A Refined H$_3$ Potential Energy Surface

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In evaluating some low temperature ($T < 1000$ K) thermal rate coefficients for inelastic rotational excitation of H$_2$ by H atoms, Sun and Dalgarno have found a marked sensitivity to the potential energy surface adopted for the calculations. We have investigated the origin of the discrepancies between previous H$_3$ potential energy surfaces and have developed a refined surface which addresses these concerns. New quasiclassical trajectory calculations of cross sections for low energy rotational excitation are reported. The refined surface is based on 8701 *ab initio* energies, most newly computed for this purpose. It has the same functional form as our earlier (BKMP) surface, but since the fit of the parameters is more fully constrained than for any previous surface it is a more accurate representation. The refined surface matches the *ab initio* energies with an overall rms error of 0.27 mE_h (i.e., 0.17 kcal/mole) and a maximum absolute deviation of 6.2 mE_h (for a very compact high energy equilateral triangle conformation). For "noncompact" conformations (no interatomic distance smaller than 1.15 bohr), the rms error is 0.18 mE_h and the maximum absolute deviation is 1.7 mE_h. The refined surface is compared critically to four previous surfaces, including the DMBE surface of Varandas *et al.*, in several respects: Legendre expansion coefficients; the interaction region for low energy rotational excitation; near the collinear saddle point; near conical intersections of the ground and first excited state surfaces; the van der Waals well; and compact geometries. We have also compared new first excited state *ab initio* energies for 1809 conformations with corresponding predictions from the DMBE surface.

I. INTRODUCTION

In this paper we present a refined H$_3$ potential energy surface which addresses an important issue raised recently by Sun and Dalgarno [1]. They carried out quantum mechanical calculations of the rotational excitation (ground vibrational state) of H$_2$ by H atoms, using the "DMBE" H$_3$ potential energy surface of Varandas *et al.* [2]. Quite surprisingly, the low temperature ($T < 1000$ K) thermal rate coefficients for the transitions $0 \to 2$ [i.e., H + H$_2(0,0) \to$ H + H$_2(0,2)$] and $1 \to 3$ were significantly higher than those found earlier by Green and Truhlar [3] and Mandy and Martin [4] based on the "LSTH" surface developed by Truhlar and Horowitz [5]. Sun and Dalgarno concluded "that the large discrepancies arise primarily from

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the different potential energy surfaces employed in the two calculations." As supporting evidence they cited unpublished quasiclassical trajectory (QCT) calculations of state-to-state cross sections by S. Lepp and by two of us (Keogh and Martin; see Sec. V) on the two potential energy surfaces, which reveal the systematic differences underlying those in the rate coefficients.

Because of the fundamental significance of this H + H_2 system in theoretical chemistry, and because of important applications to the rotational excitation and hence cooling efficiency of hydrogen-rich gas (e.g., in astrophysics of the interstellar medium), it is important to understand in what ways the potential energy surfaces are different and which is to be preferred for these rotational excitation (and other) calculations. Sun and Dalgarno comment: "It is claimed by Varandas *et al.* that their potential is superior to the LSTH potential at intermediate and long-range separations of H and H_2", from which they concluded that the DMBE surface should be preferable. However, what is meant by "intermediate and long-range" is critical to this qualitative assessment. The range of separation R_{H-H_2} (distance of H atom from center of H_2) most influential for this low energy rotational excitation is $3 - 5\, a_0$ (in this paper distances are in bohrs). One could call this range intermediate, it being well inside the longer-range van der Waals region and the very long range asymptotic region. Varandas *et al.* do argue that the DMBE surface might be better than the LSTH surface at these intermediate distances (about $3.5\, a_0$ is cited). However, neither the LSTH surface nor the DMBE surface is well constrained there, this being an interpolation region between *ab initio* data at smaller separations and experimentally-constrained descriptions of the van der Waals region.

Our interest in resolving this question stems in part from our development of the "BKMP" H_3 potential energy surface [6]. This extended the LSTH surface in several ways based on a more extensive grid of *ab initio* interaction energies. Although the BKMP surface incorporates new data extending to $R_{H-H_2} = 4\, a_0$, it too is least well constrained in the critical range of R_{H-H_2}. The BKMP surface tends to be closer to the LSTH than to the DMBE surface (see Ref. 6); comparative calculations of QCT rate coefficients at 1000 K by Lepp, Buch, and Dalgarno [7] bear this out.

Comparison of the Legendre expansion coefficients of the potential energy surfaces (see Ref. 6 and Sec. IV B) shows that the DMBE, LSTH, and BKMP surfaces have important differences in this critical unconstrained range of R_{H-H_2}, which of course explains the different derived cross sections and rate coefficients. More recent *ab initio* calculations by Partridge *et al.* [8] including $R_{H-H_2} > 4\, a_0$ begin to address this problem, giving coefficients closer to those from the LSTH and BKMP surfaces than to those from the DMBE surface. Comparison of the first expansion coefficient (spherically averaged interaction energy, V_0) shows the DMBE surface to be too repulsive. More important for the current issue of rotational excitation is the second coefficient (first anisotropic term, V_2 [9,10]). For the DMBE surface uniquely this coefficient displays a suspicious dip at $R_{H-H_2} \sim 4\, a_0$ for an H_2 molecule size near $1.4\, a_0$ (see Ref. 6, Table VIII; Partridge *et al.* [8] Table IV and Fig. 6); as discussed below (Sec. IV B), this feature is unphysical.

Initially we carried out new *ab initio* calculations for 540 conformations on a preliminary grid spanning this unconstrained region of R_{H-H_2}, confirming that there were indeed problems with the DMBE surface in the interpolation region. We found further support for this view in the *ab initio* calculations in Partridge *et al.* [8]. Therefore, as the basis for a new analytic surface that would provide a correct description of this region, we have performed further *ab initio* calculations for an extensive grid of 6548 H_3 conformations, also including good coverage in the $3 - 5.5\, a_0$ region (Sec. II A).

There are other issues to be addressed. As mentioned, such "intermediate" separations are significantly less than the extent of the van der Waals well ($R_{H-H_2} \gtrsim 6\, a_0$). Partridge *et al.* [8] have pointed out that the H_3 surfaces could also be improved in the region of the van der Waals well ($\sim 6 - 10\, a_0$; see e.g., their Figure 2). Their results are incorporated in our new analytic surface as well (see Sec. II C and Sec. IV C).

Mielke *et al.* [11] have presented low temperature ($T < 1000$ K) thermal quantal rate coefficients for the reaction D + $H_2 \rightarrow$ H + HD. For the LSTH and DMBE surfaces there is good agreement with the

experimental data. While the BKMP results agree near 1000 K, they are systematically larger for lower temperatures, differing from the values for the other surfaces by a factor 2 − 2.3 at 167 K. This behavior at low temperature is presumably related in part to the value of the classical barrier height for this reaction, which was constrained to be lower in the BKMP surface (9.54 kcal/mol) than in the LSTH and DMBE surfaces (9.80 and 9.65 kcal/mol). As described in Sec. II D, our new surface is updated to match the best current estimate of the classical barrier height, 9.61 kcal/mol. As pointed out by Garrett *et al.* [12], these rate coefficients also depend on the width of the barrier and more global characteristics of the surface which should be well constrained by our large grid of *ab initio* calculations (Secs. II A and D).

The lowest two potential energy surfaces for H_3 exhibit a seam of conical intersections for D_{3h} conformations [13] (i.e., equilateral triangles), at least for "normal" sizes (see Sec. IV G). Mielke *et al.* comment that the DMBE surface "is the only surface with the correct behavior in the region of the conical intersection" (see also Ref. 8). Certainly it represents the only attempt at an analytic continuation onto the upper surface and calculation of the associated nonadiabatic coupling. It is also the case that in developing the BKMP surface [6] we did not incorporate the *ab initio* data reported by Varandas *et al.* for 18 nonsymmetric conformations in the vicinity of D_{3h} symmetry, since there was insufficient information to bring the energies to a common consistent basis. However, this does not necessarily mean that the BKMP (or LSTH) surface has an incorrect behavior; it has simply not been constrained or modeled so explicitly. We have in fact compared the shape of the BKMP and DMBE surfaces on cuts based on the s and q symmetry coordinates of Varandas *et al.*, and the differences are not substantial (Sec. IV E). This is because conformations which apply appropriate constraints do arise in our regular grid of conformations. Nevertheless, to be assured of a good treatment of this part of the surface we have made further *ab initio* calculations (Sec. II E) to constrain the fit.

Johnson [14] pointed out that the London equation, which is used as a component of the three surfaces, can lead to unphysical discontinuities in the derivative of the potential for certain high energy isosceles triangle geometries. This is not addressed in the LSTH or DMBE surfaces, which thus exhibit this problem, but is corrected here as in the BKMP surface. A "compact" geometry is defined to be one in which any of the three distances between the nuclei is less than the distance r_R below which the Johnson correction begins to modify the H_2 triplet curve: as with the BKMP surface, $r_R = 1.15\,a_0$.

Aguado and Paniagua [15] have proposed a new way of fitting *ab initio* data for triatomic molecules. Using a FORTRAN code supplied to us by Aguado [16] we provide an assessment of their 71-parameter surface. While this "AP" surface has a low rms deviation with respect to the *ab initio* BKMP data to which it was fitted, it turns out to have several deficiencies in its shape (Sec. IV).

The surface fitting here follows that in Ref. 6 for the BKMP surface and is summarized in Sec. III; the new surface is dubbed "BKMP2". The weighted rms deviation with respect to 8701 *ab initio* energies used is only $0.27\,mE_h$. In Sec. IV we discuss the various desirable properties which the BKMP2 surface embodies. Sec. IV B focusses on how the new surface differs in shape relative to the previous surfaces, particularly in the critical intermediate region $R_{H\text{-}H_2} \sim 3 − 5\,a_0$; the deviations are largest for the DMBE surface. New QCT calculations of cross sections for rotational excitation are given in Sec. V. These show the systematic differences arising from the various surfaces; again, the DMBE values are the most discrepant. QCT cross sections should be adequate for computing thermal rate coefficients down to about 600 K [4, 17], but for lower temperatures such as treated by Sun and Dalgarno [1] new quantum mechanical calculations will be required.

II. ENERGIES CONSTRAINING THE SURFACE

The conformations and energies which we used to fit our new analytic BKMP2 H_3 surface are described in this section. There are a total of 7172 different conformations for which *ab initio* data are available. Some

of these have energies computed using two or more basis sets, for a total of 8701 *ab initio* energies; in addition 125 *ab initio* data from Ref. 8 for van der Waals conformations were also used. Tables of these data are available in electronic form from the authors [18]. For some very small and large separations, this set of energies is supplemented to ensure good behavior in those parts of the surface.

Unless otherwise specified, atomic units are used in this paper, i.e., distances are in bohrs (a_0) and energies are in hartrees (E_h), millihartrees (mE_h), or microhartrees (μE_h). Recall that $1\,a_0 = 0.529177$ Å, while $1\,mE_h = 0.0272114\,\text{eV} = 0.62751\,\text{kcal/mole}$. Unless otherwise specified, energies are expressed relative to the energy of isolated hydrogen atoms, i.e., zero energy corresponds to separated H + H + H. Relative to this, an isolated H atom plus H_2 at the equilibrium separation of $1.401\,a_0$ (*not* a ground state H_2 molecule) has an energy of $-0.174496\,E_h$ (or $-109.498\,\text{kcal/mole}$), according to the accurate analytic H_2 curve presented by Schwenke [19] which we used throughout this paper to obtain accurate H_2 energies.

A. Conformations for new *ab initio* computations

Figure 1 in the BKMP paper (Ref. 6) illustrates the coordinates used to specify our grids of H_3 conformations, which can be described by the shortest interatomic distance r_1, the next-shortest distance r_2, and the (exterior) angle between them θ_{12} (which we shall simply denote θ in this paper; $\theta = 0°$ is collinear). Alternatively, one may specify the shortest distance r_1, the distance $R_{\text{H-H}_2}$ of the third atom with respect to the *midpoint* of r_1, and the angle χ between r_1 and $R_{\text{H-H}_2}$ ($\chi = 0°$ is collinear).

In our preliminary exploration of the interpolation region, we adopted the $(9s3p1d)/[4s3p1d]$ Gaussian basis set used previously [20, 6, 21, 22]. The grid was specified as follows: r_1 was chosen from {0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.1, 2.35, 2.6 a_0}, $R_{\text{H-H}_2}$ was chosen from {3.0, 3.5, 4.0, 4.5, 5.0, 5.5 a_0}, and χ ran from $0°$ to $90°$ inclusive in increments of $10°$ (note that this grid included a few points with $r_2 < r_1$). This preliminary grid comprised 540 conformations.

For our more comprehensive grid, our $(9s3p2d)/[4s3p2d]$ basis set [22] was used; the only difference from the $[4s3p1d]$ basis set was that the single d function (with exponent $1.0\,a_0^{-2}$) is replaced by two d functions, with exponents 1.76 and $0.62\,a_0^{-2}$ (optimized for H_2 at equilibrium separation). The grid was specified as follows: r_1 and r_2 were chosen from {0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.15, 2.3, 2.45, 2.6, 2.8, 3.0, 3.2, 3.4, 3.7, 4.0, 4.3, 4.6, 5.0, 5.5 a_0}, such that $r_1 \leq r_2 \leq r_3$; θ ran from $0°$ to $90°$ inclusive in increments of $10°$, and continued from $\theta = 90°$ through $\chi = 90°$ inclusive in one, two, or three equally-spaced increments that did not exceed $10°$ (note that for $r_1 \leq r_2$, $\chi = 90°$ corresponds to $\theta \leq 120°$). This grid contained 5083 *new* conformations, as well as 32 conformations from the preliminary grid, and a number of conformations from the old grid of Ref. 6.

To investigate the bending behavior away from the collinear saddle point (Sec. II D) we computed energies for 50 new conformations with $r_1 = r_2 = 1.757 a_0$ for a range of θ. In the vicinity of D_{3h} symmetry (Sec. II E) we computed energies for the 18 conformations of Varandas *et al.* [2] and added 138 similar *new* nearly-equilateral conformations. We also computed energies for 77 *new* conformations in between grid-points for $0.7\,a_0 \leq r_1 \leq 1.0\,a_0$ (where there were few conformations from older grids) to test (and constrain) the inter-grid-point behavior of the analytic surfaces (Sec. IV G).

Our comprehensive grid comprised 6548 conformations. Compared to the grid used for the BKMP surface, it offers the following improvements: new coverage in the "interpolation region" from 4 to 5.5 a_0; better coverage at all r_1 and r_2, particularly in the ranges 0.6 to 1 a_0 and 3 to 4 a_0; and better angular coverage in θ for all separations.

For comparative tests, we computed new *ab initio* energies for *all* the conformations from the old grid and those available to us from other authors. This comprised our 403 old conformations [6], 137 conformations from Liu [23], 156 conformations from Siegbahn and Liu [20] (six of which duplicate conformations from Liu), 31 conformations from Blomberg and Liu [24] (six of which duplicate conformations from Liu), and

50 conformations from Bauschlicher *et al.* [25] (one of which duplicates a conformation from our old grid [6]). Besides the 57 conformations from Partridge *et al.* [8] which were contained in one of our above grids, we also computed energies for the remaining 330 of their conformations that had $R_{\text{H-H}_2} \leq 5.5$ (their grid had comprised 503 conformations in all). An update for some of these H_3 energies was supplied by Partridge [26].

For further checking, we also carried out computations using the $[4s3p1d]$ basis for all the conformations of other authors described above, plus the added nearly-equilateral conformations. Along with our energies from Ref. 6, this yielded 1233 conformations with $[4s3p1d]$ energies, all of which could be compared with $[4s3p2d]$ energies from the comprehensive grid, and 710 of which could be compared to energies obtained by other authors.

B. *Ab initio* computations and analysis

The *ab initio* computations and analysis of errors follow the methods described fully in our previous papers [6, 21, 22]. Here we give a brief summary and update. Energies were obtained using a workstation version of Buenker's MRD-CI program [27]. For most conformations, molecular orbitals were obtained from an open shell SCF calculation; where the open shell SCF was slow to converge, mixed shell SCF (1 closed and 1 open shell) or closed shell SCF was automatically used instead to obtain the molecular orbitals. In almost all cases a second CI energy was also obtained using molecular orbitals from one of the other two SCF types.

A fairly extensive set of reference configurations was used: the minimum size of C_R^2, the sum of reference configuration C^2 values, was 0.976, and the *average* size was 0.986. A configuration selection threshold of $T = 0.4\,\mu E_h$ was used: the extrapolation to zero threshold comprised a shift of order $0.4\,mE_h$, with an estimated rms uncertainty of $0.02\,mE_h$ (this is expected to be "random" error, in that systematic effects are probably on a smaller scale than the grid spacing of the conformations). As a check, some conformations were also computed with $T = 2\,\mu E_h$ (yielding a shift of order $1\,mE_h$, with an estimated rms extrapolation uncertainty of $0.07\,mE_h$).

A very small semi-empirical Davidson-type correction to full CI was made, similar to that described in Ref. 21, of $\Delta E_{\text{full-CI}} = \lambda_{\text{DC:H3}} \Delta E_{\text{DC}} = \lambda_{\text{DC:H3}}(1 - C_R^2)\Delta E_{sd}/C_R^2$. The values of $\lambda_{\text{DC:H3}}$ were chosen to minimize the difference between results using different SCF-types for molecular orbitals; this resulted in $\lambda_{\text{DC:H3}}^{(\text{open})} = 0.01$, $\lambda_{\text{DC:H3}}^{(\text{mixed})} = 0.19$, and $\lambda_{\text{DC:H3}}^{(\text{closed})} = 0.22$ (cf. old $\lambda_{\text{DC:H3}}$ values of 0.16, 0.3, and 0.5, respectively, used in Refs. 6 and 21). This correction is negligible for open shell cases, and of order $0.1\,mE_h$ for mixed and closed shell cases, but the estimated uncertainty for all three SCF-types is of order $0.1\,mE_h$ (largely "systematic" error, with a somewhat smaller "random" component). Comparing CI energies obtained using molecular orbitals from different SCF calculations yielded: $\text{rms}_{\text{open-mixed}} = 0.059\,\text{mE}_h$ (3891 conformations), $\text{rms}_{\text{open-closed}} = 0.065\,\text{mE}_h$ (1301 conformations), and $\text{rms}_{\text{mixed-closed}} = 0.056\,\text{mE}_h$ (658 conformations). These differences are somewhat less than the estimated errors; note, however, that with the old $\lambda_{\text{DC:H3}}$ values these rms differences would have been 0.064, 0.148, and $0.151\,mE_h$, respectively, with the closed shell cases having a systematic shift averaging $0.14\,mE_h$ with respect to the open and mixed shell cases.

An independent estimate of the combined uncertainty from the extrapolation plus full CI correction may be obtained by comparing our $[4s3p1d]$ basis results with the 186 energies computed previously [20, 23, 24] with this basis set; the rms difference between the earlier energies and ours is $0.099\,mE_h$, or $0.078\,mE_h$ if one leaves out the three energies in Ref. 20 that lie $0.2\,mE_h$ above even our *truncated-CI* energies. This suggests that an estimated uncertainty of $0.1\,mE_h$ in the extrapolation plus full CI correction is reasonable.

Because of the finite basis set, there is a small basis correction which averaged about $1.1\,mE_h$ for the $[4s3p2d]$ basis set, and $1.8\,mE_h$ for the less complete $[4s3p1d]$ basis set; in both cases, the basis correction is larger for compact conformations and smaller for noncompact conformations. As before [6, 21, 22], this correction was based on the London formula. Note that the BKMP version (see Ref. 6) of the triplet

curve (without the Johnson correction) was used in the computation of the London H_3 basis correction. Our London-based correction has been tested further by Partridge *et al.* [8] who carried out calculations with much larger basis sets, mostly $(11s5p3d1f)/[6s5p3d1f]$, and concluded that "the results confirm the accuracy of the BKMP potential and their scheme for correcting the H_3 calculations using the error in the H_2 potential." Partridge [26] has supplied us with the appropriate errors in the H_2 potential for the larger basis sets.

Partridge *et al.* [8] suggested that the correction scheme might be refined further by introducing a slight dependence on θ or χ. Note, for example, that the London basis correction is independent of angle for $r_1 = r_2$, where one might expect variation by a factor of order 1.5 from consideration of the change in the geometry. To gauge how to implement this we have computed (Sec. II A), with both of our (smaller) basis sets, energies for the 387 of their conformations with $R_{\text{H-H}_2} \leq 5.5\,a_0$. For the angular dependence it appears, empirically, that a relatively simple function $f_{\text{basis}}(\chi, r_1, r_2)$ multiplying the original correction $\Delta E_{\text{basis}}^{\text{London}}$ of Ref. [21] should suffice, namely

$$f_{\text{basis}}(\chi, r_1, r_2) = 1 - f_1\, e^{-(r_2/r_1 - 1)^2} \cos^2 \chi + f_2\, e^{-f_3(r_2/r_1 - 1)^2 - f_4(r_1 - 1.4)} \sin^2 \chi \,, \qquad (1)$$

where $r_1 \leq r_2 \leq r_3$, f_1 and f_2 are parameters that differ for different basis sets and f_3 and f_4 are simple constants. The exponential factors are largely to make $f_{\text{basis}}(\chi, r_1, r_2)$ go to unity for conformations approaching $H_2 + H$, where the London basis correction approaches the correct value (by construction). The f_1 term is used to make a small shift to obtain a collinear saddle point energy that agrees with the Monte Carlo classical barrier height of 9.613 ± 0.006 kcal/mole obtained by Diedrich [28] (see also Ref. 29 and Sec. II D). To do this for Partridge's $[6s5p3d1f]$ basis, Liu's Slater basis, our $[4s3p2d]$ basis, and our $[4s3p1d]$ basis (the latter is the same as that of Refs. 20 and 24) one needs $f_1 = 0.182, 0.09053, 0.073$, and 0.06747, respectively. Note that the resulting shift for linear symmetric geometries is $\lesssim 0.1\, mE_h$, smaller than our earlier estimate [6] of $0.15\, mE_h$ for the uncertainty in the basis correction for such geometries; this estimate still seems reasonable.

The f_2 term is used to provide additional flexibility in the angular dependence. Differencing energies obtained with $[4s3p1d]$ and $[4s3p2d]$ basis sets shows no evidence of a systematic trend as a function of angle; however, differencing energies obtained with $[4s3p2d]$ and $[6s5p3d1f]$ basis sets *does* show a significant angular effect (note that the size of the H_2 basis correction differs by a factor of ~ 1.6 for both of these pairs of bases). Since this angular effect depends on something other than the pure size of the basis set or basis correction, the most conservative assumption is that Partridge's $[6s5p3d1f]$ basis set requires no additional angular dependence beyond that introduced by setting $f_1 = 0.182$, i.e., that $f_2 = 0$ for the $[6s5p3d1f]$ basis set. In this case, one obtains $f_2 = 0.6$ and 0.35, respectively, for our $[4s3p2d]$ and $[4s3p1d]$ basis sets; values of $f_3 = 1.5$ and $f_4 = 0.8$ give the best agreement. The resulting shift reduces the rms difference between Partridge's $[6s5p3d1f]$ energies and our $[4s3p2d]$ energies from 0.37 to $0.14\, mE_h$ (387 conformations). The shift is comparable to our earlier estimate of $0.3\, mE_h$ for the uncertainty in the basis correction for nonlinear geometries; furthermore, an angular contribution to the basis correction error amounting to even half the H_2 basis correction would still be only $0.4\, mE_h$, and so our earlier estimate again seems reasonable.

For conformations that are very close to being equilateral triangles (i.e., near D_{3h} symmetry), a systematic difference remains between Partridge's energies and ours; it can be of order $0.5\, mE_h$ for $r_1 = r_2 \lesssim 2\, a_0$ and $\chi = 90°$, but vanishes for $\theta \lesssim 90°$ or $r_2/r_1 \gtrsim 1.3$. This remaining difference cannot be characterized well enough to attempt a correction; but it points out the difficulty of estimating the (systematic) error in the basis correction, which for equilateral triangles might be of order $1\, mE_h$.

In summary, our *ab initio* energies E_{final} have a total "random" error of about $0.1\, mE_h$ (from MRD-CI errors), plus a systematic error of about $0.4\, mE_h$ (mostly from basis correction errors; smaller for linear

conformations, larger for equilateral triangles). The errors are somewhat larger for the high-energy compact conformations, and smaller for conformations tending towards $H_2 + H$.

C. The van der Waals region

The Partridge *et al.* [8] *ab initio* computations also improve the van der Waals region, filling in a region at large $R_{\text{H-H}_2}$ from 5.5 to $8 - 10\,a_0$ that had been left out in previous theoretical studies. Although this region is not at the root of the discrepancies in inelastic rotational excitation, it seemed worthwhile to refine the BKMP surface here as well. In the fitting we have made use of the *ab initio* energy values for all 503 conformations of Ref. 8, of which 116 have $6\,a_0 \leq R_{\text{H-H}_2} \leq 10\,a_0$.

Partridge *et al.* [8] showed that their *ab initio* data in the well region and beyond were accurately fit by a modified Tang–Toennies (MTT) surface [this gives energies relative to $H_2(r_1) + H$ for fixed r_1]. We adopted this MTT representation; the four parameters describing the dependence on $R_{\text{H-H}_2}$ and χ were found as a function of r_1 by nonlinear least squares fitting to their *ab initio* energies for $R_{\text{H-H}_2} \geq 5.5\,a_0$, the accuracy of these fits being of order $1\,\mu E_h$. Following their recommendation, the well was deepened slightly for each r_1 (from 66 to $75\,\mu E_h$ at $r_1 = 1.449\,a_0$) by adjusting the two parameters describing the spherically symmetric radial dependence. By construction, for $R_{\text{H-H}_2} > 10\,a_0$ this representation extrapolates to the asymptotic long range dispersion interaction energies [8].

This MTT form is not incorporated explicitly in our surface. Instead, energies were computed from it (plus Schwenke's [19] H_2 potential) to be used as constraints in fitting the new surface (the BKMP surface used energies from the Gengenbach *et al.* formula [30]). The grid was as follows: r_1 was chosen from {0.7, 0.8, 1.0, 1.2, 1.449, 1.7, 2.0, 2.45, 3.0, 3.4, $4.0\,a_0$}, and $R_{\text{H-H}_2}$ was chosen from {5.5, 5.75, 6.0, 6.25, 6.5, 6.75, 7.0, 7.25, 7.5, 7.75, 8.0, 8.5, 9.0, 10.0, 12.0, $15.0\,a_0$}, subject to the constraint that $r_2 \geq 4.5\,a_0$; the angle χ ran from $0°$ to $90°$ inclusive, generally in increments of $15°$ (for $r_1 = 0.7$, 1.7, 2.45, and $3.4\,a_0$, the χ increment was $30°$, and values of $R_{\text{H-H}_2} \geq 10.0\,a_0$ were omitted). This van der Waals grid comprised 968 conformations (80 of which coincide with conformations computed in Ref. 8).

During the fitting procedure described in Sec. III, deviations of the fit for these conformations were given high weights as follows. A set of basic weights for r_1 near equilibrium ($1.4\,a_0 \leq r_1 < 1.5\,a_0$) were assigned according to $R_{\text{H-H}_2}$: 10 for Partridge *et al.* conformations with $5.25\,a_0 < R_{\text{H-H}_2} \leq 5.6\,a_0$; 20 for MMT-derived points with $5.5\,a_0 \leq R_{\text{H-H}_2} < 5.6\,a_0$; 40 for $5.6\,a_0 \leq R_{\text{H-H}_2} < 5.9\,a_0$; 80 for $5.9\,a_0 \leq R_{\text{H-H}_2} < 8.9\,a_0$; and 360 for the "distant" conformations with $8.9\,a_0 \leq R_{\text{H-H}_2}$. These were then scaled down on the basis of r_1: by 0.5 for $0.9\,a_0 \leq r_1 < 1.4\,a_0$ and $1.5\,a_0 \leq r_1 < 2.1\,a_0$; by 0.25 for $2.1\,a_0 \leq r_1 < 3.2\,a_0$; and by 0.1 for $r_1 < 0.9\,a_0$ and $r_1 \geq 3.2\,a_0$. Some of the conformations generated by the MTT representation had r_1 rather far from equilibrium and so the weight was reduced from the above by a factor 2 for $1.499 \leq r_2/r_1 < 1.7499$ and by 4 for $r_2/r_1 < 1.499$. But in no case was the weight allowed to sink below unity.

D. Collinear saddle point/classical barrier height

On the collinear cut the adopted H_3 saddle point occurs at $r_1 = r_2 = r_s = 1.7570\,a_0$ (linear symmetric conformation) and its energy is $E_{saddle} = -0.1591760\,E_h$ (relative to $H + H + H$). Using the Schwenke equilibrium H_2 energy, this matches the latest Monte Carlo result (Ref. 28) on the classical barrier height, namely, 9.613 ± 0.006 kcal/mol. This saddle point is incorporated in our surface implicitly through specification of the effective H_2 triplet curve.

Various *ab initio* estimates of the barrier height have been discussed recently by Partridge *et al.* [8]; these depend on the basis correction. Smooth agreement of our surface with the Monte Carlo result at the saddle point is achieved by fitting *ab initio* data which have been corrected using a slight reduction of the London basis correction for geometries that are not too far from linear symmetric (see discussion above in Sec. II B).

In order to tie down the asymmetric stretch and bending quadratic force constants at the collinear saddle point, two conformations with high weight (1000) were added as for the BKMP surface. We also computed energies for 50 new conformations with $r_1 = r_2 = 1.757a_0$ for a range of θ to study the angular dependence away from this saddle point (e.g., the quartic bending force constant; Sec. IV D).

E. Near D_{3h} symmetry

Varandas *et al.* report *ab initio* data for 18 nonsymmetric conformations explicitly in the vicinity of D_{3h} symmetry. These are specified using s and q symmetry coordinates which are useful in connection with analytic continuation to the upper electronic surface; q is the rms r_i, while s is a measure of the deviation from D_{3h} symmetry ($s = 1$ corresponds to the collinear limit). There is a third angular coordinate giving the direction of the deviation; only two choices of this angle were used in their conformations corresponding to two cases: (a) scalene with $r_1 = q(1 - s\cos 30°)^{1/2}$, $r_2 = q$, and $r_3 = q(1 + s\cos 30°)^{1/2}$ (an atom is moved in a direction which is initially, for small s, parallel to the opposite side, r_2, of the triangle) and (b) isosceles with $r_1 = r_2 = q(1 - s/2)^{1/2}$ and $r_3 = q(1 + s)^{1/2}$ (an atom is moved in a direction perpendicular to and toward the opposite side, r_3, of the triangle). As part of the comprehensive grid (Sec. II A) we computed in the same manner energies for 156 conformations with $q = \{0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.3, 2.5, 2.8, 3.2, 3.7a_0\}$, $s = \{0.05, 0.1, 0.2, 0.3\}$. These include the 18 conformations of Varandas *et al.*, which have $q = 1.6$, 2.0, and 2.5 a_0. We also added a third case: (c) isosceles with $r_1 = q(1 - s)^{1/2}$ and $r_2 = r_3 = q(1 + s/2)^{1/2}$ which is equivalent (geometrically – the smallest separation is denoted r_1) to using negative values of s in case (b); case (a) is of course unaffected by changing the sign of s.

The behavior of the surface in the vicinity of D_{3h} symmetry is also constrained through many other conformations in the grids described in Sec. II A (conformations with $\chi = 90°$ including equilateral triangles, and others with $\theta = 90°$ through $\chi = 90°$ in the appropriate range of r_2/r_1).

F. Extremely compact conformations

To ensure that *extrapolation* of our surface to very short distances is well behaved we added 175 *extremely* compact conformations (distances down to 0.32 a_0) with energies estimated from the (non-Johnson-corrected) London equation. The conformations were generated for $0° \leq \chi \leq 90°$, at $15°$ intervals, for $r_1 = 0.5$, 0.4, and 0.32 a_0 with r_2 taking the values $\{0.32, 0.4\ 0.5, 0.6, 0.8, 1.0, 1.2, 1.4, 1.75\ a_0\}$ (subject to the constraint $r_2 \geq r_1$), and also for $r_1 = r_2 = 0.6\ a_0$ (for overlapping angles, energies for the latter agreed with the *ab initio* energies within $\lesssim 10\%$).

III. THE FITTING PROCEDURE

Since the BKMP surface [6] is already a flexible and accurate representation we used this parametrized functional form as the basis for the fit to the new set of H_3 energies. Despite the vastly increased number of constraining energies and conformation coverage, the same number of parameters was used; the parameters were simply reoptimized. For the main steps in the fitting procedure we followed closely the same strategy as for the BKMP surface; we used the same optimization methods and we adopted the same criteria to assess the surface fit.

The overall rms error of the BKMP2 surface (as well as those of the LSTH, DMBE, and BKMP surfaces) with respect to the *ab initio* data is given in Table I, along with the rms errors for various subsets of the *ab initio* energies, corresponding to various subsections of the surface. The fitted surface has continuous first and second derivatives everywhere (the cusp at conical intersections with the first excited state surface is only rounded off by a negligible, and removable, amount, namely 1 μE_h; see Sec. IV E). Other specific qualities of the BKMP2 surface are discussed in Sec. IV.

A. The Triplet Equation and the Johnson Correction

In the first step we optimized the effective H_2 triplet curve. The form used for $r \geq r_R$ (no Johnson correction) was actually fitted to 71 *ab initio* energies for linear symmetric conformations, including 8 for compact ones. As in all subsequent stages of the fit, deviations for energies greater than $0.2\,E_h$ were given a reduced weight of $0.2/E$. In addition, energies for 14 "distant" linear asymmetric van der Waals conformations ($R_{H\text{-}H_2} = 12\,a_0$ and $15\,a_0$) for 7 values of r_1 ($0.8\,a_0$ to $4.0\,a_0$) were included in order to force the triplet curve to decay such that the London energy is not too large in the region of the van der Waals well. As described in Sec. II C, the deviations for these energies were assigned high weights producing a fit better than $2\,\mu E_h$. Of the triplet parameters only γ_3, γ_4, γ_5, and γ_6 have to be optimized. As in the BKMP and LSTH surfaces, γ_1 and γ_2 are obtained self-consistently by ensuring that the surface reproduce the collinear saddle point accurately. All linear symmetric geometries were fit very well with this modified form of the triplet potential (see Table I). The correct symmetric force constant $k_s = 0.1068\,E_h\,a_0^{-2}$ is obtained (for a summary of force constants see Table VI in Ref. 6).

The Johnson correction coefficients γ_7, γ_8, and γ_9 were calculated analytically such that the triplet curve is continuous (with continuous first and second derivatives) at the point $r_R = 1.15\,a_0$ where the Johnson correction takes over.

B. The Asymmetric Correction

The second step was optimization of the asymmetric correction V_{asym}. The optimization of the seven parameters was carried out using 850 energies for linear conformations, including all 674 *ab initio* values for noncompact geometries. A further 67 *ab initio* energies for barely compact ($1.01\,a_0 \leq r_1 < r_R$) linear conformations were included so that the V_{asym} correction term would have the correct shape through r_R. The deviations for the 70 Partridge *et al.* energies among these were assigned higher weights (the same scheme also applies in later parts of the fit). For their 22 conformations in the van der Waals range ($R_{H\text{-}H_2} > 5.25\,a_0$) the weights are as described in Sec. II C. For smaller $R_{H\text{-}H_2}$ the scheme is essentially the same except that the basic $R_{H\text{-}H_2}$-based weights at the outset are ramped down to 7 for $4.75\,a_0 < R_{H\text{-}H_2} \leq 5.25\,a_0$; 4 for $4.25\,a_0 < R_{H\text{-}H_2} \leq 4.75\,a_0$; 2 for $3.75\,a_0 < R_{H\text{-}H_2} \leq 4.25\,a_0$. No weight in this range is less than 1.0. There is no special weight for $R_{H\text{-}H_2} \leq 3.75\,a_0$. In addition, 109 energies for noncompact linear van der Waals conformations from the MTT representation were used to ensure a reasonable van der Waals well in the linear direction for a range of r_1. The correct asymmetric force constant $k_a = -0.0579\,E_h\,a_0^{-2}$ is obtained due to the constraining conformation with weight 1000.

C. Two Compact Corrections

The third step was the optimization of the terms C_{all} and C_{asym}, correction terms which have an effect only on compact geometries (which are affected by the Johnson correction). The parameters in both terms (16 in total) were optimized simultaneously using 356 energies for compact linear conformations. This included 281 *ab initio* energies from our grid and 5 from Partridge *et al.*. Using the MTT representation, 45 van der Waals conformations ensure that the van der Waals well has a stable behavior for these nonequilibrium H_2 separations. Some 25 extremely compact conformations (Sec. II F) all had $E > 0.2\,E_h$ and weights $0.007(0.2/E)$, sufficient to ensure that modest extrapolation of our surface remains well behaved (Sec. IV G).

D. The Bending Terms

The fourth step was the optimization of terms to reduce the residuals for bent geometries, $V_{bend}^{(A)}$ and $V_{bend}^{(B)}$. All of the bending terms (including the compact ones) contain an exponential decay factor to ensure the correct asymptotic behavior; the same values as for the BKMP surface were used.

The parameters in $V_{bend}^{(A)}$ and $V_{bend}^{(B)}$ (32 in total) were optimized simultaneously using 6402 energies for bent conformations, including all 5453 *ab initio* energies for noncompact bent geometries (91 of the latter

are for van der Waals conformations from Ref. 8) A further 366 *ab initio* energies for barely compact bent conformations were included to obtain the correct shape through r_R. The 390 Partridge *et al.* energies among the above were assigned higher weights by the above scheme where appropriate. Using energies from the MTT representation, 583 noncompact bent van der Waals conformations were used to ensure a reasonable van der Waals well for bent geometries for a range of r_1. The correct bending force constant $k_b = 0.0210\,E_h\,a_0^{-2}$ is obtained due to the constraining conformation with weight 1000.

E. The Compact Bending Terms

The final step was to optimize the term C_{bend}, a correction term for compact bent geometries. The 60 coefficients were optimized using 2731 energies for compact bent conformations, including 2350 *ab initio* values (12 of these are for van der Waals conformations from Ref. 8) plus 231 bent compact van der Waals conformations using the MTT representation. As mentioned in Sec. II F, we also added 150 *extremely* compact bent conformations of low weight.

IV. DISCUSSION

A FORTRAN computer subprogram which evaluates this surface and its derivatives with respect to the three internuclear distances is available from the authors [18]; it is in a form that readily replaces the routines supplied to evaluate the LSTH [31] or BKMP [6] surface. The BKMP2 surface (of the BKMP form) is simple enough that it can be used for quantum mechanical and QCT scattering calculations. Quantum mechanical calculations using the BKMP surface have been carried out by Chang and Brown [32] and QCT calculations have been reported by Keogh *et al.* [33] and Lepp, Buch, and Dalgarno [7]. As a benchmark for quasiclassical trajectory studies, a BKMP2 (or BKMP) evaluation of the interaction potential and derivatives takes typically 140 μs on a DEC 3000 workstation (Alpha 150 MHz processor).

A. Low rms for *ab initio* energies and other global comparisons

Table I summarizes some comparisons of the various surfaces with the *ab initio* data.

The quality of the fit for the BKMP2 surface is very good. It fits the entire set of 8701 *ab initio* energies with an rms error of $0.27\,mE_h$ (the maximum deviation being $6.2\,mE_h$ for a very compact equilateral triangle with $r_1 = 0.7\,a_0$). For 6077 energies for noncompact conformations the rms error is $0.18\,mE_h$ (the maximum deviation being only $1.67\,mE_h$). These rms accuracies are comparable to the estimated "random" error of $0.1\,mE_h$ for our newly-computed *ab initio* energies and are actually slightly smaller than the estimated systematic errors in the *ab initio* energies ($0.4\,mE_h$ mostly from basis correction errors; Sec. II B).

At low energies the new BKMP2 surface is quite similar to the BKMP surface, but it is based on a grid with more extensive coverage and better resolution; for example, the rms difference between the BKMP2 and BKMP surfaces is $0.26\,mE_h$ for the noncompact conformations used for the *ab initio* calculations. At higher energies we have used many more *ab initio* data than were used in the BKMP fit, and so the new BKMP2 representation should be even more accurate there; note for example the much lower rms error for compact bent conformations.

The BKMP surface fits their version (slightly different basis correction) of the energies for their 766 independent conformations with an rms error of $0.25\,mE_h$ (the maximum deviation being $1.93\,mE_h$). The BKMP fit to the new energies for this "BKMP subset" is slightly worse, having an rms error of $0.36\,mE_h$. For the same energies, the BKMP2 fit has an rms error of $0.30\,mE_h$, slightly larger that the original $0.25\,mE_h$ value in Ref. 6 because now the same number of parameters is being used to fit a much more extensive set of energies. The BKMP surface fits our entire new set of energies with an rms error of $3.76\,mE_h$ (maximum deviation $262\,mE_h$ for an equilateral triangle with $r_1 = 0.6\,a_0$); comparison with the new value $0.27\,mE_h$ for BKMP2 illustrates the overall benefit of the reoptimization of the parameters.

Not shown in Table I are values for the AP surface; for non-compact conformations, it has an rms error of $3.4\, mE_h$ (with maximum deviation $17\, mE_h$), several times worse than any of the other surfaces. The overall rms error is $6.2\, mE_h$, with a maximum deviation of $46\, mE_h$ for an equilateral triangle with $r_1 = 0.6\, a_0$. As shown below, this surface also lacks many of the desirable features seen in the other surfaces.

B. Legendre coefficients

We have computed Legendre coefficients V_{2n} for the various surfaces for several values of r_1. These are compared in Figure 1 for the case $r_1 = 1.449\, a_0$ which is representative. Also plotted are the coefficients computed by Partridge *et al.* directly from their *ab initio* data, which have less extensive angular coverage than our comprehensive grid.

Our fit surface generates a spherical average V_0 (Fig. 1a) which is in good agreement with the other surfaces, the results of Partridge et al. and the best available experimental data discussed therein. The DMBE surface stands out somewhat as being more repulsive in the intermediate (or interpolation) range near $R_{\text{H-H}_2} = 4\, a_0$. The AP surface is the most discrepant (as for all V_{2n}), having poor extrapolation characteristics beyond where it is constrained by the BKMP data.

For inelastic rotational excitation we are interested in the radial dependence of the first anisotropic coefficient V_2 (Fig. 1b) for the intermediate range $3\, a_0 < R_{\text{H-H}_2} < 5.5\, a_0$. Our *ab initio* energies (see Sec. II A) provide better radial coverage than was available to the LSTH, DMBE, and even BKMP fits for this range and also superior angular coverage; thus the BKMP2 surface should be the most accurate in the interaction region. Note how the added coverage has changed the BKMP2 coefficient slightly relative to the BKMP coefficient; both are quite close to that from the LSTH surface. The DMBE surface produces a dip near $R_{\text{H-H}_2} = 4\, a_0$; this incorrect behavior accounts for the discrepant cross sections and rate coefficients (see also Sec. V). The AP surface has the most discrepant representation of the minimum and again extrapolates poorly. There are slight discrepancies of the BKMP2 result compared to Partridge *et al.*, but only at the $0.2\, mE_h$ level comparable to the random and systematic errors of the fit (see also Fig. 2).

Calculations of V_4, V_6, and V_8 (the first two shown in Figs. 1c and 1d respectively) show the continued good behavior of the coefficients from the BKMP2 fit. Other surfaces are somewhat less precise, as for the lower order coefficients.

A complementary way of examining how surfaces differ in their basic asymmetry is to plot cuts of the interaction potential for various fixed r_1 and $R_{\text{H-H}_2}$ as a function of χ. We have done this for many combinations; three representative ones are shown in Figure 2a–c for $r_1 = 1.449\, a_0$ and $R_{\text{H-H}_2} = 3$, 4, and $5\, a_0$. The relative bulge in the DMBE potential near $R_{\text{H-H}_2} = 4\, a_0$ at $\chi = 90\deg$ (up by $\sim 1.5\, mE_h$) is reflected in the anomalous dip in V_2.

These plots also show the *ab initio* energies used in the BKMP2 fit, including the Partridge *et al.* data. The BKMP2 surface appears to have low level angular structure (which changes with $R_{\text{H-H}_2}$) somewhat larger than warranted by just these data. However, recall that the surface is required to fit simultaneously energies on a grid comprising many more separations and angles. Therefore, some of the structure just arises from the decaying tails of functions required for more compact geometries. These oscillations are constrained by data at many more angles than shown in Figure 2, but only at the level of the rms of the fit, $\sim 0.1\, mE_h$ in this region of conformation space ($R_{\text{H-H}_2} \simeq 4\, a_0$). Given this and the accuracy of the *ab initio* data, we tend to discount the details of the high order coefficients at levels below $0.1\, mE_h$. Even the derived BKMP2 V_2 coefficient is slightly different than directly computed by Partridge *et al.* from *ab initio* data for $R_{\text{H-H}_2} > 4\, a_0$ (Fig. 1b), which suggests caution in applications at very low energy (or temperature).

C. The van der Waals well

The BKMP2 functional form for the surface has sufficient flexibility that it is not necessary to join it explicitly to another description (like MTT) for larger separations ($5.5\, a_0 < R_{\text{H-H}_2} < 10\, a_0$). The BKMP

surface fit the constraining data from Gengenbach et $al.$ [30] well, but these data have been superseded by the present MTT description which also has a much more securely-based dependence on r_1. The BKMP2 fits resulted in a van der Waals well that agrees fairly closely in position, depth, and shape with the data underlying the MTT description. Figure 3 illustrates the angular dependence of the well for $r_1 = 1.449\,a_0$ for different analytic H_3 surfaces. Also shown are the ab $initio$ data from Partridge et $al.$ and the constraining data generated from our MTT formula. The BKMP2 well behaves smoothly as a function of angle and also of the size of the H_2 molecule: we have examined the well for r_1 as small $0.6\,a_0$. The BKMP2 Legendre coefficients in the van der Waals region are correspondingly well behaved. For $r_1 = 1.449\,a_0$ the minimum of V_0 is $75\,\mu E_h$ occurring at $R_{\text{H-H}_2} = 6.58\,a_0$, close to the values recommended by Partridge et $al.$

The BKMP2 analytic form of the surface (like the BKMP and the LSTH surfaces) approaches the London surface exponentially at very large distances ($R_{\text{H-H}_2} > 10\,a_0$), unlike the DMBE surface which closely mimics the asymptotic form of the interaction; however, at these distances the interaction energy is only a few μE_h. The BKMP2 surface also dissociates to give Schwenke's accurate H_2 potential curve.

D. Saddle point properties

The collinear saddle point occurs at $r_1 = 1.757\,a_0$. The classical barrier height of our fitted surface is $15.32\,mE_h$ (i.e., 9.613 kcal/mole) in good agreement with the best recent determinations (Sec. II C). As mentioned in Sec. III, all three $quadratic$ force constants for our surface agree closely with Liu and Siegbahn's values and those for the LSTH, DMBE, and BKMP surfaces.

The reactivity of the system can also depend on the angular dependence away from this collinear saddle point. In their discussion of transition state properties and the possible relevance of the zero-point corrected barrier height (which correction depends on various force constants), Garrett et $al.$ [12] used an expansion for fixed nearest-neighbor distances:

$$V(\theta) = V_{saddle} + \frac{1}{2}F\theta^2 + \frac{1}{24}A\theta^4 + \ldots \qquad (2)$$

Adopting the framework of this expansion, Figure 4 shows $2[V(\theta) - V_{saddle}]/\theta^2$ versus θ^2 for $r_1 = r_2 = 1.757\,a_0$ (1.755 a_0 for DMBE). The curves therefore have intercept F, which is the quadratic bending force constant (as expressed in mE_h radian^{-2}). For the BKMP2 surface, as for the LSTH and BKMP surfaces, this is determined by a highly weighted constraining energy (solid square); the DMBE and AP surfaces also have similar bending force constants.

The slope of the curves in Figure 4 is approximately $A/12$, where A is the quartic bending force constant (mE_h radian^{-4}) as defined by Garrett et $al.$ Clearly there is curvature to each surface, pointing to the need for additional higher-order expansion coefficients beyond $\theta \simeq 0.1$ radian. Because of this curvature, evaluation of the quartic bending constant could depend on the range of θ^2 over which the (average) slope was measured. To be precise in calculating A as one of many expansion coefficients, one can either restrict the range to very small θ^2 and fit coefficients only up to A or fit a suitably higher-order polynomial over a more extended range. The values of A calculated consistently in this way for the BKMP2, BKMP, LSTH, and DMBE surfaces are 75.6, 78.9, 16.0, and 28.7 mE_h radian^{-4}, respectively. We cannot see how to reconcile these with the values reported for the latter two surfaces in Table I of Garrett et $al.$

Away from the collinear geometry, the surfaces have slightly different curvature as illustrated in Figure 4. The detailed shape of the surface here is determined by the functional form of the analytic representation, whose parameters are in turn determined by energies for a wide variety of conformations not chosen specifically to isolate this region near the collinear saddle point. The BKMP2 (and BKMP) surface has the most angular flexibility and so shows some higher-order structure. Note that the BKMP2 surface is very close to the BKMP surface, despite many more constraining energies. In particular, we did use the ab

initio data shown in Figure 4 for the new fit, but with obviously little effect since the BKMP fit was already so good, well within the errors (largely systematic) expected for bent geometries (Sec. II B). The deviation is $0.3\,mE_h$ at $\theta \sim 1$ radian and actually decreases at smaller θ (the deviations appear amplified in Figure 4 because of division by $\theta^2/2$).

In particular the differences in the quartic bending force constant are not being determined by localized *ab initio* data. Nor is it possible to use data of this level of accuracy to choose between the surfaces in this region. This is probably not a serious issue. While a difference in the zero-point corrected barrier height, which is the transition state theory activation energy at 0 K in the absence of tunneling, could influence the relative exchange reaction rate coefficients according to the usual Boltzmann factor, Garrett *et al.* [12] also emphasize the importance of tunneling contributions for low temperature thermal rate coefficients. Low energy tunneling probabilities are sensitive to the global characteristics of the surface, not just the barrier height, including fairly large-distance interactions ($R_{\text{H-H}_2} \sim 4\,a_0$). From our ongoing discussion of both the increased constraints and the overall accuracy of the BKMP2 surface, we suggest that it should produce the most reliable results.

E. Near D_{3h} symmetry

As discussed in Sec. II E, we have computed many additional points to explore the nature of the D_{3h}-symmetry conical intersection (which for "normal" sizes occurs between the ground and first excited state surfaces; see Sec. IV F). The minimum energy conical intersection is also the saddle point for $\theta = 120°$. On the BKMP2 surface it occurs at $r_1 = 1.9711\,a_0$ with energy $74.33\,mE_h$, or $62.85\,$kcal/mole relative to the equilibrium H_2 energy; the corresponding values for the DMBE surface are $1.973\,a_0$ and $63.36\,$kcal/mole.

Figure 5 shows two cuts of the surfaces near this intersection, specified using the Varandas *et al.* symmetry coordinates q and s (see Sec. II E). Both have $q = 2.0\,a_0$ rather than $1.9711\,a_0$ in order to display the *ab initio* data. The two cuts are for cases (a) and (b)+(c) of Sec. II E (scalene and isosceles, respectively). We have examined such plots for many different values of q (not shown). Except for the AP surface, which does not even have a cusp in its formulation and which for other values of q often does not pass through the *ab initio* energy for the equilateral triangle geometry, the surfaces all fit the *ab initio* energies fairly well. This is true even of the LSTH and BKMP surfaces, whose shapes were not constrained by the data shown in Figure 5 (except for the equilateral triangles); this agreement is possible because of a sufficiently flexible and apt functional form (not the case for the AP surface) and because conformations which apply appropriate constraints do arise in a regular grid of conformations even if not explicitly generated in symmetry coordinates.

Quantitatively the BKMP2 surface, with constraints including these new *ab initio* data, provides the most accurate fit. For noncompact geometries (i.e., with shortest distance $r_1 \geq 1.15\,a_0$) near the conical intersection ($|s| \leq 0.3$) the rms errors for 325 *ab initio* energies are $0.29\,mE_h$ for BKMP2, $0.62\,mE_h$ for BKMP, $0.82\,mE_h$ for DMBE, $1.2\,mE_h$ for LSTH, and $9.4\,mE_h$ for AP. For 54 compact *ab initio* energies for $q \geq 0.85\,a_0$ (see Sec. IV G for the reason for this cut) and $|s| \leq 0.3$, the rms errors are $0.91\,mE_h$ for BKMP2, $2.4\,mE_h$ for BKMP, $5.9\,mE_h$ for DMBE, $7.9\,mE_h$ for LSTH, and $20\,mE_h$ for AP. For the very high-energy points with $q < 0.85\,a_0$, only the BKMP2 surface remains accurate (Sec. IV G.)

F. The DMBE first excited state surface

Porter, Stevens, and Karplus [13] showed that for D_{3h} symmetry (equilateral triangles) the doubly-degenerate E' state of H_3 corresponds to a conical intersection between two surfaces. For H_3 systems of "normal" size the two states intersecting at D_{3h} symmetry (of symmetry A_1 and B_2 for isosceles triangles and otherwise A' for scalene triangles) define the ground and the first excited potential energy surfaces.

The DMBE surface is intended to be a consistent analytic representation of the two lowest potential energy surfaces for H_3, explicitly making an analytic continuation based on this conical intersection for D_{3h}

geometries. The comparison in Figure 5 (for $q = 2\,a_0$) with the *ab initio* energies for the first excited state that we have computed shows that the DMBE representation is indeed quite good near D_{3h} symmetry. However, away from the conical intersection it becomes less accurate, as might be expected because the first excited state surface was not constrained by these (or any) *ab initio* energies. As q decreases, the predicted surface is not as asymmetric in s (for isosceles triangles) as the *ab initio* data indicate.

Having computed *ab initio* excited state energies for 1809 of our conformations (these excited state energies are also available from the authors [18]), we can examine more globally the accuracy of the DMBE excited surface prediction; the overall rms error for these energies is $19\,mE_h$. Near the conical intersection, for $|s| \le 0.3$ where the surface is best, there is an rms error of $1.1\,mE_h$ for 71 noncompact points and $1.9\,mE_h$ for 20 compact points with $q \ge 0.85\,a_0$. With no restriction on s the overall rms error is $7.9\,mE_h$ for all 1246 noncompact points and $30\,mE_h$ for 531 compact points with $q \ge 0.85\,a_0$.

G. Compact conformations

Except for our studies, the high energy interaction region has received little attention. For compact conformations ($r_1 < 1.15\,a_0$), the BKMP2 surface should be fairly accurate up to at least the energy of our highest *ab initio* points, of order $1\,E_h$ above the energy of $H + H + H$. The grid coverage (Sec. II A) is more extensive than for the BKMP surface. Energies up to $200\,mE_h$ above the energy of $H + H + H$ are given full weight in the fit. Our weighting scheme gives lower weight to the deviations for conformations with very high *ab initio* energies, but only by a factor of six at the very most, thus ensuring that the absolute error at high energy is acceptable. Energies above $\sim 1\,E_h$ require extrapolation, and, of course, any fitted surface is best used for interpolation rather than extrapolation; however, we did ensure (Sec. II F) that our H_3 surface does not differ too greatly from the non-Johnson-corrected London equation, even when extrapolated in to very short distances where we did not have *ab initio* energies. For $r_1 = r_2$ the surface is monotonically increasing for all θ up to energies $\sim 3\,E_h$, down to distances slightly shorter than $0.35\,a_0$. Below this, for sufficiently bent geometries, the analytic surface turns over and drops steeply.

Our multiple-root MRDCI calculations near and including D_{3h} symmetry show some interesting changes as the geometry becomes more compact. For $q = 0.9\,a_0$, the energy of the doubly-degenerate E' root is $341\,mE_h$ (all energies relative to $H + H + H$). The third root at D_{3h} symmetry is single, with state symmetry A_1'; away from D_{3h}, the symmetry becomes A_1 for isosceles triangles and otherwise A' for scalene triangles. The energy of the A_1' root is $347\,mE_h$. In Varandas symmetry coordinates (s and their angle 3θ) the lowest three surfaces defined by these states are all fairly convex ("bowl"-shaped) for such compact geometries. As q decreases the upper surface associated with A_1' rises in energy, but the two formerly lower surfaces associated with E' rise even more quickly. The A_1' and E' roots at D_{3h} symmetry coincide at $q = 0.844\,a_0$ (energy $438\,mE_h$).

For even smaller q the A_1' root is lower than the E' root. For example, by $q = 0.8$ the energy of the A_1' root is $525\,mE_h$, clearly separated from the energy $530\,mE_h$ for the doubly-degenerate E' root. In fact the surface associated with A_1' remains the ground state for most s and 3θ, except for an isolated intersection with the first excited state for a squashed isosceles triangle geometry at $s \approx 0.225$ (i.e., $r_1 = r_2 \approx 0.754\,a_0$, $r_3 \approx 0.885\,a_0$), having an energy $\sim 549\,mE_h$ ($24\,mE_h$ up from the bottom of the "bowl"). The conical intersection between the surfaces through E' at D_{3h} symmetry is now between the first and second excited state surfaces.

We can conclude that the DMBE first excited state surface should not be extrapolated to such compact geometries. The first reason is technical, since the representation depends explicitly on the existence of the D_{3h}-symmetry conical intersection with the ground state surface; the second reason is practical, since the rms error with respect to our *ab initio* energies increases to $30\,mE_h$ for 531 compact points with $q > 0.85\,a_0$, and $50\,mE_h$ for 32 compact points with $q < 0.85\,a_0$. (For near-D_{3h} points with $|s| \le 0.3$, corresponding rms

errors are $1.9\,mE_h$ for 20 points with $q > 0.85\,a_0$, and $64\,mE_h$ for 15 points with $q < 0.85\,a_0$.) Of course, the DMBE ground state representation is also becoming less accurate when extrapolated to compact geometries, having an rms error of $5.6\,mE_h$ for 2118 compact points with $q > 0.85\,a_0$, and $40\,mE_h$ for 51 compact points with $q < 0.85\,a_0$.

Even our more accurate BKMP2 surface, which provides a much better fit to the small-q (compact) *ab initio* data, still exhibits a slight cusp at small-q D_{3h} geometries (rather than, for example, shifting it to the isosceles-triangle geometry where the actual intersection takes place when $q = 0.8\,a_0$). This cusp at D_{3h} symmetry arises from the London term which appears explicitly in the analytic surface, as it does for the LSTH and DMBE surfaces. For compact geometries this London term is increasingly overwhelmed by the three compact correction terms (see Ref. 6) in the BKMP2 surface, but a D_{3h} cusp, now relatively insignificant, must still appear. The size of both the spurious D_{3h} cusp and features like the missing isosceles-triangle cusp for small q are of order a few mE_h, like the error in the fit, so that while the BKMP2 surface is qualitatively incorrect, it is quantitatively still acceptably close.

V. CROSS SECTIONS FOR INELASTIC ROTATIONAL EXCITATION

In this section we report on quasiclassical trajectory calculations carried out to assess low energy state-to-state cross sections for rotational excitation (nonreactive rotationally inelastic scattering). The method of calculation generally follows that described by Mandy and Martin [4, 17] and references therein. We use a revised three-body trajectory code written to incorporate several different optional surfaces and to make use of a state-of-the-art Runge-Kutta variable step integrator [33]. Cross sections are computed for transitions in the downward direction [e.g., for $H + H_2(0,2) \rightarrow H + H_2(0,0)$]; the upward cross sections are determined from these using detailed balance [34]. With the QCT method, cross sections involving nonreactive excitation and exchange are distinguished. For the low energy transitions of interest here, only the former are important for parity-conserving transitions; these are the values reported.

Results for $H + H_2(0,0) \rightarrow H + H_2(0,2)$ are shown in Figure 6. This example is sufficient to contrast the results from different surfaces. Like the original DMBE quantum cross sections [1], the QCT cross sections for the DMBE surface remain substantial to a much lower relative kinetic energy than encountered (in QCT calculations) for other surfaces (LSTH, BKMP, and now BKMP2).

The relatively high DMBE cross sections at low energy are of course what cause the discrepantly high rotational rate coefficients at low temperature. The origin of the high cross sections is the abnormally large asymmetry in the DMBE surface through the intermediate (interpolation) region $R_{\text{H-}H_2} \sim 4\,a_0$ (Sec. IV B; Figs. 1 and 2). We have been able to verify this explicitly with our QCT calculations as follows. First the trajectories (specified by particular initial conditions) which produce the low energy excess cross section for the DMBE surface were isolated. Then the time development of these trajectories was examined in detail. The H atom approaches the H_2 molecule and is strongly deflected in an interaction region which is seen to be $R_{\text{H-}H_2} \simeq 4\,a_0$, leaving behind a rotating molecule. For the same initial conditions, but for the other potential energy surfaces, there is little deflection or induced rotation.

The smooth curves in Figure 6 are from nonlinear least squares fits of the data to the Le Roy class II excitation function [35]. The thermal rate coefficient for rotational excitation can be obtained in analytic form by the appropriate integral of this excitation function over the Maxwell-Boltzmann distribution [35]. For the LSTH surface we verified that these rate coefficients are within a few percent of those previously calculated [4, 17] for temperatures up to 2000 K (coefficients for higher temperatures would require an extrapolation of the new cross section data to higher energies than computed). Our rate coefficients also compare well with the QCT results by Lepp, Buch, and Dalgarno [7] for the BKMP, DMBE, and LSTH surfaces. For the DMBE surface the QCT rate coefficients also agree well with the quantum values above 600 K.

In summary, we have shown that these rate coefficients for nonreactive rotational excitation using the DMBE surface are indeed too large; quantitatively this is by a factor 10 at 1000 K and growing toward lower temperatures (more than a factor 30 discrepancy at 600 K). We have identified the reason for this excess. Since new BKMP2 surface is the most directly constrained by *ab initio* calculations for conformations in the relevant interaction region and shows less extraneous structure there (previous surfaces relied on interpolation), it should be the most reliable for these calculations. The rate coefficients for temperatures 600, 800, 1000, 1400, and 2000 K are 0.076, 0.32, 0.76, 2.0, and 4.0×10^{-11} cm^3 s^{-1}, respectively, up to 30% lower than the LSTH results at the lower temperatures.

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Table I. Accuracy of the analytic H_3 potential energy surfaces: rms errors and maximum deviations for various subsets of the 8701 *ab initio* data (125 energies for van der Waals conformations from Ref. 8 are not included). "Compact" geometries are those having at least one distance less than $1.15\,a_0$. Note that different authors used slightly different H_3 basis corrections to the *ab initio* energies.

Description of subset	N_{data}	BKMP2 surface		BKMP surface		LSTH surface		DMBE surface	
		rms (mE_h)	Max dev[a] (mE_h)	rms (mE_h)	Max dev[a] (mE_h)	rms (mE_h)	Max dev[a] (mE_h)	rms (mE_h)	Max dev[a] (mE_h)
All H_3 energies	8701	0.27	6.22	3.76	261.62	10.87	-169.35	4.34	-168.93
BKMP subset[b]	766	0.30	-2.23	0.36[c]	2.98	10.54	-98.98	3.53	-47.93
LSTH subset[b]	283	0.22	-1.78	0.24	0.97	0.60[d]	2.40	0.66	4.07
DMBE subset[b]	308	0.23	-1.78	0.23	0.97	0.60	2.40	0.66[e]	4.07
Compact	2624	0.42	6.22	6.82	261.62	19.76	-169.35	7.84	-168.93
Noncompact	6077	0.18	-1.67	0.28	2.58	0.71	4.06	0.69	2.72
Linear	1001	0.15	-1.26	0.22	-2.82	10.35	-169.35	1.58	9.01
Linear symmetric	74	0.18	-1.26	0.38	-2.82	20.33	-169.35	0.84	-3.98
Linear asymmetric	927	0.14	-0.54	0.20	-1.24	9.09	-116.38	1.63	9.01
Linear compact	286	0.19	-1.26	0.30	-2.82	19.36	-169.35	2.91	9.01
Linear noncompact	715	0.13	-0.37	0.18	-0.47	0.22	0.52	0.35	-1.55
Bent	7700	0.29	6.22	3.99	261.62	10.93	-165.88	4.58	-168.93
Bent compact	2338	0.44	6.22	7.23	261.62	19.81	-165.88	8.24	-168.93
Bent noncompact	5362	0.19	-1.67	0.29	2.58	0.76	4.06	0.72	2.72

[a] Largest deviation—analytic surface energy minus *ab initio* energy.

[b] The numbers of energies for these sets are slightly lower than those in the BKMP paper (Ref. 6), due to elimination of duplicate geometries here and, for the LSTH and DMBE subsets, to leaving out three Siegbahn and Liu energies (Refs. 20 and 23) that are inaccurate by about $0.5\,mE_h$. Differences in rms values with respect to the BKMP values for these subsets are due largely to the different basis correction (Sec. II B).

[c] Boothroyd *et al.* (Ref. 6) fitted the BKMP surface to *their* version of these data with an rms error of $0.25\,mE_h$, and a maximum deviation of $1.93\,mE_h$.

[d] Truhlar and Horowitz (Ref. 5) fitted the LSTH surface to *their* version of these data with an rms error of $0.27\,mE_h$, and a maximum deviation of $0.88\,mE_h$.

[e] Varandas *et al.* (Ref. 2) fitted the DMBE surface to *their* version of these data with an rms error of $0.39\,mE_h$.

FIGURE CAPTIONS

Fig. 1. Legendre expansion coefficients for the representative case $r_1 = 1.449\,a_0$ evaluated for various surfaces: BKMP2 (solid), BKMP (dashed), LSTH (dotted), DMBE (dashed–dotted), and AP (dashed–triple dotted). $R_{\text{H-H}_2}$ spans the intermediate range inside the van der Waals well. Open circles present values from Partridge $et\ al.$ [8] at certain $R_{\text{H-H}_2}$. Note the change in energy range for the successive panels. (a) Spherical average V_0. (b) First anisotropic term, V_2, important for rotational excitation. (c) V_4. (d) V_6.

Fig. 2. Cuts of the various potential energy surfaces as a function of χ for fixed $r_1 = 1.449\,a_0$ and selected $R_{\text{H-H}_2}$. Interaction energy plotted is relative to $R_{\text{H-H}_2} = \infty$ for this r_1 (cf. Fig. 1a). Line types as in Fig. 1. $Ab\ initio$ data are from our calculations (squares) and from Partridge $et\ al.$ (open circles). Note the change in energy range for the successive panels. (a) $R_{\text{H-H}_2} = 3\,a_0$. (b) $R_{\text{H-H}_2} = 4\,a_0$. (c) $R_{\text{H-H}_2} = 5\,a_0$.

Fig. 3. Profile of the van der Waals well as a function of $R_{\text{H-H}_2}$ for fixed $r_1 = 1.449\,a_0$ and selected values of χ. Interaction energy plotted is relative to $R_{\text{H-H}_2} = \infty$ for this r_1. Line types as in Fig. 1. $Ab\ initio$ data are from our calculations (squares) and from Partridge $et\ al.$ (open circles). Bullets are from our MTT representation. (a) $\chi = 0°$. (b) $\chi = 45°$. (c) $\chi = 90°$.

Fig. 4. Angular dependence of the potential with fixed $r_1 = r_2$ for bent geometries relative to the energy for the collinear saddle point. The representation plotted is motivated by the expansion in equation 2. Line types as in Fig. 1. The solid square on the BKMP2 (and BKMP and LSTH) curve is the high weight conformation used to constrain the quadratic force constant. $Ab\ initio$ results are shown as open squares.

Fig. 5. Cuts of the potential energy surfaces near the conical intersection at fixed $q = 2\,a_0$ as a function of symmetry coordinate s ($s = 0$ is the equilateral triangle, whereas $s = 1$ is the collinear limit). Line types as in Fig. 1. Note that all surfaces but AP have a cusp. $Ab\ initio$ results for the ground electronic state are shown as open squares. DMBE analytic extension onto the upper surface is shown for comparison with our $ab\ initio$ results for the first excited state (bullets). See Sec. II E for definition of cases (a) scalene and (b) isosceles (squashed for positive s).

Fig. 6. QCT cross sections for rotational excitation (without exchange) of H_2 by H atoms for the transition $(0,0) \rightarrow (0,2)$ as a function of relative translational energy. Symbols are circle, square, cross, and diamond for the BKMP2, BKMP, LSTH, and DMBE surfaces, respectively. Smooth curves (with line types as in Fig. 1) of the Le Roy class II form have been fitted to the data. The cross sections from the DMBE surface are too high at low energies.