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Selective Vibrational Pumping of Molecular Hydrogen via Gas Phase Atomic Recombination[†]

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Formation of rovibrational excited molecular hydrogen from atomic recombination has been computationally studied using three body dynamics and orbiting resonance theory. Each of the two methods in the frame of classical mechanics, that has been used for all of the calculations, appear complementary rather than complete, with similar values in the low temperature region, and predominance of three body dynamics for temperatures higher than about 1000 K. The sum of the two contributions appears in fairly good agreement with available data from the literature. Dependence of total recombination on the temperature over pressure ratio is stressed. Detailed recombination toward rovibrational states is presented, with large evidence of importance of rotation in final products. Comparison with gas-surface recombination implying only physiadsorbed molecules shows approximate similarities at $T = 5000$ K, being on the contrary different at lower temperature.

Introduction

Large interest is presently devoted to the understanding of vibrational excitation of molecular hydrogen under plasma conditions. The reason for this interest is linked to the production of negative ions through the dissociative attachment process,[1] i.e.,

$$e + H_2(v,j) = H + H^- \tag{1}$$

where $H_2(v,j)$ represents a hydrogen molecule characterized by vibrational and rotational quantum numbers v and j, respectively (w and k will denote, respectively, the final vibrational and rotational quantum numbers). Different mechanisms have been so far proposed for the production of rovibrationally excited states including the so-called e-V and E-V processes, i.e.,

$$e + H_2 = H_2^- = e + H_2(w,k) \tag{2}$$

$$e + H_2 = H_2^* = e + H_2(w,k) \tag{3}$$

The first mechanism is a resonant process involving a transient negative ion molecular species followed by rovibrational excitation.[1] The second mechanism is an indirect process implying the excitation of electronically (singlet states) excited states followed by radiative decay over rovibrationally excited states.[2] Both mechanisms have been widely investigated.

Surface recombination constitutes a third class nowadays studied of rovibrational excitation. Two mechanisms are presently investigated, the Eley−Rideal mechanism and the Langmuir−Hinshelwood mechanism.[3,4] The first considers the recombination as occurring between a gas phase atomic hydrogen and an adsorbed atomic hydrogen H_w, i.e.,

$$H + H_w = H_2(w,k) + W \tag{4}$$

The Langmuir−Hinshelwood mechanism considers recombination through two adsorbed atomic hydrogen, i.e.,

$$H_w + H_w = H_2(w,k) + W \tag{5}$$

A further pumping mechanism is represented by the atomic recombination in gas phase, i.e.,

$$H + H + H_2 = H_2(w,k) + H_2 \tag{6}$$

$$H + H + H = H_2(w,k) + H \tag{7}$$

This mechanism, while being the oldest one being investigated (see, for example, refs 5−7), has been scarcely considered as a pumping process. In principle, the rovibrational distribution generated by the heterogeneous recombination should be very similar to the one generated by the Eley−Rideal and Langmuir−Hinshelwood mechanisms when the adsorbed atoms are physiadsorbed, i.e., when the adsorption well is very small.

The vibrational distribution coming from processes 6 and 7 can be investigated through a molecular dynamics approach either using quantum mechanical or classical methods. In this paper, our detailed database of quasiclassical calculations[8−11] concerning some atom−molecule collision processes has been exploited to produce rate coefficients for process 7 either using (in a sense specified below) three body dynamics or kinetics of quasibound states. New data will be presented concerning the vibrational distribution generated by homogeneous recombination, and a comparison will be shown with the corresponding distribution generated by the heterogeneous recombination.

General Considerations and Strategy of Computation

Termolecular recombination is rarely obtained directly from a dynamical calculation, because of the relative difficulty in the practical implementation of a three body collision with respect to a two body one. In principle, since recombination is the inverse process of dissociation:

$$A + BC \rightarrow A + B + C$$

(A, B, C atoms for simplicity) it should be easy to obtain recombination by applying the detailed balance principle to dissociation rates directly calculated: only the equilibrium constant is needed. Difficulties arise for two reasons: first, it

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can be difficult to obtain numerically dissociation results in the low temperature regime, where recombination is expected to be relevant and dissociation very low; second, not simply continuum states contribute to dissociation, but also some other states are more or less "evanescent", that is, not bound and in some way intermediate between bound and continuum states. Using (quasi- or semiclassical) methods in which no quantum tunneling is allowed strictly separates the possible exit channels of the A + BC(v,j) collision (v/j initial vibrational/rotational quantum numbers, w/k final ones):

1. A + BC(w,k) (and analogously other rearrangements B + AC, C + AB), being final molecule bound (internal energy below the asymptotic dissociation limit, obtained from the diatomic potential without any rotational contribution);
2. A + BC*(w,k) (and other rearrangements) with quasibound (QB) final molecule, that is, with an internal energy above the dissociation limit but below the top of the rotational barrier. A quasibound molecule is exactly bound from a quasiclassical point of view but can escape quantum mechanically from the rotational barrier with a certain finite probability, contributing (eventually) to dissociation;
3. A + B + C, direct three body dissociation, for internal energy above the rotational barrier.

Quantum mechanically, only two cases are strictly distinguishable, the bound case from the others, while the transition between quasibound and unbound states is smooth, because quasibound states can escape from the barrier and unbound states with energy near the top of the rotational barrier are partially trapped above the barrier. The quantum unbound (UB) states are essentially included in classical free particle motion. As a consequence in an idealized calculation, one could obtain the outcomes of the A + BC collision on the whole ladder of possible final states, ranging from bound states to continuum. Anyway, not bound states (quasibound, unbound, and continuum states) should be treated differently when computing dissociation (or recombination): while continuum states (CS) contribute directly to dissociation, the remaining ones have finite lifetimes that complicate the calculation. Lifetimes of these borderline states vary on a range of many orders of magnitude: therefore, depending on the typical collision time of the studied system, some quasibound states can be considered as dissociated, others as bound, and others as indeterminate. Only kinetics can solve this part of the problem. Probably the most famous and used kinetic scheme for recombination is the orbiting resonance theory (ORT[5]), based on the following scheme:

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AB}^*(v,j) \qquad (8)$$

$$\mathrm{C} + \mathrm{AB}^*(v,j) \xrightarrow{k_2} \mathrm{C} + \mathrm{AB}(w,k) \qquad (9)$$

The first equation describes an equilibrium between the quasibound state AB* (or orbiting resonance, hence the name of the method) and its free conponents, equilibrium not disturbed in the ORT philosophy by the second equation, the collision with the third body, which stabilizes the excited AB* to a bound state AB. Actually, this is the energy transfer mechanism of ORT.[5] It is possible that an intermediate QB state is formed by A and C, with successive exchange of particles in the second step and formation of bound AB and free C: this is called the bound complex mechanism. The ORT method is subject to some restrictions: the rate of decomposition k_{-1} of AB* to free particles, directly linked to AB*(v,j) lifetime $\tau_{v,j}$ by the relation: $k_{-1} = 1/\tau_{v,j}$, has to be much higher than k_2[C]:

$$k_{-1}^{v,j} = \frac{1}{\tau_{v,j}} \gg \sum_{w,k} k_2^{v,j\to w,k}[\mathrm{C}] \qquad (10)$$

(here, the sum over final products has been considered, for fixed quasibound state AB*(v,j)) and this can occur of course for some selected QB states, given the reactants and the concentration of C. In fact, specific QB states have to be chosen in order to satisfy this requirement, with the implicit hypothesis that all of the others are not of importance for recombination. For example, in the hydrogen case from a set of about 50 QB states, only six states are commonly used for ORT application.[5,13] In this work, these six states are indicated as "RBC states" (from the authors of ORT, Roberts, Bernstein, and Curtiss). However, other possibilities have been explored here, selecting QB states only on the basis of relation 10. Lifetimes of QB states have been calculated by the semiclassical WKB method (Table 1), and are at most within 1 order of magnitude (often much less) when compared to some accurate lifetime values available in ref 12: this accuracy is sufficient for the purpose. Various possible concentrations of third body [C], obtained as a function of the ratio of temperature over pressure, $[\mathrm{C}] = 1/(R\cdot T/P)$, and of the rate coefficient sum in eq 10, $\sum_{w,k} k_2^{v,j\to w,k}$. This last has been approximated with the constant value 5×10^{-10} cm^3/s, deduced from data in this work. By equating the two terms in eq 10, one can obtain a critical value of lifetime: the allowed QB states must have lifetimes much less than this critical value, at least 10 times less just for fixing a sharp criterion. In this way, from a given T/P ratio, one can extract a list of QB states suited for ORT application.

On the other hand, it should be emphasized that in eq 9 the reverse path is neglected, on the hypothesis that the direct one, being invariably in the exothermic direction, is of larger importance. All of these restrictions could be overcome by applying, as suggested in ref 14, a steady state approximation to the AB* intermediate (instead of equilibrium), allowing the participation of all QB states available to the kinetics and also the introduction of other possible paths in the reaction scheme. However, the ORT method or other possible variants concern exclusively the QB role in the recombination/dissociation dynamics, with the introduction of some UB states using further approximations. Analogously, classical direct three body dissociation (and recombination obtained by this last using detailed balance) involves exclusively CS. It has been proposed[15] that if all of the possible final not bound states could be included in each scheme, each scheme would be complete and correct. This is interesting but hardly applicable, because of the very different nature of the various components of the set of final states. The reason for the unsatisfying performance of both direct classical dissociation and ORT in obtaining recombination/dissociation rates relies just on the underneath hypothesis that only a fraction of the complete spectrum of initial/final states is sufficient in describing the process. A reliable recombination calculation, however, could be feasible in two possible ways:

1. By carefully summing up the contributions from various methods involving QB, UB, and CS. "Carefully" means that it is fundamental not to include more than one time some states "common" to different methods.[16]
2. By using a "unifying" method of calculation in which all of the possible states (QB, UB, and CS) are "uniformly" treated. A good example with an approximate quantum method is given in ref 14. Smith theory[16] about recombination in principle treats all of the possible states

TABLE 1: Lifetimes of Quasibound States on the BKMP2 PES, Calculated by the Authors by the WKB Semiclassical Method

rotational quantum number	vibrational quantum number	lifetime (fs)
4	14	2.0421×10^6
5	14	337.23
8	13	1914.7
9	13	213.63
11	12	1454.8
12	12	167.03
13	11	1.0414×10^6
14	11	195.20
15	10	1.3907×10^9
16	10	1394.2
17	9	1.3560×10^{11}
17	10	121.97
18	9	8695.4
19	8	3.9334×10^{11}
19	9	110.15
20	8	29197.
21	7	1.4245×10^{11}
21	8	96.586
22	7	52257.
23	6	2.4821×10^{10}
23	7	119.79
24	6	59441.
25	5	4.0213×10^9
25	6	139.05
26	5	51513.
27	4	7.9137×10^8
27	5	149.89
28	4	40300.
29	3	2.0959×10^8
29	4	155.22
30	2	4.0805×10^{13}
30	3	32343.
31	2	8.0993×10^7
31	3	165.98
32	1	3.1240×10^{12}
32	2	30256.
33	1	5.0971×10^7
33	2	198.23
34	0	1.0037×10^{12}
34	1	38313.
35	0	7.0465×10^7
35	1	302.81
36	0	91914.
36	1	65.679
37	0	820.94
38	0	58.717

on an equal footing (actually, it deals with characterization of CS, and an extension to QB and UB states should be obvious), but it does not seem to have reached a practical implementation.

In this paper, the first route is attempted on the basis of this quite simple consideration. As already pointed out, classical dynamics separates neatly QB from UB and CS: therefore, by performing a quasiclassical calculation of the collision process A + BC(v,j) including all possible QB and CS states as final states, one should be capable of obtaining (1) direct dissociation and then recombination by detailed balance (DEB), (2) transition to/from QB states, that with separate calculation of equilibrium constants, can be treated with the ORT (or more accurate) method, giving essentially a separate (and directly additive) contribution with respect to direct three body recombination obtained by DEB. This logical path is totally feasible for us because of the calculations in past years[8−11] of a detailed rovibrational state-to-state database of cross sections for atom−diatom collisions concerning hydrogen:

$$\mathrm{H} + \mathrm{H}_2(v,j) \rightarrow \begin{cases} \mathrm{H} + \mathrm{H}_2(w,k) & \text{non-reactive} \\ \mathrm{H}_2(w,k) + \mathrm{H} & \text{reactive} \\ \mathrm{H} + \mathrm{H} + \mathrm{H} & \text{dissociation} \end{cases} \qquad (11)$$

including also QB both as initial and final states.

Method of Calculation

The dynamical calculations for collision process 11 has been performed with an implementation of the quasiclassical method developed by one of us[17] on the quite accurate BKMP2 potential energy surface (PES).[18] The energy interval of cross sections is from 0.001 to 9 eV, largely allowing an accurate rate calculation (in the quasiclassical limit) in the temperature range from 300 to 10 000 K, as reported in this work. Translational energy has been sampled in a continuous way, with fine discretization of the energy axis (1500 bins), for optimal determination of thresholds. The density of trajectories is 24 000 per Å of impact parameter and per eV of translational energy, with application of stratified sampling. Each step of each trajectory is checked in phase space with a second integration using a reduced time interval, which allows also an optimal ratio between accuracy and computational cost (see ref 19 for details). Tolerance in error checking is typically of 10^{-9} Å for lengths and 10^{-9}Å/fs for velocities. The validity of our quasiclassical code as well as our cross section data and rate coefficients have been proved with comparisons with both theoretical and experimental results in some papers[8−11] but generally for averaged quantities (thermal rates), due to the difficulty of finding reliable rovibrationally detailed data. There is a similar detailed calculated database by Martin et al.[20] on a slightly less accurate potential energy surface (LSTH[21]). Some comparisons with that database will be shown, in order to assess the validity of data used in the successive calculations but also to emphasize the differences existing between the rates calculated on the two PESs (this discussion is done with manipulation of data from the analytical fit given in ref 20). In Figure 1, the sum of rate coefficients for the process is shown: H + $\mathrm{H}_2(v=12,j=11) \rightarrow \mathrm{H} + \mathrm{H}_2(w,k=\mathrm{all})$, including only bound states as final products. The selected initial state is one of the quasibound states used in the application of orbiting resonance theory; therefore, the rate sum shown, if multiplied by the appropriate equilibrium constant, gives exactly the contribution to ORT recombination by the cited quasibound state. In Figure 1a, the temperature is 300 K, while, in Figure 1b, $T = 3000$ K: it is clear that, while the general trend is quite similar in both cases, the lower T data on the LSTH PES are higher by roughly a factor of 2 from $w = 4$ to $w = 12$ and about 5 times lower for $w = 0$. At higher temperature, discrepancies are much less important. Discrepancies between results on the two potential energy surfaces have already been put in evidence for rotational transitions at low temperature;[18] therefore, the comparison in Figure 1 is compatible with already known differences, taking into account that QB states are by definition the highest rotational states. Disagreement at low temperature seems also confirmed for dissociation data, as can be seen in Figure 2, with $T = 600$ K and $T = 3000$ K, respectively, for panel a and b. Here, dissociation rate coefficients from almost all rovibrational states with only even j (for clarity) are shown, with the only limitation of the lower limit fixed to 10^{-30} cm^3/s in panel a. It can be observed that circles (results in this work) are very often superposed to crosses (Martin et al. database) but for low temperature and high lying rotational states, where the agreement

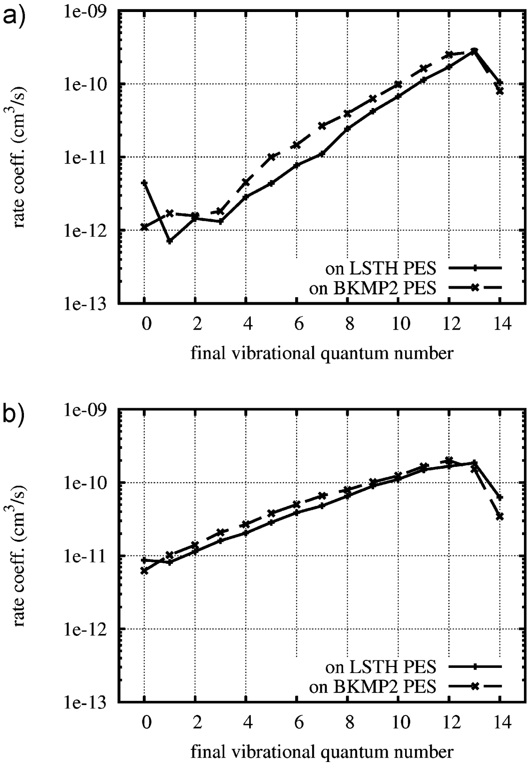

Figure 1. Comparison of the summed rate of stabilization from the same quasibound state ($v = 12, j = 11$) toward each final vibrational state: (a) $T = 600$ K; (b) $T = 3000$ K.

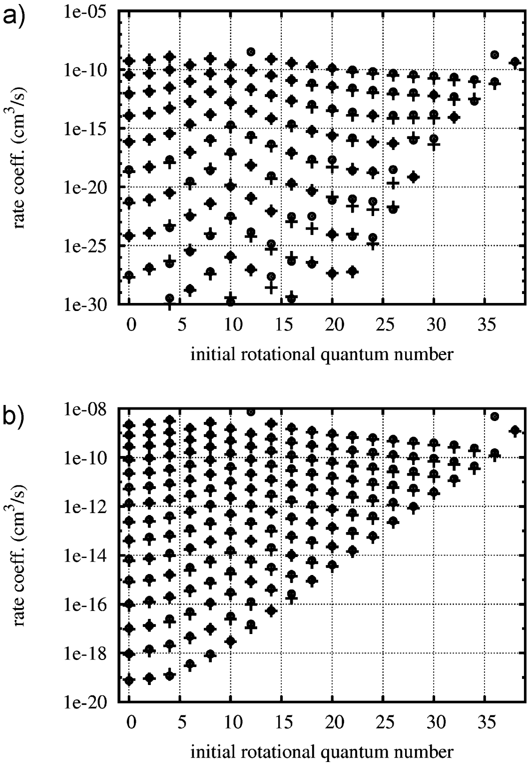

Figure 2. Comparison of dissociation rate coefficients as a function of initial rotational quantum number calculated on BKMP2 (circles) and on LSTH (crosses) for (a) $T = 600$ K and (b) $T = 3000$ K.

is only within 1 order of magnitude in some cases. Moreover, some quasibound states are not present at all in the LSTH PES (some circles without the corresponding crosses in Figure 2 for $j = 12$ and 36). All of these differences are the justification for using the accurate BKMP2 PES in this work.

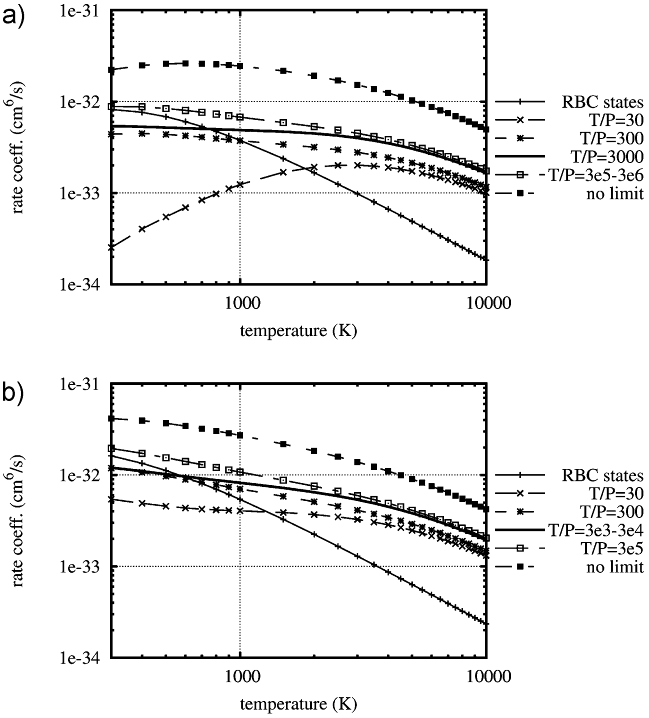

Figure 3. Recombination by ORT: dependence on selection of quasibound states involved in the kinetic scheme. In part a, on LSTH, and in part b, on BKMP2.

Figure 3 shows a comparison among different ORT calculations, as a function of temperature, using different sets of QB states. As anticipated, the “RBC states” result, shown in Figure 1, has been performed using the original six states in ref 5, while the other graphs are relative to different values of the ratio T/P (T temperature in kelvin, P pressure in bar). In Figure 1a, results on the LSTH PES are shown, taking into account that two RBC states are not present on this PES ($v = 14, j = 5$; $v = 12, j = 12$). Four different trends can be observed: the decreasing one for “RBC states”, an increasing trend from very low initial value for $T/P = 30$ and a maximum at $T = 3000$ K, very high values for unlimited use of QB states with a maximum of 800 K, and similar intermediate trends for T/P within the range $300-3 \times 10^6$. In panel b of Figure 1, the same results are displayed using data calculated on the BKMP2 PES. While for $T > 2000$ K the two sets appear very similar, they differ substantially in the lower temperature range, with results on the LSTH PES more than 1 order of magnitude smaller at $T = 300$ K and $T/P = 30$. It is very clear also that the very limited selection of QB states operated in ref 5 alters deeply the trend of recombination when considered on a large range of temperature. Actually, the original selection of QB states in ref 5 was really restricted by the necessity of reducing to a minimum the number of calculations required, excluding some QB states only for their relatively high energy in comparison to the typical temperature range of that study (about 300 K), and not for lifetime consideration. In this work, only relation 10 has been applied, and the significant differences at low temperature between LSTH and BKMP2 rates are due principally to the selection of QB states, to the differences of their lifetimes on the two PESs, and to the presence or lacking of some QB states in the two sets. When comparing recombination obtained by a detailed balance of dissociation on the two PESs, as in Figure 4, the values are very similar in the whole temperature range, despite the significant differences for the dissociation data already presented in Figure 2. Therefore, proper selection of QB states appears

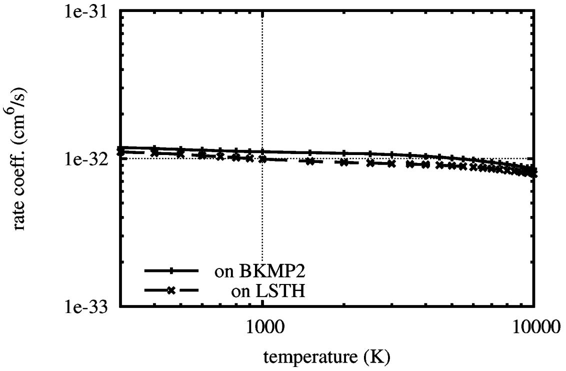

Figure 4. Comparison of total recombination rate obtained by detailed balance from dissociation, calculated on the BKMP2 PES in this work and on the LSTH PES by Martin et al.

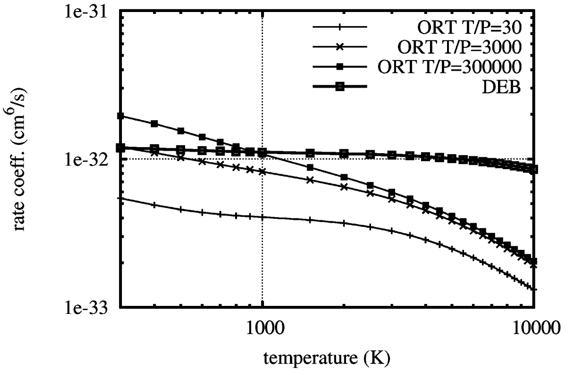

Figure 5. Comparison of recombination by ORT mechanism and by true three body collision. Different ORT results depend on the temperature over pressure ratio *T*/*P*.

of fundamental importance when obtaining recombination rates, also more important than accuracy of input data (state-to-state and dissociation rate coefficients).

In this work, also the bound complex mechanism is included, due to the availability of reactive rates for H + H_2. Concerning nonreactive rates, parity conservation of molecular momentum has been applied. We have actually studied also the application of steady state approximation to QB concentration, including other possible channels to the reaction path, that will be presented in another paper.

Results

In Figure 5, we report direct three body recombination (applying DEB to direct dissociation from bound states) in comparison with ORT recombination, choosing for this the last three ratio values T/P = 30, 3000, 300 000. DEB contribution is almost flat in the whole range shown, with a slightly decreasing value from 1.19×10^{-32} cm^6/s at 300 K to 8.53×10^{-33} cm^6/s at 10 000 K, while ORT has a more pronounced decreasing trend, that in the intermediate case T/P = 3000 starts from 1.20×10^{-32} cm^6/s (almost identical to the DEB value) to 1.94×10^{-33} cm^6/s (clearly lower than DEB). This is compatible with what one can expect, because QB states should be more efficient as "recombinators" at low temperature. For T/P values of the order of 3×10^5 or higher, ORT is slightly predominant on the DEB mechanism for $T < 1000$ K. The sensitivity of the ORT recombination contribution to specific conditions of the system studied can probably partially explain the large incertitude about recombination data in the literature. In Figure 6, we show the sum of ORT (T/P = 3000) and DEB, on the basis of what was already explained, in comparison with various experimental and theoretical results. In panel a, the comparison is with the minimum, maximum, and typical values of atomic hydrogen recombination recommended by Wetzel and Solomon:[22] the agreement (for the specific T/P value) is quite good over the whole range. It is important to note, however, the really large incertitude in recombination data, given by the difference between maximum and minimum recommended values, extending from 2 to 3 orders of magnitude from 300 to 10 000 K. Other data are from Levitskii and Polak,[23] the only direct three body recombination classical dynamics example in the literature, as far as we know, calculated on a semiempirical PES:[24] their result is higher by a factor variable from less than 5 (low T) to 2 (T = 10 000 K), with a similar general trend in the whole temperature range. The experimental result of Kondratev[25] appears in good agreement between 1000 and 10 000 K (it is worth noting that almost all recombination experiments have been performed in the high temperature regime). In panel b, the experimental result from Jacobs et al.,[26] fitted by Palla et al.,[27] is in good agreement for $T > 2000$ K, as well as the Schwenke result[28] in the limited range 3000−5000 K. Concerning this last, it has been obtained from a very large and complex kinetic study including H_2 as the third body (not only H). The conclusions of the Schwenke work are that for hydrogen atomic recombination the ORT mechanism has limited importance with respect to direct three body recombination in the range T = 1000−5000 K: these conclusions are compatible with this study, as can be inferred from Figure 5. In Figure 6b, there is also the recombination calculated by Shui[29] using the Keck method (trajectories started in the strong coupling region and propagated forward and backward in time to reach products and reagents, respectively): in this case, it seems that the agreement is remarkably satisfying in the range 300−5000 K. The only very different and very low recombination result is that of Krstic et al.,[30] obtained with an infinite order sudden approximation method which neglects rotation. Probably this is not a suited method for treating recombination, because rotation is absolutely fundamental in this case, as will be seen

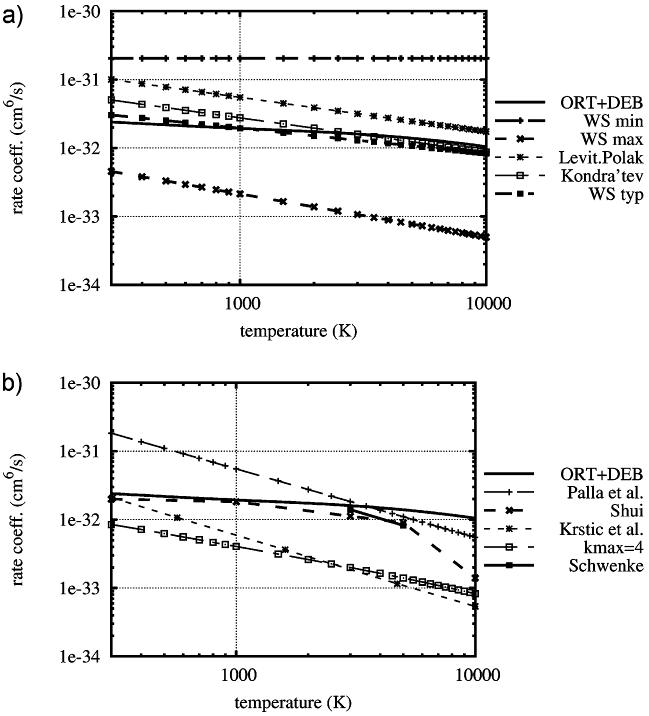

Figure 6. Comparison of calculated total recombination rate at T/P = 3000 with various results from the literature.

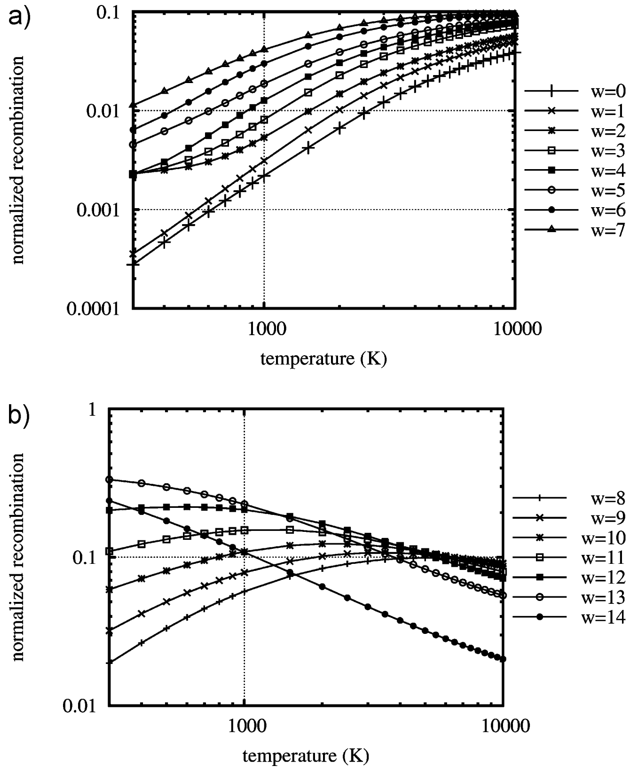

Figure 7. Recombination rate coefficient toward selected final vibrational states normalized to total recombination as a function of temperature: (a) final vibrational states from $w = 0$ to $w = 7$; (b) from $w = 8$ to $w = 14$.

in the next figures. For proving this point, a comparison of recombination data from this work, limiting the maximum final rotation to $k_{\max} = 4$, is presented in the same figure, with significant agreement with the Krstic et al. data. At low temperature and only for the ORT result, it is worth noting the agreement of total recombination from this work at $T = 300$ K: 1.6×10^{-32} cm^6/s with the Orel ORT result[13] at the same temperature: 1.19×10^{-32} cm^6/s, obtained both with the six QB "RBC states".

Globally, it seems that our summed recombination, obtained from both ORT and dissociation with DEB, shows quantitative agreement and correct slope in comparison with significant heterogeneous results from the literature, and this encourages us to use this sum as a basis for all of the subsequent more detailed data presented in the following of this paper.

The relative weight of different vibrational states w in hydrogen atomic recombination is put in evidence in Figure 7, in which rates toward selected final w, normalized to total recombination, are shown as a function of temperature. It is clear that at low temperature only high lying w states are significant, but this changes gradually when the temperature increases, with much more similar weights among rates relative to all w for $T = 10\,000$ K. It seems that for each w there is a smooth maximum which moves toward higher temperatures as a function of w. The trends are very smooth: this is quite normal for DEB results, but not necessarily for ORT results, because of the presence of only selected QB states as "recombinators". Quasi-elastic transitions (for example, between two states differing only in one rotational quantum) with QB states can bring into recombination sum some unexpected peaks, as can be seen using the six "RBC states" as QB. This is not the case in Figure 4, where normalized recombination is presented as a function of w, for three temperature values, $T = 300$, 1000, and 10 000 K: in this case, as throughout the entire work, many QB states have been used, limiting them as already explained. For $T = 300$ K, there is a clear prevalence of high w, which is less pronounced for $T = 1000$ K. At $T = 10\,000$ K, the distribution is roughly an inverted parabola with a maximum at $w = 7$.

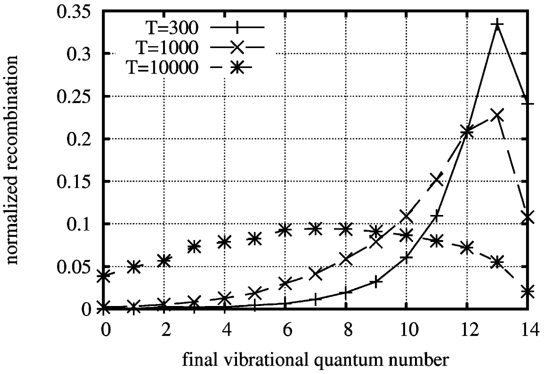

Figure 8. Recombination rate coefficient toward selected final vibrational states normalized to total recombination as a function of final vibrational quantum number for $T = 300$, 1000, and 10 000 K.

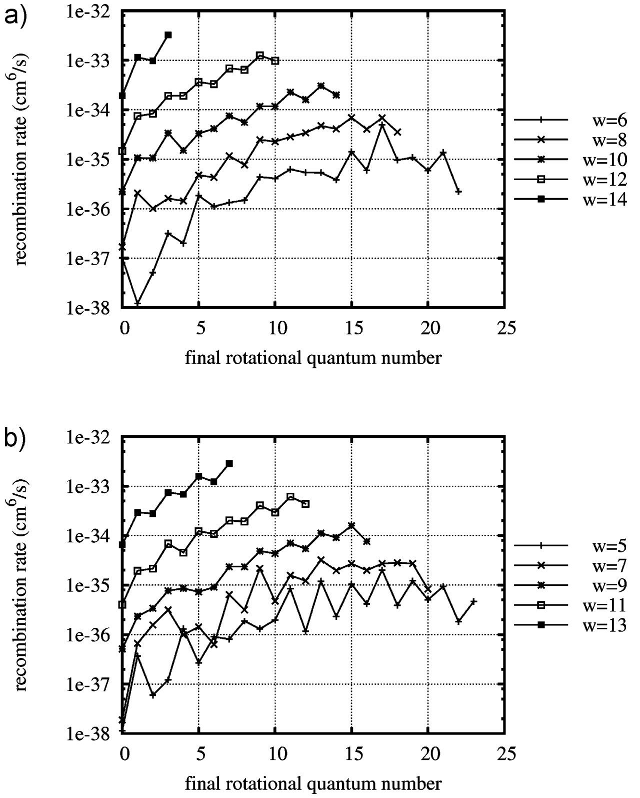

Figure 9. Recombination rate coefficients toward selected final rovibrational states for $T = 300$ K: (a) final vibrational states from $w = 6$ to $w = 14$ even values; (b) from $w = 7$ to $w = 13$ odd values.

Distributions of recombination among final rotational states for fixed temperature and final vibrational states are shown in Figure 9 for $T = 300$ K and Figure 10 for $T = 3000$ K. In these two figures, the large importance of rotation in the recombination process is absolutely evident, with variation of 2 or 3 orders of magnitude among $k = 0$ and the maximum rotational quantum number compatible with the selected final vibration. The alternating trend as a function of k is due to the application of conservation of parity to non-reactive rates and ortho−para coefficients in partition function. Differences among various k-depending results, for given w, decrease as temperature is

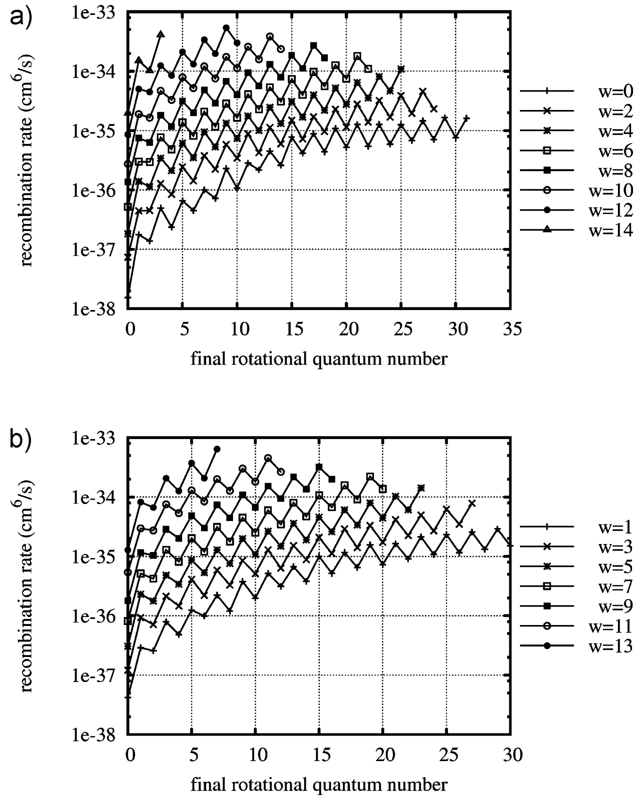

Figure 10. Recombination rate coefficients toward selected final rovibrational states for $T = 3000$ K: (a) final vibrational states from $w = 0$ to $w = 14$ even values; (b) from $w = 1$ to $w = 13$ odd values.

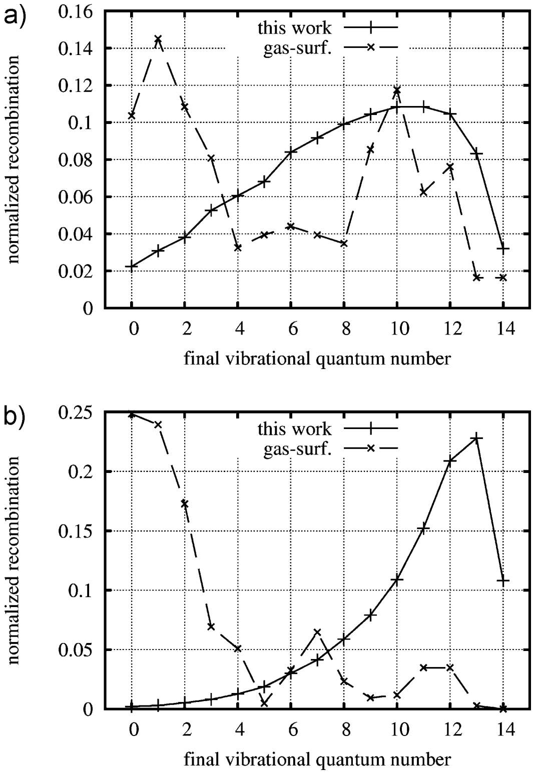

Figure 11. Comparison of normalized recombination rate coefficient in gas phase and gas surface at two temperatures: (a) $T = 5000$ K; (b) $T = 1000$ K.

increased, in particular, for the high lying rotational states, which for low *w* states are more numerous, contributing significantly to uniformly redistributing recombination among vibrational states at high *T*.

Finally, a comparison of gas phase recombination with gas-surface recombination data concerning the H with Cu surface from Billing[3] is presented in Figure 11 for $T = 5000$ K (a) and $T = 1000$ K (b). It is interesting to note that, from $w = 4$ on, the two normalized distributions at $T = 5000$ K are roughly similar. This is due essentially to the weak interaction with the surface (atoms are physisorbed). On the contrary at $T = 1000$ K, only a very limited central part of the vibrational spectrum is similar, with totally opposite trends outside that interval (largest importance of low lying states for gas surface, the opposite for gas phase).

Conclusions

Gas-phase atomic hydrogen recombination has been calculated by including contributions from quasibound and unbound states by means of ORT kinetics, and from continuum states through direct calculated dissociation with detailed balance application. Initial data have been taken entirely from a detailed atom-molecule hydrogen database, constructed by the authors with intensive calculations in the past years. The total thermal rate of recombination is in fairly good agreement with available literature data, with interesting possibilities of improving the result by modifying the kinetics of quasibound states. Dependence of ORT kinetics on temperature over pressure ratio has been put in evidence. Detailed rates have been also presented as a function of final vibrational and rotational states, showing a large dependence from final rotation. An attempt of comparing these data with gas-surface recombination has given similar vibrational distributions of recombination at $T = 5000$ K, evidencing a general behavior not very far from the gas phase but opposed distributions at lower temperature.

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