry that characterizes the nascent photoexcited species of the half-collision experiments, (2) along its own streambed path in which R is varied from ca. 4 Å inward to 1.6 Å with r "optimized" to produce the minimum 1B_1 energy for each such R value [this path describes qualitatively how flux would most probably evolve if placed on the (weakly attractive) 1B_1 surface], and (3) along this same 1B_1 path, focusing on where an intersection with the 3A_1 state is detected in the entrance valley.

III. RESULTS AND DISCUSSION

A. Calibration of calculated results

A feel for the accuracy with which the basis sets and *ab initio* methods used here reproduce experimental energies was obtained by calculating the $^1S \rightarrow ^1P$ atomic excitation energies of cadmium and the bond dissociation energy D_e of the hydrogen molecule. In addition, *ab initio* calculations were performed for the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of CdH. For the excitation energies, the calculated values of 125.9 and 78.4 kcal/mol can be compared with the experimental values of 124.9 and 87.6 kcal/mol.²⁶ Because the relative positions of singlet and triplet surfaces that derive from the 1,3P levels of Cd are of utmost importance, we later must consider the effects of "shifting" our calculated triplet-state surfaces upward by $87.6 - 78.4 = 9$ kcal/mol to achieve better representations of these relative energies.

The calculated H_2 well depth of 96.0 kcal/mol is some-

what smaller than the experimental D_e value of 109.5 kcal/mol,²⁷ again by an amount that is not entirely satisfactory. The calculated vibrational frequencies ($^{114}\text{Cd } ^1\text{H}$) for the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of CdH 1278, 1428, and 895 cm^{-1} , respectively, qualitatively reproduce the experimental values²⁷ 1337, 1700, and 1000 cm^{-1} . A prior theoretical relativistic computation²⁸ of the geometry of the linear H–Cd–H molecule gave a Cd–H bond length of 1.733 Å, which is in very good agreement with our calculated value of 1.741 Å. All of the *relevant energies* obtained for stable species $\text{Cd}(^1S, ^1,3P) + H_2$, $\text{HCdH}(^1\Sigma_g^+)$, $\text{CdH}_2(^1A_1, ^1B_2, ^3B_2)$, $H + \text{Cd} + H$, and $\text{CdH}(X^2\Sigma^+, B^2\Sigma^+, \text{and } A^2\Pi) + H$ are summarized in Table I.

B. Long-range interaction energies relevant to the van der Waals region

To estimate the large- R (i.e., van der Waals region) interaction energies of the various states that arise from 1P Cd or 3P Cd interacting with H_2 , we performed the following calculations:

(i) We used the same six-orbital CASSCF procedure used to map out all of the potential surface features reported here to compute the energies of ground 1A_1 , and excited 1,3A_1 , 1,3B_1 , and 1,3B_2 CdH_2 all for $r = 0.76$ Å (the equilibrium bond length of H_2) and $R = 50$ Å (i.e., essentially infinitely far away). These energies are reported in Table II.

(ii) In each such calculation, we allowed the six valence orbitals to be optimized to produce the lowest total energy for the state under study. The physical natures of these valence orbitals are also given in Table II.

(iii) We then calculated the energies of these same 1A_1 , 1,3A_1 , 1,3B_1 , and 1,3B_2 states at $R = 4.4$ Å, $r = 0.76$ Å, the presumed geometry of the ground-state van der Waals complex.

(iv) At the van der Waals geometry, we also employed the Boys and Bernardi²⁹ counterpoise method to calculate the basis-set superposition errors (BSSE) for each of the seven states. These errors ranged from 0.13 to 0.19 kcal/mol.

TABLE II. Relative energies of CdH_2 species used to evaluate long-range interaction energies.^a

Species	Nature of six valence orbitals	Calc. energy (kcal/mol) ^b
$\text{CdH}_2(^1A_1)$	$5s, 5p, \sigma_g, \sigma_u$	0
$\text{CdH}_2(2^1A_1)$	$5s, 5p_x, 5p_z, \sigma_g, \sigma_u, \pi_x$	123
$\text{CdH}_2(^1B_1)$	$5s, 5p_x, 1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u$	121
$\text{CdH}_2(^1B_2)$	$5s, 5p_z, 1\sigma_g, 1\sigma_u, 2\sigma_g, \pi_x$	119
$\text{CdH}_2(^3A_1)$	$5s, 5p_z, 1\sigma_g, 1\sigma_u, 2\sigma_u, \pi_x$	75
$\text{CdH}_2(^3B_1)$	$5s, 5p_x, 1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u$	73
$\text{CdH}_2(^3B_2)$	$5s, 5p_z, 1\sigma_g, 1\sigma_u, 2\sigma_g, \pi_x$	71

^a All energies in kcal/mol relative to $\text{Cd}(^1S) + H_2$.

^b As calculated in this work.

(v) By subtracting from our BSSE-corrected energies at $R = 4.4 \text{ \AA}$, $r = 0.76 \text{ \AA}$ our $R = 50 \text{ \AA}$, $r = 0.76 \text{ \AA}$ energies, we obtain an estimate of the interaction energies for the seven electronic states.

These results are given in Table III and are summarized qualitatively in Fig. 1(a). In Table III, we also show the interaction energies that would obtain if one were to include only the quadrupole-quadrupole interactions between H_2 and the various states of Cd. These data show clearly that the $^{1,3}A_1$ states' interaction energies are *not* entirely quadrupole-quadrupole at these geometries (repulsions due to orbital overlaps are present), but the $^{1,3}B_{1,2}$ have strong or even dominant quadrupole-quadrupole components here.

Our CASSCF wave function contains no configurations capable of describing dispersion interactions among H_2 and the various states of Cd. Our wave functions are capable of describing the dominant (because it varies as R^{-5}) long-range electrostatic interaction deriving from the quadrupole moment of H_2 interacting with the quadrupole moments of the various states of Cd. For these reasons, our interaction energies can be considered as reasonable at large R , but subject to increased attractions amounting to $< 2 \text{ kcal/mol}$ (due to dispersion) as R decreases, with the largest such corrections thus arising at small R .

The data of Table III show the following in the van der Waals region: (i) the excited $^{1,3}A_1$ surfaces are repulsive (by amounts that are not likely to be reversed when dispersion is included), (ii) the $^{1,3}B_2$ surfaces are more attractive than the $^{1,3}B_1$ surfaces, and (iii) the singlet surfaces are more attractive than their corresponding triplet surfaces (due to the larger quadrupole moments of $^1P \text{ Cd}$). In Fig. 1(a), the behavior of these states in the van der Waals region is denoted by the $R > 3 \text{ \AA}$ region.

In the same fashion, we determined the CASSCF interaction energies for the $2^1\Sigma^+$ and $^1\Pi$ colinear states in the van der Waals region ($r = 0.76 \text{ \AA}$ and $R = 4.4 \text{ \AA}$). We found that the $2^1\Sigma^+$ surface is strongly repulsive (3.19 kcal/mol) despite its attractive quadrupole-quadrupole interaction (-0.65 kcal/mol). As in the case of the $^{1,3}A_1$ states, the repulsive overlap effects dominate in the region where the photoexcitation places the CdH_2 species on the $2^1\Sigma^+$ surface.

The interaction energy for $^1\Pi$ state is also found to be repulsive (0.13 kcal/mol) as is the quadrupole-quadrupole

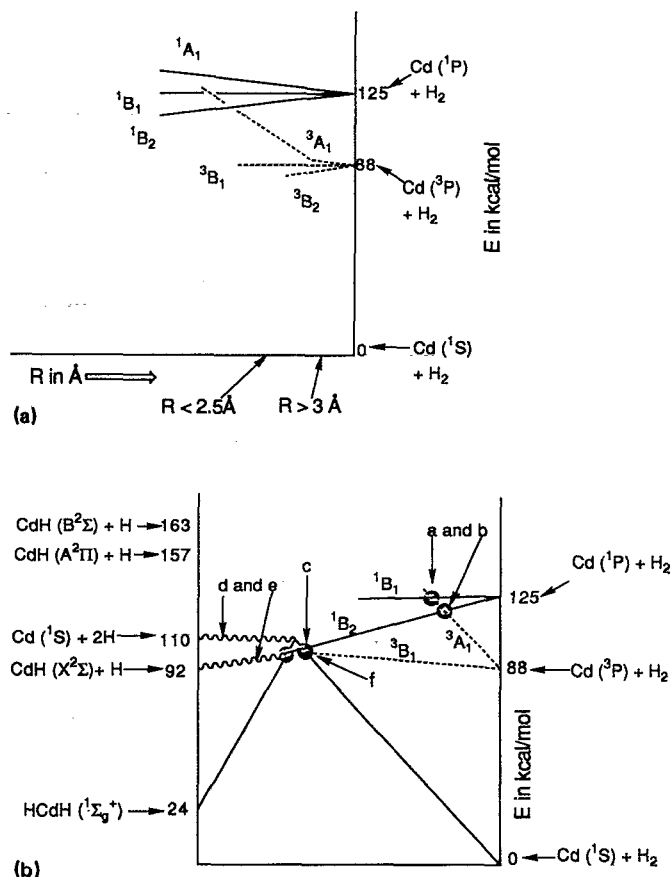


FIG. 1. (a) Qualitative energy-level diagram showing the behavior of the excited singlet and triplet states for large R values; $R > 3 \text{ \AA}$ characterizes the near-asymptotic region, and $R < 2.5 \text{ \AA}$ is where chemical valence interactions become important (see Figs. 2 and 3). (b) Qualitative energy-level diagram showing primary surface intersections (marked by ●) that lead to various reaction products. All energies are in kcal/mol and are relative to the ground state of $\text{Cd}(^1S) + \text{H}_2$. The intersections labeled a and b may produce $^3P_j \text{ Cd}$ via intersections of the 1B_1 (at $R = 2.0 \text{ \AA}$, $r = 0.9 \text{ \AA}$) and 1B_2 (at $R = 2.25 \text{ \AA}$, $r = 0.79 \text{ \AA}$) surfaces by the 3A_1 surface; c labels the 1B_2 and 1A_1 intersection that leads to formation of $^1S \text{ Cd} + 2\text{H}$ via path d, and to $\text{CdH}(X^2\Sigma^+) + \text{H}$ via the b_2 -mode instability path e; f labels the intersection of the 1B_2 and 1A_1 surfaces by the 3B_1 surface (near $R = 1.85 \text{ \AA}$, $r = 1.02 \text{ \AA}$) in the chemically reactive region.

interaction energy (by 0.32 kcal/mol). As with the $^{1,3}B_{1,2}$ states, the remaining components of the $^1\Pi$ state's interaction energy stabilize the complex.

In view of the repulsive interactions for the colinear complexes, the remainder of our study was focused on the attractive C_{2v} 1B_1 and 1B_2 surfaces.

C. The surfaces at geometries where chemical valence forces are strong

In Fig. 1(b) we describe the qualitative features of the ground and lowest excited singlet and triplets PESs in the van der Waals region and the chemical-interaction region (which then connect to product channels). This presentation is not meant to provide a highly accurate representation of these three-dimensional PESs, but to help the reader view the relative energies and geometries of the various asymptotic states and most important surface intersections.

TABLE III. CAS-SCF interaction energies^a ΔE .

State	1^1A_1	2^1A_1	1^1B_1	1^1B_2	3^1A_1	3^1B_1	3^1B_2
ΔE^b	0.11	3.45	-0.17	-0.38	1.06	-0.03	-0.11
ΔE^c	0.0	0.31	-0.08	-0.24	0.14	-0.04	-0.11

^aIn kcal/mol determined at $R = 4.4 \text{ \AA}$, $r = 0.76 \text{ \AA}$ in C_{2v} geometry.

^bFrom our *ab initio* quantum calculations.

^cPure quadrupole-quadrupole interaction for $\text{Cd}(^1P) + \text{H}_2$ computed as $Y(\Theta_{\text{Cd}}\Theta_{\text{H}_2}/R^5)$, where $Y = 9/4$ for B_2 symmetry, $Y = 3/4$ for B_1 symmetry, and $Y = -3$ for A_1 symmetry. The computed quadrupole moments are $\Theta_{\text{Cd}}(^3P) = -7.8 \text{ a.u.}$, $\Theta_{\text{Cd}}(^1P) = -18.0 \text{ a.u.}$, and $\Theta_{\text{H}_2} = 0.38 \text{ a.u.}$

1. The lowest 1A_1 potential-energy surface

(a) *Global C_{2v} picture at 1100 geometries.* The calculated lowest-energy 1A_1 potential-energy surface of CdH_2 is depicted in Fig. 2 as a function of R , the distance between the H_2 midpoint and the cadmium atom, and r , the H-H distance. A contour version of this same surface is given in Fig. 3. There are three asymptotic regions of interest in Figs. 2 and 3: the van der Waals minimum of the cadmium atom and H_2 molecule ($R = 4.4 \text{ \AA}$, $r = 0.76 \text{ \AA}$), the three separated cadmium and hydrogen atoms ($R = 4.4 \text{ \AA}$, $r = 3.5 \text{ \AA}$), and the linear H-Cd-H molecule ($R = 0.0 \text{ \AA}$, $r = 3.5 \text{ \AA}$). The total electronic energies (i.e., not including zero-point corrections) for these geometries are included in the data of Table I.

(b) *HCdH formation is endothermic.* Comparison of the energies of $\text{Cd} + \text{H}_2$ and H-Cd-H shows that formation of H-Cd-H (which was proven to be a local minimum by demonstrating that the Hessian matrix is positive definite) is *endothermic* by 24.4 kcal/mol. This is in contrast to the isovalent systems $\text{Be} + \text{H}_2$ and $\text{B}^+ + \text{H}_2$, where formation of the corresponding linear triatomic molecules is predicted (also at the CASSCF level of theory) to be exothermic by 23 (Ref. 18) and 47 (Ref. 17) kcal/mol, respectively. The harmonic vibrational frequencies of H^{114}CdH were found to be 540 (bending), 1620 (asymmetric stretch), and 1640 (symmetric stretch) cm^{-1} .

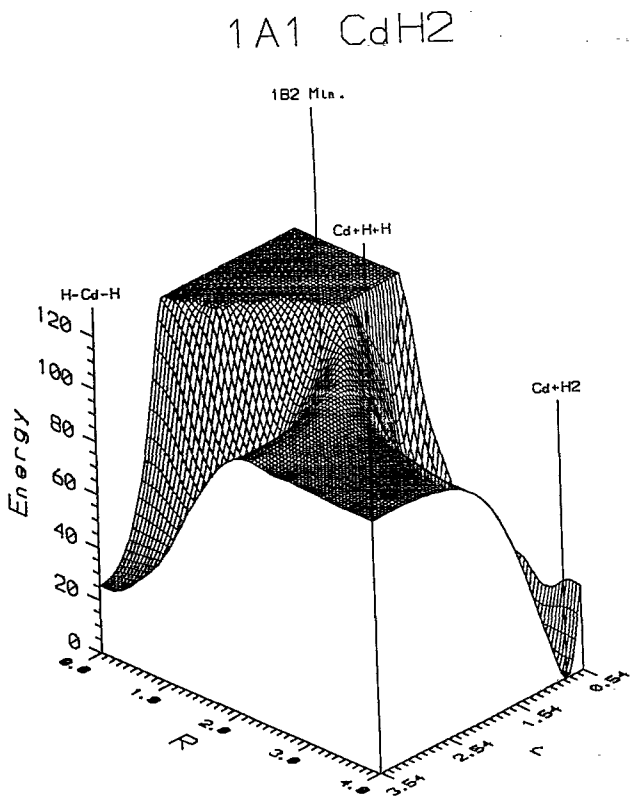


FIG. 2. The ground-state 1A_1 potential-energy surface. R denotes the distance between the Cd atom and the H_2 midpoint and r denotes the H-H distance. The point labeled " 1B_2 Min" indicates the geometry of the minimum on the 1B_2 surface.

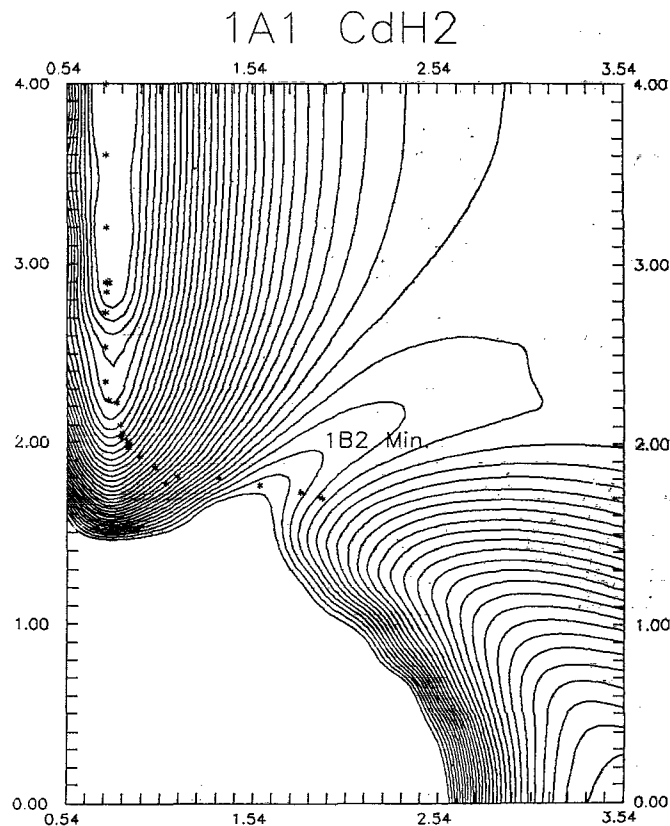


FIG. 3. Contour plot of the same surface shown in Fig. 2. r is the horizontal axis and R is the vertical axis (both in \AA). The spacing between contours is 5 mhartrees (ca. 3 kcal/mol). The points marked by asterisks denote geometries in a streambed on the 1B_2 surface and the point labeled " 1B_2 Min" indicates the geometry of the minimum on this surface. The geometries that characterize the streambed on the 1B_1 surface (not shown here) closely parallel the asterisks.

(c) *There is no well-defined saddle leading from $\text{Cd} + \text{H}_2$ to HCdH.* Essential features of the CdH_2 1A_1 PES shown in Figs. 2 and 3 are the two channels (one leading to linear H-Cd-H and the other to a cadmium atom and an H_2 molecule) which are divided by a ridge. Of particular interest is the lack of a stationary point along this ridge (apart from the asymptotic region corresponding to $\text{Cd} + \text{H} + \text{H}$). This, too, is in contrast to the BeH_2 and $\text{B}^+ \text{H}_2$ systems, where a stationary point with an imaginary-frequency vibrational mode of a_1 symmetry connecting the two channels is observed. The lack of such a stationary point for CdH_2 implies that there is no saddle point for the direct insertion of Cd into the H_2 molecule, on the 1A_1 surface. Rather, the most energetically favorable means of insertion on this surface within this C_{2v} symmetry is by initial dissociation of the H_2 molecule, followed by concerted addition of the two hydrogen atoms to cadmium.

2. The 1B_1 surface

Calculations on the weakly attractive (see Table III) 1B_1 state for C_{2v} geometries have been carried out as a function of R , with the H-H distance r optimized for each such R value, to generate a "streambed" path. The energies of this

1B_1 state along such a path, as well as the variations of R and r , are described in Table IV.

The geometries lying in this streambed closely parallel those of the 1B_2 surface streambed from $R = 4$ Å in to $R = 2.1$ Å (compare the asterisks of Fig. 3 with the R , r values of Table IV) although the energy variation of the 1B_2 state is much stronger than that of the 1B_1 state. Past $R = 2.1$ Å, the two paths differ markedly; the 1B_2 surface curves into the “chemically reactive” region where it intersects and couples strongly to the lowest 1A_1 state to produce $\text{CdH} + \text{H}$, HCdH , and $\text{Cd} + 2\text{H}$. In contrast, the 1B_1 path remains “straight” (i.e., with r varying little from $r = 0.76$ Å) and rather “flat” until $R < 2.4$ Å, at which time it becomes quite repulsive; flux on this surface does not enter the chemically reactive region for the total energies appropriate here (125 kcal/mol).

In addition to characterizing the streambed on this 1B_1 surface, we found that, along this path, the repulsive 3A_1 PES intersects it near $R = 2.0$ Å, $r = 0.80$ Å, at which these surfaces lie ca. 10 kcal/mol above the $\text{Cd}(^1P) + \text{H}_2$ asymptote. See Fig. 4 where the 1B_1 surface and the underlying triplet surfaces are depicted along such a path. The (less-repulsive) 3B_1 surface lies ca. 38 kcal/mol lower at the 1B_1 - 3A_1 crossing geometry. Addition of dispersion interaction terms to the 1B_1 energy could move this intersection point to somewhat longer R values, thereby also moving its energy below the 10 kcal/mol value. Moreover, if we “shift” the entire 3A_1 curve upward to force the asymptotic 1P - 3P splitting to be $126 - 88 = 38$ kcal/mol rather than the calculated (see Table II $121 - 75 = 46$ kcal/mol), the crossing point moves outward to only ca. 2.2 Å, at an energy that is still above the 1B_1 asymptote.

In summary, it seems likely that the 3A_1 - 1B_1 intersection will occur for $R > 2.2$ Å and at energies somewhat above the 1B_1 state’s asymptote. If any flux were to reach this crossing point, it could “hop” to the repulsive triplet surface and dissociate to produce $\text{Cd}(^3P_J) + \text{H}_2$.

3. The 1B_2 surface

Flux created on the 1B_2 excited state via photon excitation near the geometry of the ground-state van der Waals complex experiences strong forces that “drive” it along a 20

TABLE IV. Interaction energies on the 1B_1 surface.^a

R (Å)	r^b (Å)	E (kcal/mol)
1.6	0.7833	40
2.0	0.7655	10
2.4	0.7611	2
2.8	0.7579	1
3.2	0.7538	0
3.6	0.7545	0
4.0	0.7538	0

^aRelative to the $\text{Cd} + \text{H}_2$ asymptote reported in Table II.

^bFor each R value, the distance r was varied to minimize the energy on this 1B_1 surface.

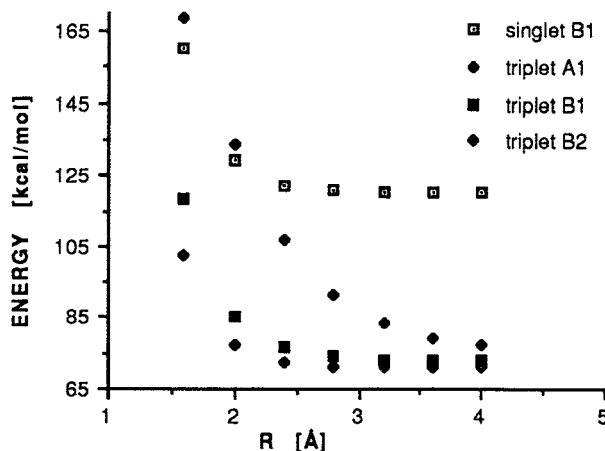


FIG. 4. Singlet-triplet crossings along the streambed of the 1B_1 state.

kcal/mol deep, narrow valley streambed whose locus is depicted by the asterisks in Fig. 3. This path leads to the minimum (denoted 1B2 min in Figs. 2 and 3) on this 1B_2 surface at $R = 1.69$ Å and $r = 1.92$ Å and at an energy of 106 kcal/mol.

Along the path leading from the van der Waals geometry to the minimum, the 1B_2 PES is intersected by the repulsive 3A_1 surface near $R = 2.25$ Å, $r = 0.79$ Å (see Fig. 5), where the 1B_2 state’s energy is ca. 3 kcal/mol below its asymptotic value (i.e., the “deep” chemically reactive basin has not yet been entered). At this crossing point, flux can move onto the 3A_1 surface and dissociate to produce 3P_J Cd atoms. At such geometries, the less-repulsive 3B_1 surface lies ca. 38 kcal/mol lower in energy.

Flux that progresses on the 1B_2 surface toward smaller R values experiences a different fate. It moves on to approach the minimum on the 1B_2 surface, at which the lowest

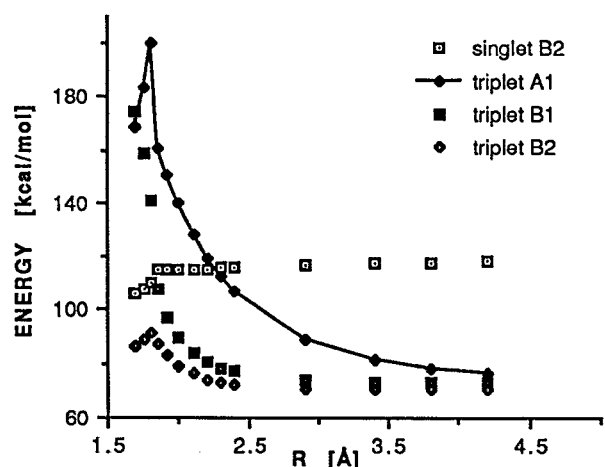


FIG. 5. Singlet-triplet crossings along the streambed of the 1B_2 state. The 3A_1 points have been connected by a curve to more easily follow the rapid change of energy that results from the “avoided crossing” discussed in the text.

1A_1 surface is slightly (7 kcal/mol) lower in energy. At nearby geometries (e.g., where $R = 1.69$ Å and $r = 1.54$ Å), the 1B_2 surface lies 3.5 kcal/mol below the 1A_1 surface. Therefore, a 1A_1 - 1B_2 surface intersection seam lies in this neighborhood of the ridge separating the $\text{Cd}\cdots\text{H}_2$ and HCdH channels in Fig. 2, beginning near $R = 1.7$ Å, $r = 1.6$ Å and extending to smaller R and smaller r values. Flux encountering such intersection points can do either one of the following.

(i) Remain on the 1B_2 PES which, after passing below the 1A_1 surface, develops b_2 -mode instability as a result of coupling to the higher-energy 1A_1 state as discussed in Sec. I F, thereby generating $\text{CdH}(X^2\Sigma^+) + \text{H}$.

(ii) "Hop" to the 1A_1 PES as the intersection is traversed, and subsequently move on to produce vibrationally "hot" HCdH , which can then decompose to $\text{Cd} + \text{H} + \text{H}$.

We also find that, in the neighborhood of the close approach and intersection of the 1A_1 and 1B_2 surfaces, the 3B_1 surface intersects near $R = 1.85$ Å, $r = 1.02$ Å (see Fig. 5); these intersections provide one more path to forming $\text{Cd}(^3P_J) + \text{H}_2$, for flux that enters this region and hops to the 3B_1 surface.

4. Treatment of 1A_1 - 1B_2 nonadiabatic coupling to produce b_2 -mode instability

Clearly, in the neighborhood of the close approach and intersections of the 1B_2 and 1A_1 surfaces discussed above, it is essential to verify the b_2 -mode instability (or lack thereof) of each of these surfaces. To examine the b_2 -mode stability of the 1B_2 state at its own minimum, we proceeded as follows:

(i) Because the GAMESS program cannot compute analytical second energy derivatives, we introduced a small (0.005 29 Å) asymmetric distortion of the two Cd-H bond lengths.

(ii) After which the CASSCF energy of the lowest-energy singlet state (the 1A_1 state lies ca. 7 kcal/mol lower here) was evaluated.

(iii) First, a CASSCF calculation on the lower-lying 1A_1 state was performed, and the negative curvature on this 1A_1 surface was verified via the small b_2 -mode distortion noted above.

(iv) Second, a state-averaged CASSCF process, in which the 1A_1 and 1B_2 states are equally weighted in the energy functional being optimized, was performed and the energy of the resulting 1A_1 state was examined under the small b_2 -mode distortion to again verify its negative curvature.

The results of both such calculations were the same: the 1A_1 state is unstable with respect to b_2 -mode motions at the geometry where the 1B_2 state has its minimum but lies above the 1A_1 state. Likewise, the 1B_2 state will be b_2 -mode unstable when it has intersected and now lies below the 1A_1 state. We thought it prudent to carry out both sets of CASSCF calculations because the former, which optimizes orbitals and configuration mixing coefficients for the 1A_1 state, differentially stabilizes the 1A_1 state relative to the 1B_2 state. On the other hand, the state-averaged CASSCF calculation probably underestimates the energy gap between the two states. Because the strength of coupling, as given by the formula in Sec. I F, depends strongly on this energy gap, it was

important to verify the negative b_2 -mode curvature for situations in which this gap is overestimated and underestimated.

5. The 3B_2 and $^3\Sigma^+$ surfaces and relation to full-collision experiments

We found the 3B_2 and $^3\Sigma^+$ surfaces to display behavior that may be useful in interpreting earlier "full-collision" experiments^{11,12} in which 3P_1 Cd atoms were allowed to collide with H_2 molecules and $\text{CdH}(X^2\Sigma^+) + \text{H}$ products were detected.

In particular, the 3B_2 surface, which was not discussed in earlier sections since its PES does not intersect the 1B_2 or 1B_1 surfaces in regions where flux in the half-collision experiments is likely to flow, has been found to (i) be attractive in the van der Waals region as noted earlier, and (ii) to have a minimum at $R = 1.70$ Å, $r = 2.12$ Å whose energy lies 8 kcal/mol above our computed $\text{Cd}(^3P) + \text{H}_2$ asymptote.

These two facts imply that there must be a minimum on the 3B_2 potential surface at long range (probably in the van der Waals region), separated by a transition state that connects to the minimum at $R = 1.70$ Å, $r = 2.12$ Å. We found such a transition state to occur at $R = 1.84$ Å, $r = 1.28$ Å and to have an energy of 92 kcal/mol. The transition state is visible in Fig. 5 (because the streambed paths on the 1B_2 and 3B_2 surfaces are quite similar for $R > \text{ca. } 1.8$ Å).

It should also be noticed in Fig. 5 that the energy of the 3A_1 state falls drastically near $R = 1.8$ Å as the result of an avoided crossing between the $1a_1^2 2a_1 3a_1$ and $1b_2^2 1a_1 2a_1$ configurations. We speculate that the second-order Jahn-Teller coupling discussed in Sec. I F, and now applied to the 3A_1 and 3B_2 states, causes negative b_2 -mode curvature on the (lower-lying) 3B_2 surface and opens the $\text{CdH}(X^2\Sigma^+) + \text{H}$ channel for $R < 1.7$ Å with a 3B_2 -state energy between 8 and 14 kcal/mol above the $\text{Cd}(^3P) + \text{H}_2$ asymptote.

Another possibility to produce $\text{CdH}(X^2\Sigma^+) + \text{H}$ in the "full-collision" experiments comes through the $^3\Sigma^+$ surface. Even though the colinear paths are less probable than the C_{2v} paths, we considered this option in view of the activation barrier detected on 3B_2 surface in C_{2v} geometry. On the $^3\Sigma^+$ surface we also found a transition state which lies at 102 kcal/mol [i.e., even higher than the 3B_2 transition state (see Table 1)].

In conclusion, we expect an activation barrier for the $\text{Cd}(^3P) + \text{H}_2 \Rightarrow \text{CdH}(X^2\Sigma^+) + \text{H}$ reaction. Earlier full-collision data indeed demonstrate that this reaction, which is essentially thermoneutral, proceeds with a nonzero activation.^{11,12}

IV. CONCLUSIONS AND SUMMARY OF FINDINGS

This paper has attempted to provide a more detailed understanding of the reaction dynamics of 1P cadmium with the ground-state hydrogen molecule. At the energy of 1P $\text{Cd} + \text{H}_2$ [ca. 125 kcal/mol above ground-state $\text{Cd}(^1S) + \text{H}_2$ reactants], it is possible to access products via the ground-state 1A_1 surface (i.e., $\text{HCdH}(^1\Sigma_g^+)$ at 24 kcal/mol and $\text{Cd}(^1S) + \text{H} + \text{H}$ at 110 kcal/mol) or products

that require b_2 -mode instability to occur somewhere along the path from 1P Cd + H₂ (i.e., CdH(${}^2\Sigma^+$) + H at 92 kcal/mol). Of course, quenching to produce Cd(3P_J) + H₂ at 88 kcal/mol is also energetically possible. Formation of CdH($A^2\Pi$) + H or CdH($B^2\Sigma$) + H is *not* energetically possible.

To explain the formation of CdH($X^2\Sigma^+$) + H, we propose the following. (i) Flux starts on the excited 1B_2 electronic state and (ii) moves under strongly attractive forces to a region where the 1B_2 surface penetrates the lowest 1A_1 surface (see Figs. 2 and 3 for an example of such a region), (iii) where asymmetric (b_2 -mode) instability on this 1B_2 surface is induced by the presence of the nearby but higher-lying 1A_1 surface, (iv) as a result of which distortion along this b_2 mode and hence dissociation to CdH(${}^2\Sigma^+$) + H products occurs from the 1B_2 surface.

It is also possible that flux "hops" to the 1A_1 surface, and evolves on this surface to geometries where this 1A_1 surface lies just below the 1B_2 PES, at which point b_2 -mode instability will occur on the 1A_1 surface, thereby allowing CdH(${}^2\Sigma^+$) + H products to be formed from this 1A_1 surface.

To explain the formation of Cd + H + H, we propose the following. (i) Flux starts on the excited 1B_2 electronic state and again moves to a region where the 1B_2 and 1A_1 surfaces approach one another, (ii) at which time the flux can "hop" to the underlying 1A_1 state, either through an intersection of the two surfaces or via nonadiabatic coupling mediated by an asymmetric vibration, (iii) after which the flux moves "downhill" directly into the HCdH potential well (with ca. 125 – 24 = 101 kcal/mol of internal vibrational energy) on this 1A_1 surface, (iv) from which it has enough energy to escape and produce Cd(1S) + H + H.

To explain the formation of Cd(3P_J) + H₂ ($X^1\Sigma_g^+$), we find that both the 1B_1 and 1B_2 surfaces may be involved. In these cases, we propose the following.

(i) Flux prepared on the 1B_1 or 1B_2 surface is moved by attractive forces (weak in the former case, and strong in the latter) from $R = 4$ Å inward (toward $R = 2.0$ – 2.2 Å, $r = 0.77$ Å for the 1B_1 surface and to $R = 2.25$ Å, $r = 0.79$ Å for the 1B_2 surface) to where the repulsive 3A_1 PES crosses from below.

(ii) The crossing point ($R = 2.0$ – 2.2 Å, $r = 0.8$ Å) for the 1B_1 surface may lie above the Cd(1P) + H₂ asymptote (it is difficult for us to determine this precisely due to the restricted treatment of the electron correlation and neglect of spin-orbit coupling), so this point may not easily be accessed (without tunneling) by flux on the 1B_1 PES.

(iii) However, the 3A_1 – 1B_2 crossing ($R = 2.25$ Å, $r = 0.79$ Å with an energy ca. 3 kcal/mol below the Cd(1P) + H₂ asymptote) is accessible, and flux can hop onto the 3A_1 surface and dissociate to yield Cd(3P_J) + H₂.

(iv) Flux that remains on the 1B_2 surface past this intersection with the 3A_1 PES has another chance to produce Cd(3P_J) + H₂ because the 1B_2 surface is intersected by the

3B_1 PES in the chemically reactive region (near $R = 1.85$ Å, $r = 1.02$ Å) where close approach of the 1A_1 and 1B_2 PESs occurs.

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