J. Phys. Chem. A **2009,** *113,* 1995–1998

Calculations of V−V Transfer Rates in H_2 and Comparison with Experiment[†]

J. D. Kelley*

The University of Missouri—St. Louis, St. Louis, Missouri 63121-4400

Received: September 19, 2008; Revised Manuscript Received: November 18, 2008

Recent observations on VV transfer in H_2 have shown interesting results. For nonresonant processes, comparison of the experimental rate constants with the results of previous semiclassical calculations, quantum oscillators/classical rotors coupled via classical collisions, showed the theoretical rate constants to be too slow by a factor of 3 or more. The semiclassical rate constant of the resonant VV process ($v = 1 + v = 0 \rightarrow v = 0 + v = 1$) was also found to be too slow, by more than an order of magnitude, compared with the experimental rate. Further, the semiclassical model predicted the value of $k(1,1\rightarrow0,2)$ to exceed that of $k(1,0\rightarrow0,1)$, but the experimental data shows it to be a factor of approximately 2 less. In this work we employ an accurate interaction potential for the H_2-H_2 system, and treat both rotation and vibration of the diatoms as coupled quantum-mechanical degrees of freedom. These new calculated results are in better overall agreement with the near-resonant experimental values, but the calculated rate constants are a factor of 2 to 3 larger than experiment for the nonresonant processes

Introduction

Recent results from Ahn, Adamovich and Lempert[1] (AAL) on vibration-to-vibration (VV) transfer in H_2 have shown interesting behavior. The measured rate constant for the nonresonant process,

$$H_2(v=1) + H_2(v=1) \rightarrow H_2(v=0) + H_2(v=2) \quad (1)$$

is consistent with the previously reported experimental values of Kreutz et al.[2] (K) and Saiki et al.[3] (S). However, for nonresonant processes, comparison of the experimental rates with the results of previous semiclassical calculations[4] showed the theoretical rate constants to be too slow, by a factor of approximately 3. The semiclassical rate constant for the resonant VV process,

$$H_2(v=1) + H_2(v=0) \rightarrow H_2(v=0) + H_2(v=1) \quad (2)$$

was also found to be too slow, by an order of magnitude or more, compared with the experimental rate constants obtained in AAL and S. The resonant rate constant value was also measured by Farrow and Chandler[5] (FC). Both the FC and S values are somewhat smaller than that given by AAL, but agree within their stated error bars. The previous semiclassical model[4,6] predicted the value of $k(1,1\rightarrow0,2)$ for process (1) to exceed that of $k(1,0\rightarrow0,1)$ for process (2), but the experimental data show it to be smaller. In this work we employ an accurate interaction potential for the H_2-H_2 system and recognize the effects of the large anharmonicity constant and rotational constant for H_2. These two parameter values set H_2 apart from other homonuclear diatomics, and necessitate a treatment in which both rotation and vibration are coupled and treated quantum-mechanically. The rotational states are not indicated in reactions (1) and (2), but they play a role in both the experiments and calculations, and are discussed below.

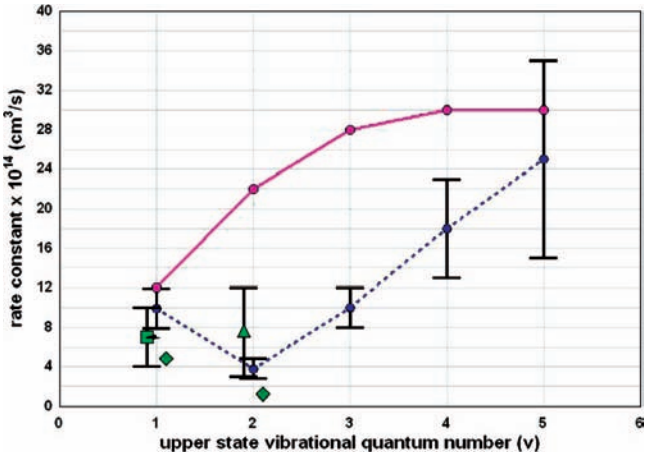

Figure 1. Comparison of experimental VV rate constant values reported in AAL ● (ref 1), FC ■ (ref 4), K ▲ (ref 2), and S ◆ (ref 3). The values are rotation-averaged and represent $v_1 = 1$, $v_2 = v - 1 \rightarrow v_1 = 0$, $v_2 = v$. The FC values were obtained at 295 K and the others at 298 K. The FC, K and S points are offset for clarity. The calculated VV rate constants at 298 K are shown in the upper curve.

Summary of Experimental Results and Theoretical Approach

Experimental Summary. Figure 1 summarizes the various experimental rate constant values for VV transfer in collisions between H_2 molecules, one of which is in the first excited vibrational state, $v = 1$, and the other in vibrational states ranging from $v' = 0$ through $v' = 4$. The rate constants are for vibrational exchange in the vibrationally exothermic direction, i.e. $v = 1$ collides with v' to yield $v = 0$ and $v' + 1$. The figure also shows theoretical results that will be discussed later. The most complete set of data is that of AAL,[1] who used Raman techniques to pump hydrogen from $v = 0$ to $v = 1$, and then the time evolution of the vibrational population to higher v-states was followed. The data analysis involved solving a set of coupled equations with variable vibrational exchange rate constants until a "best fit" to the observed time evolution of the vibrational state distribution was obtained.

[†] Part of the "Max Wolfsberg Festschrift".

* E-mail: jdanielkelley@sbcglobal.net.

10.1021/jp808355y CCC: $40.75

TABLE 1: Transitions, Defects and Rate Constants

transition (v, $J + v'$, J' $\rightarrow v{-}1$, $J + v' + 1$, J')	defect (cm^{-1})	rate constant ($\mathrm{cm}^3\ \mathrm{s}^{-1}$)
1, 1 + 0, 0 → 0, 1 + 1, 0	5.9	1.2×10^{13}
1, 1 + 0, 2 → 0, 1 + 1, 2	−12.0	1.3×10^{13}
1, 1 + 1, 1 → 0, 1 + 2, 1	−239	2.2×10^{13}
1, 1 + 2, 1 → 0, 1 + 3, 1	−465	2.8×10^{13}
1, 1 + 3, 1 → 0, 1 + 4, 1	−694	3.1×10^{13}
1, 1 + 4, 1 → 0, 1 + 5, 1	−922	3.0×10^{13}

The vibrational pumping process in AAL exclusively populated the $J = 1$ rotational state of $v = 1$ in H_2. This fact allowed measurement of reaction (2), because one can observe the collisional population of $v = 1$, $J = 0$ or 2. Coupling of vibration and rotation splits the $v = 1$ state energy enough so that the $J = 0$ and $J = 2$ states are distinguishable from $J = 1$. There is no collisional mixing of the even and odd rotational states of H_2 because the nuclear spin symmetry, ortho or para, forbids this process. Therefore, the appearance of $v = 1$, $J = 0$ or 2 must be the result of vibrational energy exchange from $v = 1$, J = 1. The same underlying physics allowed FC to measure the rate constant for reaction (2), also with a Raman method. Rotationally state-specific constants for nonresonant processes such as reaction (1) and reactions involving higher v-states, i.e. ($v_1 = 1$, $v_2 = v - 1 \rightarrow v_1 = 0, v_2 = v$) are not available, and the experimental values in Figure 1 represent an average over a thermal distribution of J-states. The $J = 1$ state is the most probable J-state in a thermal distribution of normal hydrogen at temperatures around 300 K, and it dominates the thermal average. As noted above, the AAL, FC and S rate constants for the resonant VV process agree within their respective error bars, as do the K and AAL values for the first nonresonant process ($v = 1$, $v' = 1 \rightarrow v = 0$, $v' = 2$); the value in S is a bit lower. The energy differences between initial and final states, the vibrational energy defects, are shown in Table 1 for specific initial and final v, J states (negative values signify exothermic processes). The rate constant values in Table 1 are those calculated in this work as described below.

Theoretical Approach. This study was initiated in response to a suggestion in AAL that the results in Figure 1 could be explained by attributing the rate constant behavior as a function of v-state to the interplay between vibrational and rotational motion. To execute a reasonably rigorous calculation of the collisional transfer of energy between H_2 molecules, one must assemble several pieces. First, a description of the separated molecule motion is required. In this work the H_2 wave functions are eigenfunctions of the RKR potential for the H_2 electronic ground state,[7] and thus they are rotating anharmonic oscillators with rotation and vibration coupled.[8] Molecular constants for H_2 were obtained from Huber and Herzberg.[9] The defect data in Table 1 were obtained using these constants. Next, a sufficiently accurate interaction potential must be used to describe the collisional interaction of the two H_2 molecules. The potential used here was constructed by Kelley and Bragg[10] to describe collision broadening and line shifting in the quadrupole spectrum of molecular hydrogen. This potential gave good agreement between measured and calculated broadening and shifting coefficients in numerous transitions in the H_2 fundamental and overtone bands, and is used here without modification. This interaction potential was based on an *ab initio* potential[11,12] for collision between two H_2 rigid rotors with the H−H separation fixed at r_0, the average separation for a molecule in $v = 0$. This potential in a space-fixed coordinate system gives the interaction dependence on intermolecular distance R, the orientation angles of each molecule θ_1,ϕ_1 and θ_2,ϕ_2, and the relative orientation angles Θ,Φ. The dependence on the H_2 vibrational coordinates r_1,r_2 was obtained from an *ab initio* potential for He−H_2..[13,14] The r-coefficients from the He−H_2 potential were adjusted in ref 10 to optimize the fit to line shift data. As stated above, the resulting interaction potential successfully described collision phenomena in the H_2 quadrupole spectra. This potential, V_I, can be written as an expansion in spherical harmonics, denoted Y_λ

TABLE 2: Potential Parameters in Atomic Units[10]

	V_{000}	V_{202}[a]
A	3.726	0.1315
c	1.471	1.6
d	0.0224	0
α	0.91	2.26
C_6	12.14	0.254
α_6	0.57	1.35
C_8	215.2	12.18
α_8	0.86	2.0
C_{10}	4813.0	307.2
α_{10}	1.15	1.6

[a] V_{202} was used only in preliminary calculations.

$$V_\mathrm{I}=V_{000}(r_1,r_2,R) + V_{202}(r_1,r_2,R)Y_2(\theta_1\varphi_1)Y_0(\theta_2\varphi_2)Y_2(\Theta\Phi) + V_{022}(r_1,r_2,R)Y_0(\theta_1\varphi_1)Y_2(\theta_2\varphi_2)Y_2(\Theta\Phi) + \text{(higher terms)...} \tag{3}$$

The first term in V_I represents the collision of two radially vibrating spheres; it can produce VV transfer, but it does not produce any change in the J-state of either molecule. Any rotational participation in the VV process, or even pure rotational excitation, is a result of the higher terms in the expansion. The magnitude of the spherical V_{000} term is substantially greater than that of the higher terms[10] (see Table 2), and preliminary calculations quickly established that the higher terms did not contribute significantly to any of the VV rate constants calculated here. Only the spherical term is important in this context. With this in mind, we write the V_{000} term in more detail and set it equal to V_I

$$V_\mathrm{I}(r_1,r_2,R) = A\exp(-cR - \mathrm{d}R^2)(1 + \alpha\Delta r_1 + \alpha\Delta r_2 + \alpha^2\Delta r_1\Delta r_2 + ...) - f(R)\Sigma_n C_n/R^n(1 + \alpha_n\Delta r_1 + \alpha_n\Delta r_2 + \alpha_n^{\,2}\Delta r_1\Delta r_2 + ...) \tag{4}$$

where $n = 6, 8, 10$ and Δr is $r - r_0$. The function $f(R)$ serves to damp the contribution of the long-range attractive terms for small R, and is discussed in ref 10. The values of the potential parameters are given in Table 2. Vibrational excitation and energy transfer result from Δr terms in eq 4. The linear terms allow vibrational excitation of one H_2 or the other. This process requires an energy transfer of about 4000 cm^{-1} to or from the relative motion, and is much less likely than VV transfer, which requires only a few hundred cm^{-1} (see Table 1). The VV transfer process is effected by the bilinear $\Delta r_1\Delta r_2$ term, which allows simultaneous changes in the vibrational states of both colliding molecules.

The next step in the calculation is to describe the collision process and its results. A semiclassical method is used here, but one that is different from that usually employed. In its more common formulation, as in ref 4 for example, the relative intermolecular motion and the rotational motion of the colliding molecules are treated classically. The resulting collision trajectory produces a time-dependent perturbation on the vibrational motion, which is treated quantum-mechanically. This perturbation results in vibrational state changes through the Δr terms in the interaction. Such an approach is valid for diatomics such as O_2 and CO, because the rotational level separations are only a few tens of wavenumbers and the interaction potentials are more anisotropic that that for H_2-H_2. The rotational excitation rates for these heavier diatomics, even at room temperature, are comparable with the gas kinetic collision rate and multiquantum rotational changes are the rule. It is then reasonable to consider rotation to be a classical variable, directly coupled to the collisional motion which is also treated classically.

Hydrogen is a special case because its small mass leads to rotational level spacings of hundreds rather than tens of wavenumbers. Moreover the rotational quantum number J must change by at least $\Delta J = 2$ as a result of the nuclear spin symmetry restriction mentioned above. As a result, rotational excitation is much more difficult than for heavier diatomics, and the rates are less than 1/100 of the gas kinetic collision rate at room temperature.[15] Given these circumstances, a better semiclassical treatment for H_2-H_2 is one in which both vibration and rotation are treated quantum-mechanically, and only the relative collision motion is classical. This is the approach used here. Using eq 4 for the interaction potential, the collision coordinate R becomes $R(t)$, and the resulting time-dependent perturbation yields transitions between initial state v_1J_1,v_2J_2 and final state v'_1J_1,v'_2J_2 where the J's are unchanged. The probability in a particular collision that a given final state f is produced from the initial state i can be obtained from first-order perturbation theory

$$P_{if} = |(i/\hbar) \int \langle i|V_{\mathrm{I}}(r_1,r_2,t)|f\rangle \exp[i(E_i - E_f)t/\hbar]G(t)\,\mathrm{d}t|^2 \tag{5}$$

where $V_{\mathrm{I}}(r_1,r_2,t)$ is obtained from eq 4 by substituting $R(t)$ obtained by integrating the classical equations of motion for an H_2-H_2 collision proceeding via $V_{\mathrm{I}}(r_1=r_0,r_2=r_0,R)$; $E_i - E_f$ is the energy difference between the initial and final state, and $G(t)$ is given by

$$G(t) = \exp[(i/h)\int^{t} (V_{ff} - V_{ii})\,\mathrm{d}t'] \tag{6}$$

This G-factor was described by Mies[16] and represents the contribution of the difference between the diagonal matrix elements of the interaction potential between the initial state and the final state. This term is sometimes omitted, but the omission is incorrect except for systems described by harmonic oscillators for which $G(t) = 1$ and therefore $V_{ii} = V_{ff}$ when the interaction potential is linear and bilinear in the separations Δr. For the anharmonic rotating oscillators used in this calculation, $V_{ff} - V_{ii}$ is small, but not zero, and the G-factor makes an increasing contribution to the calculated probabilities and rate constants for VV transfer as v increases. The use of first-order perturbation theory for this H_2-H_2 system is justified by the fact that the probabilities for all the state-changing processes, pure rotation and rotation−vibration, are small for the collisions that contribute to a room-temperature V−V rate constant average. The sum of these probabilities is much less than unity for these collisions, and this is the criterion for validity of a first order calculation.

The probabilities generated via eq 5 are for a single collision with specified relative collision energy and angular momentum. In order to obtain rate constants, we choose an initial collision energy and angular momentum, and numerically solve the classical equations for relative motion. The resulting time-dependent interaction matrix element is multiplied by the exponential factor and $G(t)$, and the integral in eq 5 is evaluated. This process is repeated for a set of relative angular momenta (equivalently, impact parameters) sufficiently large that the results become invariant to further increase. The collision energy is then changed, and the process repeated. At each collision energy, an integration over impact parameter yields a cross section for the process $i \rightarrow f$. This energy dependent set of cross sections is then averaged over a Maxwellian distribution of energy to obtain a thermal rate constant for the particular process. The rate constants discussed below were obtained in this way. One further detail should be mentioned. For these inelastic collision processes, a "symmetrized" energy is used in obtaining the probabilities given by eq 5. The symmetrized energy is obtained by adding to the initial collision energy half the energy lost or subtracting half the energy gained by the internal degrees of freedom. This procedure accounts for the addition or loss of energy in relative motion because of the transition.[16] The accuracy of the classical trajectories, which were obtained using fourth-order Runge−Kutta algorithm,[17] is ensured by checking conservation of energy and angular momentum, varying the time step, integrating a subset of trajectories backward from the final to initial state, and increasing the range of impact parameters and energies until the rate constants did not change.

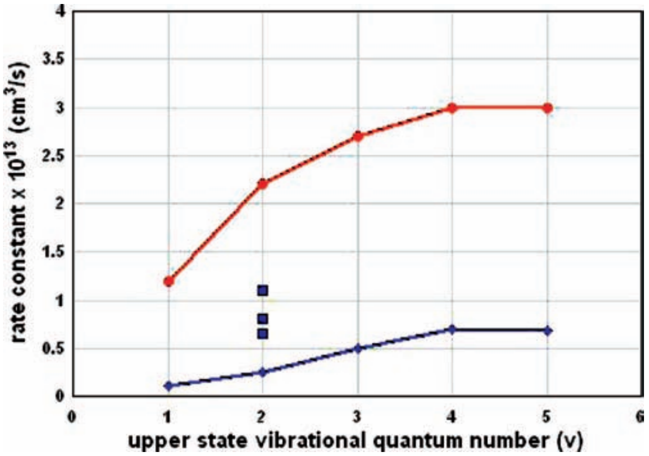

Figure 2. Comparison of calculated rate constants ● with Billing et al. values ◆ (ref 4) and ■ (ref 6) at $T = 298$ K. The rate constants are given in the exothermic direction, 1, $v - 1 \rightarrow 0$, v.

Results and Discussion

Calculated rate constants are shown in Table 1 for specific transitions, along with the associated vibrational defects. Typically, only the constants for molecules in $J = 1$ are shown in Table 1 because these dominate the room-temperature average over J, and the average values do not differ much from these values. For the resonant case, rate constants for transfer to molecules in both $J = 0$ and $J = 2$ are shown; the values are essentially the same. Figure 2 shows a comparison of the J-averaged values calculated here with the set of rate constants calculated by Cacciatore and Billing (CB),[4] along with values from Billing and Kolesnick[6] for the process $v = 1 + v = 1 \rightarrow v = 0 + v = 2$. The values are for rate constants in the exothermic direction. The rate constants from Billing's group are appreciably smaller than those calculated here. The major contribution to this difference is the difference in interaction potentials used in the two calculations. The effective α-values in the earlier work[4] are smaller than those employed here (Table 2), and the calculated rate constants depend on the square of the matrix elements for the bilinear term, or on α^4. The various values at $v = 2$ from Billing's group result from fits to different *ab initio* potential surfaces; this is discussed in detail in ref 6. A point of interest is that the three points shown by "■" represent results from different fits to the H_2-H_2 surface obtained by Schwenke.[18] The factor of three variation in the rate constants dramatically illustrates the sensitivity of the V−V calculation to the r-dependence of the surface and the quality of the fit.

The rate constants calculated in this work are also shown in Figure 1 along with the various experimental values and error bars as discussed above. The calculated values are in reasonable agreement with the data for the "resonant" process, but they are 2−3 times larger than experiment for the nonresonant transitions. Moreover, the drop in the experimental rate constant from the resonant $v = 1$ to the first nonresonant $v = 2$ value is not seen in this calculation, nor is it seen in the CB results (Figure 2). The origin of the drop in the experimental rate constant from $v = 1$ to $v = 2$ is unknown. There is no obvious alteration in the interaction potential which would produce this behavior.

Summary and Conclusions

This paper describes a set of semiclassical calculations of the rate constants for VV energy transfer in collisions between hydrogen molecules. Unlike most semiclassical treatments, molecular vibration and rotation are coupled and treated quantum mechanically using RKR wave functions for each v,J state. The calculations used an intermolecular interaction potential for the H_2-H_2 that had been previously shown to accurately describe collisional line broadening and shifting in the quadrupole spectrum of H_2. This potential was used here without any alteration. The results are mixed, in that the calculated rate constant for the resonant $v = 1 + v = 0 \rightarrow v = 0 + v = 1$ process are accurate, but the calculated and observed values differ for the non resonant VV processes. In addition, the drop in rate constant from the resonant to first nonresonant VV process is not captured in the calculation. The results obtained here are compared with earlier calculations in which rotation was treated classically. The differences among the calculations can be at least qualitatively attributed to differences in the interaction potentials employed. It is not obvious that the different dynamics in a system with classical rather than quantum rotors plays an important role. In general, these older calculations do not agree with the data as well as the calculations developed here. A significant result in this work is that the anisotropic potential terms did not play a role; the rotational degree of freedom does not significantly participate in the VV processes. This observation is apparently not true for VT energy transfer[19] in H_2, a process dominated by higher energy collisions in the thermal rate constant average. The VV transfer rates with their relatively small defects depend on collisions with energies well below 0.1 eV, as do the line broadening and shifting processes for which the interaction potential given by eq 4, with the parameters in Table 2, was optimized. It is not surprising that an interaction potential optimized for higher energies is more anisotropic than that used in this work. Note that the interaction potential used in this work, despite its partial lack of *a priori* rigor, does in fact fit a large amount of spectroscopic[10] and VV transfer data for H_2 reasonably well.

There are a few lessons to be learned from the attempt to describe this deceptively simple system and process. First, the fact that the calculated V−V rates depend on the potential parameter α to the fourth power presents a challenge to anyone attempting an "exact" calculation. The value of α represents the slope of the change in interaction potential as the intramolecular H−H distance is varied from r_0. The α^4 dependence means that a 20% uncertainty in α implies a factor of 2 uncertainty in the rate constant, and thus requires the interaction potential to be very accurately calculated for small displacements around r_0 in order to approach 10−20% accuracy in the rate constants. A second related challenge is obtaining an accurate value for the difference in diagonal matrix elements of the interaction potential between initial and final states. Neglect of the "G-factor" (eq 6) decreases the calculated rate constant (Figure 1) about 10% at $v = 3$, 40% at $v = 4$ and a factor of 3 at $v = 5$; this reduction becomes quite sensitive to $V_{ff} - V_{ii}$ as the defect increases with upper state v-level. At this point it seems that the appropriate next step for H_2 VV calculations is to undertake a fully quantum mechanical scattering calculation with the best interaction potential available and employing vibrotational wave functions for H_2 generated by the RKR method. Given that the number of states required is much smaller than for other diatomics, this is a feasible calculation. In fact, a beginning has been made in this direction by Panda et al.[20] This work included fully quantum mechanical calculations of cross sections for $H_2(v_1{=}0,j_1{=}0) + H_2(v_2{=}1,j_2{=}1) \rightarrow H_2(v_1{=}1,j_1') + H_2(v_2{=}0,j_2')$ for collision energies between 0.1 and 1.0 eV. This collision energy range is too high to allow rate constants at 298 K to be obtained, and vibrational quantum numbers greater than unity were not considered, but the results are still useful in comparison with the present study. The cross section for the resonant, rotationally elastic VV process $j_1' = 0$, $j_2' = 1$ is an order of magnitude larger than the values for rotationally inelastic processes, e.g. $j_1' = 2$, $j_2' = 1$, at 0.1 eV collision energy.[20] This is consistent with the neglect of such processes at lower collision energies in the present study. The value for the resonant VV cross section at 0.1 eV calculated by Panda et al.[20] is 0.013 au^2 and the value calculated using the methods here is 0.027 au^2, fair agreement considering that a different potential energy surface[21] was used in ref 20.

Acknowledgment. I thank Profs. Don Thompson and Walter Lempert for helpful comments on this work.

References and Notes

(1) Ahn, T.; Adamovich, I.; Lempert, W. R. *Chem. Phys.* **2007**, *335*, 55.

(2) Kreutz, T. G.; Gelfand, J.; Miles, R. B.; Rabitz, H. *Chem. Phys.* **1988**, *124*, 359.

(3) Saiki, D. J.; Cureton-Chinn, S.; Kelly, P. B.; Augustine, M. P. *J. Chem. Phys.* **2005**, *123*, 104311.

(4) Cacciatore, M.; Billing, G. D. *J. Phys. Chem.* **1992**, *96*, 217.

(5) Farrow, R. L.; Chandler, D. W. *J. Chem. Phys.* **1988**, *89*, 1994.

(6) Billing, G. D.; Kolesnock, R. E. *Chem. Phys. Lett.* **1993**, *215*, 571.

(7) The Δr matrix elements for H_2 were calculated by Prof. R. J. LeRoy, U. of Waterloo, using his program LEVEL 7.7; a subset of these values appears on his Web site at http://scienide.uwaterloo.ca/~rleroy/potentials/H2D2HD/.

(8) A preliminary version of this work was presented at the 39th AIAA Lasers and Plasmadynamics Conference, paper AIAA-2008-3779, June 2008. That work used rotating Morse oscillator wave functions to evaluate the transition matrix elements. Unfortunately, an error in the wave function program led to Δr matrix element values that were too low by almost 30%. The resulting rate constants, which depend on Δr^4, were therefore a factor of 3 or more too small. The reported results appear online in the Conference summaries and should be ignored.

(9) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*; Van Nostrand and Reinhold: New York, 1979; p 250.

(10) Kelley, J. D.; Bragg, S. L. *Phys. Rev. A* **1986**, *34*, 3003.

(11) Norman, M. J.; Watts, R. O.; Buck, U. *J. Chem. Phys.* **1984**, *81*, 3500.

(12) Schaefer, J.; Meyer, W. *J. Chem. Phys.* **1979**, *70*, 344.

(13) Meyer, W.; Hariharan, P. C.; Kutzelnigg, W. *J. Chem. Phys.* **1980**, *73*, 1880.

(14) Senff, U. E.; Burton, P. G. *J. Phys. Chem.* **1985**, *89*, 797.

(15) See for example: Sultanov, R. A.; Guster, D *Chem. Phys.* **2006**, *326*, 641.

(16) Mies, F. H. *J. Chem. Phys.* **1964**, *41*, 903.

(17) Press, W. H., Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in FORTRAN*, 2nd ed.; Cambridge University Press: Cambridge, 1992.

(18) Schwenke, D. W. *J. Chem. Phys.* **1988**, *89*, 2076.

(19) Pogrebnya, S. K.; Mandy, M. E.; Clary, D. C. *Int. J. Mass Spectrom.* **2003**, *335*, 223–224.

(20) Panda, A. N.; Otto, F.; Gatti, F.; Meyer, H-D. *J. Chem. Phys.* **2007**, *127*, 114310–1.

(21) Boothroyd, A. I.; Martin, P. G.; Keogh, W. J.; Peterson, M. J. *J. Chem. Phys.* **2002**, *116*, 666.

JP808355Y