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# Comparison of variational transition state theory and quantum sudden calculations of three-dimensional rate coefficients for the reactions $\text{D(H)} + \text{BrH} \rightarrow \text{DBr(HBr)} + \text{H}$

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We calculate rate coefficients for the three-dimensional reactions  $\text{H} + \text{BrH} \rightarrow \text{HBr} + \text{H}$  and  $\text{D} + \text{BrH} \rightarrow \text{DBr} + \text{H}$  using two different dynamical methods but with the same potential energy surface. One method is a three-dimensional quantum mechanical technique in which the energy sudden approximation is used for the entrance reaction channel and the centrifugal sudden approximation is applied to the exit reaction channel. The second method is improved canonical variational transition state theory with small-curvature-tunneling semiclassical adiabatic ground-state transmission coefficients. The potential energy surface is an empirically adjusted diatomics-in-molecules surface which has a very narrow barrier to reaction. The rate coefficients predicted by the two very different dynamical theories are in excellent agreement—they differ by less than 20% over the temperature range from 150 to 500 K.

## I. INTRODUCTION

The prediction of reliable rate coefficients for gas-phase bimolecular reactions is a major goal in theoretical chemistry.<sup>1</sup> Variational transition state theory (VTST) with semiclassical ground-state transmission coefficients<sup>2-5</sup> is a general method for computing reliable rate coefficients for a wide variety of bimolecular gas-phase reactions. This has been demonstrated by testing VTST rate coefficients against accurate quantum-mechanical ones for several collinear atom-diatom reactions.<sup>6-11</sup> Comparisons of this type for atom-diatom reactions in three dimensions are limited by the lack of accurate quantum mechanical results. In the only case for which such results are available,<sup>12</sup> the  $\text{H} + \text{H}_2$  reaction, the agreement between the quantum-mechanical and VTST results is quite good.<sup>13</sup> Direct comparisons of theoretical and experimental rate constants are complicated by uncertainties in the potential energy surfaces; however, in one reaction for which an accurate *ab initio* surface has been computed—the  $\text{H} + \text{H}_2$  system<sup>14</sup>—VTST calculations have been successfully compared to experimental results.<sup>13,15</sup> This same potential has also been used to predict rate coefficients for the  $\text{Mu} + \text{H}_2$  reaction which are in good agreement with experiment.<sup>11,16</sup>

A new three-dimensional quantum-dynamical approximation for atom-diatom exchange reactions of the light-heavy-light type was recently formulated<sup>17</sup> and applied to the exchange reactions of hydrogen halides with H and D atoms.<sup>18,19</sup> This technique, to be called the ESA-CSA approximation, involves applying the energy sudden approximation<sup>20</sup> (ESA) to the entrance channel Hamiltonian and the centrifugal sudden approximation<sup>21</sup> (CSA) to the exit channel Hamiltonian. The re-

sulting quantum-dynamical equations are then solved by using a close-coupled expansion of adiabatic vibration functions, multiplied by orbital spherical harmonics for the entrance channel and rotational spherical harmonics for the exit channel. The matching between entrance and exit channel wave functions is done analytically.

Rate coefficients have been calculated using this method for the  $\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$ ,  $\text{D} + \text{ClH} \rightarrow \text{DCl} + \text{H}$ ,  $\text{H} + \text{ClD} \rightarrow \text{HCl} + \text{D}$ , and  $\text{D} + \text{ClD} \rightarrow \text{DCl} + \text{D}$  reactions with a LEPS potential energy surface.<sup>19</sup> These agree well with quasiclassical trajectory results<sup>22</sup> and with those obtained using variational transition state theory<sup>23</sup> for a temperature of 295 K. This finding is not surprising as quantum-mechanical tunneling is not important for this surface at this temperature.<sup>18,23</sup> However, the LEPS surface is thought to be inadequate for these reactions,<sup>18,24</sup> and quantum calculations on the  $\text{D} + \text{ClH}$  reaction using a diatomics-in-molecules plus three-center terms (DIM-3C) potential energy surface<sup>25</sup> give much better agreement<sup>18</sup> with experimental differential cross sections<sup>26</sup> and with available rate coefficient data.<sup>27,28</sup> A DIM-3C surface has also been optimized<sup>19</sup> so that the approximate quantum-dynamical method gave good agreement with the experimental<sup>29</sup> room temperature rate coefficient for the  $\text{D} + \text{BrH} \rightarrow \text{DBr} + \text{H}$  reaction. The calculated<sup>19</sup> differential cross sections for this reaction once again agreed well with experiment.<sup>28</sup>

In the present paper we compare rate coefficients for the three-dimensional  $\text{H(D)} + \text{BrH} \rightarrow \text{HBr(DBr)} + \text{H}$  reactions calculated using both the ESA-CSA quantum-dynamical method and variational transition state theory. Both sets of calculations use the previously optimized DIM-3C surface.<sup>19</sup> This surface is collinearly dominated and has

a very narrow barrier to reaction; thus, quantum mechanical tunneling is very significant at room temperature. Also, the potential for bending away from collinear geometries is very steep. The skew angles for the H and D reactions with BrH are  $89.3^\circ$  and  $89.0^\circ$ , respectively, and are larger than for any of the systems for which VTST has been tested against accurate collinear results. The relative importance of tunneling effects offers a severe test of methods of treating quantum effects, especially for a threshold-dominated quantity like the thermal rate coefficient. Because the approximations inherent in each of these methods are so different, we view agreement between the two theories for three-dimensional rate coefficients as evidence of the validity of these approximations for the systems studied. As a separate check we also compare VTST rate coefficients to accurate quantum-mechanical ones for the collinear reactions  $H(D) + BrH \rightarrow HBr(DBr) + H$ .

Section II briefly summarizes the three-dimensional ESA-CSA and variational transition state theories and the essential details of the DIM-3C potential energy surface. Sections III and IV present practical details of the calculations and results, and Sec. V discusses and compares the calculated rate coefficients. The main conclusions are summarized in Sec. VI.

## II. THEORY

### A. ESA-CSA method

The details of the three-dimensional quantum approximation for light-heavy-light reactions are described in Ref. 17. Equations of motion are solved for a single reaction path. The reaction is divided up into an entrance ( $\alpha$ ) channel and an exit ( $\beta$ ) channel, and curvilinear reaction coordinates<sup>30,31</sup> are used. The ESA<sup>20</sup> is applied to the  $\alpha$  channel Hamiltonian, and this involves replacing the rotational angular momentum operator  $j_z^2$  by  $\hbar^2 j(j+1)$ , where  $j$  is the initial rotational quantum number. A close-coupling expansion of adiabatic vibrational basis functions multiplied by the orbital spherical harmonics  $\{Y_l^m(\theta, 0)\}$  is then made, where  $l$  is an orbital angular momentum quantum number and  $\theta$  is the atom-diatom orientation angle.

For the  $\beta$  channel, the CSA<sup>21</sup> is applied. This involves replacing the orbital angular momentum operator  $l_z^2$  by the eigenvalue  $\hbar^2 l'(l'+1)$ , where the primes represent the product state. The close-coupling expansion for the  $\beta$  channel is then constructed from adiabatic vibrational functions multiplied by the rotational spherical harmonics  $\{Y_{l'}^{M'}(\theta, 0)\}$ . The quantum number  $M$  is the total angular momentum projection along the body-fixed  $z$  axis,<sup>17</sup> which is identical for both entrance and exit channels.

The close-coupling equations are solved using the  $R$ -matrix propagation method.<sup>31</sup> After setting  $j = l'$ ,<sup>32</sup> the wave functions in the  $\alpha$  and  $\beta$  channels are matched analytically, and the  $S$  matrix elements  $S_{v'v}^{jM}$  are obtained. Here  $v$  is a vibrational quantum number, and  $v'$  denotes the final vibrational quantum number. Degeneracy-averaged integral reaction cross sections are then obtained from<sup>17</sup>

$$\sigma^R(v, j \rightarrow v', j') = \frac{\pi}{k_{vj}^2} \sum_M \sum_l |S_{v'v}^{jM}|^2, \quad (1)$$

where  $k_{vj}$  is the initial wave number. Rate coefficients can be obtained by averaging these cross sections over Maxwell-Boltzmann distributions of relative translational energy and, if necessary, over initial states.

The method was originally programmed<sup>17,18</sup> for general light-heavy-light reactions for the CDC 7600 computer. The calculations reported here were performed on the CRAY-1 computer and an enhancement in CPU time by a factor of 5 was achieved by using vector-optimized matrix multiplication, diagonalization, and inversion subroutines. This enabled calculations to be performed with larger basis sets so that computations could be carried out at higher energies than had been possible on the CDC 7600 computer.

### B. Accurate collinear quantum calculations

The one-dimensional quantum calculations were performed with our own version<sup>17</sup> of the  $R$ -matrix propagation method of Light and Walker.<sup>31</sup> For this calculation the locally adiabatic vibrational basis functions were determined numerically by the Cooley<sup>33</sup> method.

### C. Variational transition state theory

We performed calculations using conventional transition state theory (TST), improved canonical variational theory<sup>6</sup> with classical reaction-coordinate motion (ICVT), and improved canonical variational theory with small-curvature-tunneling semiclassical adiabatic ground-state transmission coefficients (ICVT/SCTSAG). The small-curvature-tunneling approximation semiclassical adiabatic ground-state (SCTSAG) transmission coefficient<sup>34,35</sup> represents a reliable calculational method for including quantum mechanical tunneling and nonclassical reflection into VTST. Calculations using both ICVT and ICVT/SCTSAG are reported to give a measure of the importance of reaction-coordinate quantal effects in the reaction studied.

The procedures for these calculations have been described in detail elsewhere.<sup>6,34,35</sup> Here we give a very brief review. All partition functions are treated quantum mechanically; the Morse approximation  $\tilde{I}^6$  is used for the stretching degree of freedom, and a harmonic-quartic approximation<sup>37</sup> is used for the bending degree of freedom. The adiabatic potential curve for the ground state  $V_a^G(s)$  is given by

$$V_a^G(s) = V_{MEP}(s) + \epsilon_{str,0}(s) + 2\epsilon_{b,0}(s), \quad (2)$$

where  $V_{MEP}(s)$  is the value of the potential energy surface along the minimum energy path, and  $\epsilon_{str,0}(s)$  and  $\epsilon_{b,0}(s)$  are the zero-point energy levels for the stretching and bending degrees of freedom at the position  $s$  along the minimum energy path. The probabilities for transmission through and over the one-dimensional ground-state adiabatic barrier are then obtained by a semiclassical calculation,<sup>38</sup> including the path-shortening effect of reaction-path curvature by the small-curvature approximation<sup>34</sup> at tunneling energies and neglecting the effect of reaction-path curvature at classically allowed energies.<sup>35</sup> The transmission probabilities are used to calculate the transmission coefficients.

TABLE I. Saddle point properties for HBrH and DBrH on the DIM potential energy surface.

	HBrH	DBrH
$R_{HBr}^{\ddagger} (a_0)^a$	2.99	2.99
$V^{\ddagger} (eV)^b$	0.238	0.238
$\hbar\omega_{st}^{\ddagger} (cm^{-1})^c$	1794	1524
$\hbar\omega_I^{\ddagger} (cm^{-1})^d$	1281i	1073i
$\hbar\omega_b^{\ddagger} (cm^{-1})^e$	359	312
$[V^{AG} - V_a^G(s = -\infty)] (eV)^f$	0.232	0.209
$\kappa(s=0) (a_0^{-1})^g$	0.66	0.88

<sup>a</sup>H to Br bond distance at the saddle point.

The saddle point is symmetrically located.

<sup>b</sup>Potential energy at the saddle point. The zero of energy is the bottom of the asymptotic reactant vibrational well.<sup>c</sup> $\hbar$  times the harmonic frequency for the stretching degree of freedom at the saddle point.<sup>d</sup> $\hbar$  times the imaginary harmonic frequency for the unbound normal mode at the saddle point.<sup>e</sup> $\hbar$  times the harmonic frequency of the bending degree of freedom at the saddle point.<sup>f</sup>Difference in energy between the ground-state adiabatic energy at the saddle point and the reactant zero-point energy, including anharmonicity in both places, for the three-dimensional reaction. The maximum in the adiabatic barrier occurs at the saddle point for both systems.<sup>g</sup>Curvature of the reaction path at the saddle point.

### D. Potential energy surface

The details of the DIM-3C potential energy surface for the HBrH system are presented in Ref. 19. The surface is denoted  $B$  in that paper, with the  $g$  factor, as defined by Last and Baer,<sup>25</sup> having the value of 0.22. Properties of the potential energy surface at the saddle point are summarized in Table I. The saddle point is symmetrically located at a collinear geometry with  $R_{HBr}$  equal to  $2.988a_0$ , and a height of 0.238 eV (the zero of energy is taken to be the bottom of the asymptotic reactant vibrational well). The maximum of the ground-state adiabatic barrier for the three-dimensional  $H + BrH$  reaction occurs at the saddle point and is 0.232 eV above the reactant zero point energy. The potential energy curve along the MEP  $V_{MEP}(s)$  and the ground-state adiabatic potential curve  $V_a^G(s)$  as defined in Eq. (2) are shown in Fig. 1 for the three-dimensional HBrH reaction. Also shown is  $V_a^G(s)$  for the collinear reaction. This is defined by the first two terms on the right-hand side of Eq. (2).

### III. CALCULATIONS

In the ESA we choose an average value for the initial rotational state  $j$ . For the present calculations we used  $j = 3$ , which is, on the average, the most likely initial  $j$  state for the temperature range considered. In the ESA-CSA calculations the accuracy of the computed  $S$  matrix elements depends on several convergence pa-

rameters, and the convergence tests used will be presented in a separate publication.<sup>39</sup> These tests suggest that the cross sections reported here should be converged to within 5%. The maximum number of basis functions required was 76; with 27, 19, 11, 10, 7, and 2 rotors in the vibrational states 0 to 5, respectively. The maximum value of  $M$  needed in Eq. (1) was 15, and a total of 104  $R$ -matrix sectors<sup>31</sup> were required in solving the close-coupling equations.

The previous calculations of cross sections for the  $D + HBr$  reaction were carried out for initial translational energies from threshold up to 0.295 eV.<sup>19</sup> To obtain converged rate coefficients at a temperature of 500 K, it was necessary to extend these cross section calculations to translational energies up to 0.585 eV. For the  $D + BrH$  reaction, a total of 16 different energies were used in calculating the cross sections, while for the  $H + BrH$  reaction, 23 energies were used. For the temperature range considered here, the  $HBr(v=1)$  reaction only contributes to the one-dimensional and three-dimensional rate coefficients in, at most, the third significant figure, and it was therefore only necessary to consider the  $HBr(v=0)$  reactions in calculating the rate coefficients. To average the cross sections over a thermal distribution of initial translational energies, we interpolated them by fitting their logarithms to a cubic spline function and the rate constants were obtained from a Simpson's rule integration.

The accurate quantum mechanical rate constants for the one-dimensional reactions are based on reaction probabilities calculated at 140 translational energies from threshold to 0.617 eV for each reaction. Table II gives convergence tests for the collinear rate coefficients for  $D + BrH$ . This table shows that the quantum collinear rate coefficients are converged to within 2% with respect to numerical parameters used in the quantum scattering calculation, and with respect to the num-

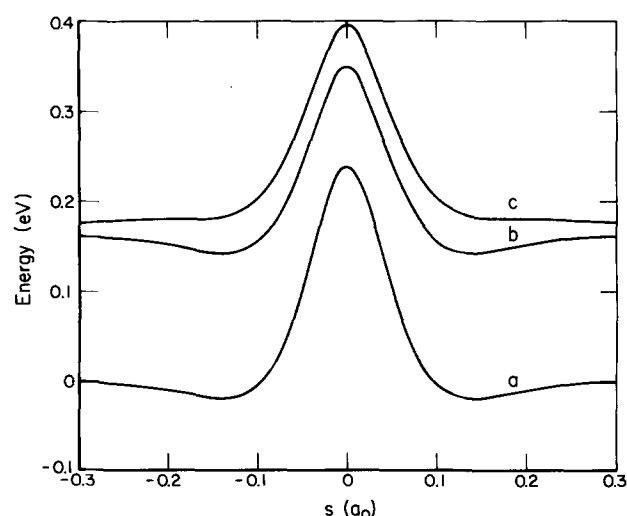


FIG. 1. Potential energy curve along the minimum-energy-path  $V_{MEP}(s)$  and ground-state adiabatic potential barriers  $V_a^G(s)$  as a function of reaction coordinate  $s$  for the  $H + BrH \rightarrow HBr + H$  reaction. Curve a is the potential along the MEP, curve b is the collinear adiabatic potential barrier, and curve c is the three-dimensional adiabatic potential barrier.

TABLE II. Convergence tests for the rate coefficients for the collinear reaction  $D + BrH \rightarrow DBr + H$ .<sup>a</sup>

T(K)	Rate coefficients (cm molecule <sup>-1</sup> s <sup>-1</sup> )		
	Calculation A	Calculation B	Calculation C
150	5.52(0) <sup>b</sup>	5.51(0)	5.42(0)
300	1.84(1)	1.85(1)	1.85(1)
500	1.68(3)	1.68(3)	1.68(3)

<sup>a</sup>In each case the translational energies are equally spaced from threshold to 0.617 eV; A: 80 energies, six adiabatic vibrations, 164 *R* matrix sectors. B: 140 energies, six adiabatic vibrations, 164 *R* matrix sectors. C: 140 energies, five adiabatic vibrations, 108 *R* matrix sectors.

<sup>b</sup>Numbers in parentheses are powers of ten.

ber of energies used in the Boltzmann average. Similar results were obtained for the  $H + BrH$  reaction. Estimates of the errors in the three-dimensional rate coefficients are much more difficult to obtain. Calculations of the collinear rate coefficients for  $D + BrH$  were repeated using the identical set of translational energies used in the three-dimensional reactions and these results were shown to be accurate to within 9%. Using this as a rough estimate, and combining it with the 5% convergence estimates for the ESA-CSA three-dimensional cross sections, we expect the three-dimensional rate coefficients to be accurate to within 14% for both systems.

## IV. RESULTS

The cross sections used to calculate the ESA-CSA rate coefficients for the three-dimensional reactions are pre-

TABLE III. Cross sections used in calculating the rate coefficients for the three-dimensional reaction  $H + BrH \rightarrow HBr + H$ .

Initial translational energy (eV)	Reaction cross section ( $\text{\AA}^2$ )
0.005	3.5(-7) <sup>a</sup>
0.025	2.8(-5)
0.045	6.3(-5)
0.065	2.2(-4)
0.085	7.9(-4)
0.105	2.5(-3)
0.125	6.1(-3)
0.145	1.4(-2)
0.165	3.3(-2)
0.185	7.1(-2)
0.205	1.3(-1)
0.225	2.1(-1)
0.245	3.0(-1)
0.325	8.5(-1)
0.335	9.2(-1)
0.355	1.06(0)
0.375	1.21(0)
0.425	1.63(0)
0.455	1.89(0)
0.475	2.08(0)
0.515	2.46(0)
0.545	2.73(0)
0.585	3.10(0)

<sup>a</sup>Numbers in parentheses are powers of ten.

TABLE IV. Cross sections used in calculating rate coefficients for the three-dimensional reaction  $D + BrH \rightarrow DBr + H$ .

Initial translational energy (eV)	Reaction cross section ( $\text{\AA}^2$ )
0.015	5.7(-6) <sup>a</sup>
0.045	4.0(-5)
0.075	3.1(-4)
0.125	5.8(-3)
0.175	6.1(-2)
0.245	3.8(-1)
0.295	7.4(-1)
0.325	9.6(-1)
0.345	1.04(0)
0.365	1.13(0)
0.395	1.52(0)
0.425	1.78(0)
0.475	2.28(0)
0.495	2.44(0)
0.545	2.76(0)
0.585	3.32(0)

<sup>a</sup>Numbers in parentheses are powers of ten.

sented in Tables III and IV. More detailed results, such as product-state distributions and differential cross sections, will be presented in a separate publication,<sup>39</sup> in which results for both  $HBr(v=0)$  and  $HBr(v=1)$  will be reported. The rate coefficients for the three-dimensional reactions are presented in Tables V and VI, and those for the collinear reactions are shown in Tables VII and VIII. Rate coefficients for the ESA-CSA calculations, for conventional TST (denoted by TST in the text and ‡ in the tables), and for the ICVT/SCTSAG calculations are compared over the temperature range 150 to 500 K for the three-dimensional reactions and 150 to 600 K for the collinear reactions. We found that improved canonical variational theory with unit transmission coefficient (ICVT) is identical to conventional TST for the cases studied in this paper.

## V. DISCUSSION

### A. Three-dimensional reactions

The ICVT/SCTSAG results are in excellent agreement with the ESA-CSA results for both reactions over the whole temperature range of 150 to 500 K. However, the conventional TST rate coefficients are in poor agree-

TABLE V. Rate coefficients (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for the three-dimensional reaction  $H + BrH \rightarrow HBr + H$ .

T (K)	‡, ICVT	ICVT/SCTSAG	ESA-CSA
150	3.8(-19) <sup>a</sup>	4.0(-16)	3.4(-16)
200	3.2(-17)	1.7(-15)	1.5(-15)
250	4.7(-16)	6.0(-15)	5.6(-15)
300	2.9(-15)	1.7(-14)	1.6(-14)
350	1.1(-14)	3.9(-14)	3.8(-14)
400	3.0(-14)	7.9(-14)	7.8(-14)
450	6.6(-14)	1.4(-13)	1.4(-13)
500	1.3(-13)	2.4(-13)	2.4(-13)

<sup>a</sup>Numbers in parentheses are powers of ten.

TABLE VI. Rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the three-dimensional reaction  $D+BrH \rightarrow DBr+H$ .

$T(K)$	$\ddagger$ , ICVT	ICVT/SCTSAG	ESA-CSA
150	1.2(-18) <sup>a</sup>	1.9(-16)	1.8(-16)
200	6.8(-17)	1.0(-15)	1.0(-15)
250	7.9(-16)	4.2(-15)	4.2(-15)
300	4.2(-15)	1.3(-14)	1.3(-14)
350	1.4(-14)	3.2(-14)	3.2(-14)
400	3.6(-14)	6.7(-14)	6.6(-14)
450	7.5(-14)	1.2(-13)	1.2(-13)
500	1.4(-13)	2.1(-13)	2.0(-13)

<sup>a</sup>Numbers in parenthesis are powers of ten.

ment. For the HBrH system, the ICVT/SCTSAG and quantum rates differ by 18% at 150 K, whereas for the DBrH system these two theories differ by only 6% at 150 K. Comparison of the TST and ICVT/SCTSAG results show that tunneling is very important in the HBrH system—the SCTSAG transmission coefficient  $\kappa^{\text{SCTSAG}}(T)$  is 1050, 53, 13, and 5.9 at 150, 200, 250, and 300 K, respectively. Tunneling is slightly less important for the DBrH system,  $\kappa^{\text{SCTSAG}}(T)$  is 160, 15, 5.3, and 3.1 at 150, 200, 250, and 300 K, respectively. Considering the importance of tunneling in these systems, the agreement between the ICVT/SCTSAG and ESA-CSA methods is very encouraging. Notice that conventional transition state theory (neglecting tunneling) predicts an inverse isotope effect (the  $D+BrH$  reaction has the larger rate coefficient) over the entire temperature range. However, in the ICVT/SCTSAG and ESA-CSA calculations, the  $H+BrH$  reaction has the larger rate coefficient because of the importance of tunneling as discussed above.

The calculated Arrhenius activation energies and pre-exponential factors for the temperature range 300 to 500 K are 0.175 eV and  $1.39 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the  $H+BrH$  reaction and 0.176 eV and  $1.18 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the  $D+BrH$  reaction. The activation energies for both reactions are much smaller than the adiabatic barriers (see Table I) because of the large amount of tunneling at low temperatures.

## B. Collinear reactions

Although the agreement of the ICVT/SCTSAG results with the accurate quantal results for the collinear re-

TABLE VII. Rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the collinear reaction  $H+BrH \rightarrow HBr+H$ .

$T(K)$	$\ddagger$ , ICVT	ICVT/SCTSAG	Accurate
150	2.5(-2) <sup>a</sup>	2.7(1)	1.2(1)
200	1.1(0)	6.5(1)	3.8(1)
250	1.0(1)	1.5(2)	1.1(2)
300	4.7(1)	3.0(2)	2.5(2)
350	1.4(2)	5.5(2)	5.0(2)
400	3.3(2)	9.2(2)	8.9(2)
450	6.4(2)	1.4(3)	1.4(3)
500	1.1(3)	2.1(3)	2.1(3)
600	2.5(3)	3.9(3)	4.0(3)

<sup>a</sup>Numbers in parentheses are powers of ten.TABLE VIII. Rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the collinear reaction  $D+BrH \rightarrow DBr+H$ .

$T(K)$	$\ddagger$ , ICVT	ICVT/SCTSAG	Accurate
150	6.4(-2) <sup>a</sup>	1.1(1)	5.5(0)
200	2.0(0)	3.4(1)	2.3(1)
250	1.6(1)	9.3(1)	7.3(1)
300	6.4(1)	2.2(2)	1.9(2)
350	1.8(2)	4.3(2)	3.8(2)
400	3.8(2)	7.5(2)	7.0(2)
450	7.0(2)	1.2(3)	1.1(3)
500	1.2(3)	1.8(3)	1.7(3)
600	2.5(3)	3.3(3)	3.2(3)

<sup>a</sup>Numbers in parentheses are powers of ten.

actions is not quite as good as in the three-dimensional systems, the results still agree within a factor of 1.2 for both reactions at 300–600 K and within a factor of 1.7 for both reactions at 200 K. Temperatures as low as 150 and 200 K present a real challenge for the approximate tunneling methods used and it is not surprising to find errors of a factor of 2 at these low temperatures. At higher temperatures the agreement in the collinear reactions is almost perfect. The fact that the ICVT/SCTSAG results overestimate the rate constants at the lower temperatures is not too surprising because our previous tests<sup>5,6</sup> have shown a tendency for the SCTSAG, as well as the related Marcus-Coltrin-path method,<sup>13,35,40</sup> to slightly overestimate the low-temperature tunneling contributions in large-skew-angle systems and slightly underestimate them in small-skew-angle systems. Thus, although ICVT/SCTSAG rate overestimates for  $D+BrH$  at 200 K are larger than we have seen in previous tests at this temperature, they are understandable in terms of the large skew angle and the very high tunneling contributions. It is also interesting that the SCTSAG transmission coefficients for the collinear system are very similar to those found in the three-dimensional reactions. For the collinear HBrH system,  $\kappa^{\text{SCTSAG}}(T)$  is 1080, 59, 15, and 6.4 at 150, 200, 250, and 300 K, respectively, whereas for the collinear DBrH system the corresponding numbers are 170, 16, 5.8, and 3.4. The close agreement between the transmission coefficients in the collinear and three-dimensional calculations can be understood in terms of the very similar shapes of the adiabatic barriers for the collinear and three-dimensional reactions (see Fig. 1).

The good agreement we obtain between variational transition state theory with small-curvature-tunneling transmission coefficients and the accurate quantum mechanical collinear rate coefficients for both reactions may be considered as strong evidence that the excellent agreement between the ICVT/SCTSAG and ESA-CSA results for the same reactions in three dimensions is not merely fortuitous.

## VI. CONCLUSIONS

Variational transition state theory, with a small-curvature-tunneling transmission coefficient, and an

approximate three-dimensional quantum mechanical method that uses the energy sudden approximation in the entrance channel and the centrifugal sudden approximation in the exit channel, both using the same DIM-3C potential energy surface, give three-dimensional rate coefficients for the  $H + BrH \rightarrow HBr + H$  and  $D + BrH \rightarrow DBr + H$  reactions which show excellent agreement for the temperature range of 150 to 500 K. These results are particularly remarkable because the two methods used are very different and because quantum mechanical tunneling effects are very important in these systems, increasing the rate constants by over three orders of magnitude for  $H + BrH$  at the lowest temperature. Our findings suggest that both these methods should be reliable for calculating rate coefficients for light-heavy-light reactions in three dimensions.

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