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Trajectory Calculations of Intermolecular Energy Transfer in H_2O + Ar Collisions

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The collisional deactivation of H_2O by Ar has been studied by using classical trajectory calculations, with an initial vibrational energy of 50, 75, and 100 kcal/mol, rotational temperatures in the range 0−10 000 K, and translational energies corresponding to the Boltzmann distribution at 298 K. Some results at 1000 K are also presented. The effect of internal energy on the first and second moments is examined. Increasing the initial vibrational energy enhances the intermolecular relaxation. However, the rotational temperature has a complex effect. The results are analyzed using a cumulative probability distribution of the amount of energy transferred in deactivating collisions, $Q(\Delta E)$, obtained by direct count of the number of trajectories that transfer an amount of energy equal to or greater than a certain amount, ΔE. The transition probability for energy transfer, $P(E',E)$, is then obtained by differentiation of the cumulative function. Scaling of $Q(\Delta E)$ in terms of the mean down energy lost in deactivating collisions, $\langle \Delta E \rangle_d$, for each group of trajectories, results in a unique distribution. This function then allows us to obtain a global $P(E',E)$ which depends on $\langle \Delta E \rangle_d$ as a single parameter.

I. Introduction

Despite the progress made in experimental and theoretical studies, collisional energy relaxation of highly excited molecules is not a well-understood process.[1−3] The overall average energy transferred per collision with a bath molecule, $\langle \Delta E \rangle$, has been measured for a variety of molecules, using different experimental techniques.[4−7] The results obtained provided useful information about the dependence of $\langle \Delta E \rangle$ on internal energy and the nature of both the parent molecule and the bath gas. However, insight into the dynamics of the relaxation process requires information on the amount of energy transferred in activating and deactivating collisions, $\langle \Delta E \rangle_{up}$ and $\langle \Delta E \rangle_d$, which are not directly obtained from experiments. In addition, the energy transfer probability function from initial state E to final state E', $P(E',E)$, which is the most relevant function in energy transfer processes, is very difficult to obtain. This function is needed not only to attain a better comprehension of the relaxation process but also for the solutions of master equations to fit experimental data.[8] Considerable advances have recently been made in this direction, using sophisticated spectroscopic techniques.[9−12] However, the results obtained rely, to some extent, on the use of assumed functions, so a certain level of ambiguity still remains.

On the theoretical side, quasiclassical trajectory calculations are increasingly used to provide new insights into the dynamics of the relaxation process.[13−24] These calculations allow us to obtain the values of $\langle \Delta E \rangle$, $\langle \Delta E \rangle_{up}$, and $\langle \Delta E \rangle_d$, usually separated in their rotational and vibrational components, as a function of the initial energy in the different degrees of freedom of the system. Higher moments as well as the width of $P(E', E)$ can also be calculated.[23,25] Histograms of the fraction of trajectories that transfer an amount of energy, $\Delta E = E' - E$, are usually fitted to some physically reasonable function to provide an educated guess of $P(E',E)$.

Several authors have properly addressed the question of the difficulties found in fitting the histograms.[19,26−29] All these difficulties emanate from the finite number of trajectories computed to construct them.

Very recently, an interesting new method to calculate $P(E',E)$ from trajectory simulations was proposed.[26] In the present work trajectories are analyzed in terms of a cumulative transition probability, $Q(\Delta E)$, which is a probability distribution of ΔE.[30] This function is calculated by direct count of the trajectories that transfer an amount of energy equal to or greater than a certain value of ΔE. The cumulative functions for the different sets of trajectories, when scaled to $\epsilon = \Delta E/\langle \Delta E \rangle_d$, become a single function, $Q(\epsilon)$, from which $P(E',E)$ is obtained as a function of $\langle \Delta E \rangle_d$.

Trajectory calculations of the collisional relaxation of water by Ar were previously studied by Stace and Murrel[21] and by Hase et al.[20] The major difference between their calculations and the present work is in the initial conditions. The calculations of Stace and Murrel were made at the initial vibrational, rotational, and translational energies corresponding to equipartition at 2500, 6000, and 10 000 K, while in the results reported in ref 20, the vibrational energy of the water molecule was 100 kcal/mol with zero rotational temperature and translational energy of 3 kcal/mol. Our calculations were performed over a broader range of initial conditions, with vibrational energy of 50, 75, and 100 kcal/mol, rotational temperatures in the range 0−10 000 K, and translational energy corresponding to the Boltzmann distribution at 298 and 1000 K. Also, a larger number of trajectories were computed.

II. Trajectory Calculations

A. Potential Energy Surface. The potential energy surface was identical to that of Hase et al.[20] It was constructed as the sum of an intramolecular term $V(H_2O)$, corresponding to H_2O and an intermolecular contribution $V(X_i, Ar)$, due to the interaction of H_2O with Ar:

$$V(H_2O{-}Ar) = V(H_2O) + V(X_i,Ar) \qquad (1)$$

where X_i represents H or O. The intramolecular potential was constructed as the addition of a Morse potential, used to describe

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TABLE 1: Parameters for the Intramolecular and Intermolecular Potentials of H_2O + Ar

H_2O intramolecular potential		Lennard−Jones intermolecular potential	
Morse potential	bending potential		
$D = 125$ kcal/mol $\beta = 2.19$ Å^{-1} $r_o = 0.957$ Å	$f = 0.688$ mdyn Å/rad^2 $\theta_o = 104.52°$	σ(H−Ar) = 3.09 Å σ(O−Ar) = 3.06 Å	ϵ(H−Ar) = 29.4K ϵ(O−Ar) = 70.0K

the O−H stretching motions and a quadratic harmonic potential, used for the bending mode:

$$V(H_2O) = D\{1 - \exp[\beta(r - r_0)]\}^2 + {}^1/_2 f(\theta - \theta_0)^2 \qquad (2)$$

Parameters were chosen to reproduce the equilibrium geometry, normal-mode frequencies, and dissociation energy to OH + H and are shown in Table 1.

The intermolecular potential was represented as the sum of atom−atom pair potentials. For each pair a Lennard−Jones 6−12 function was used:

$$V(X_i,Ar) = 4\epsilon_{X_i}\left[\left(\frac{\sigma_{X_i,Ar}}{R_{X_i,Ar}}\right)^{12} - \left(\frac{\sigma_{X_i,Ar}}{R_{X_i,Ar}}\right)^{6}\right] \qquad (3)$$

The parameters used are shown in Table 1.

B. Initial Conditions and Computational Details. The calculations were performed with the general Monte Carlo classical trajectory computer program Mariner.[31]

The impact parameter, b, was calculated as $b = R_a^{1/2} b_{max}$, where R_a is a random number between 0 and 1 and b_{max} is a necessary cutoff, selected so that the product $\langle \Delta E \rangle \pi b_{max}^2$ converged. The value used in the present calculations was $b_{max} = 0.6$ nm.

The initial conditions were specified by a vibrational energy E_V; a rotational temperature, T_R; and a translational temperature, T_T. The initial vibrational energies studied were 50, 75, and 100 kcal/mol and the rotational temperatures were 0, 298, 700, 1000, 2000, 5000, and 10 000 K. The initial translational energy was selected from the appropriate thermal energy distribution at 298 K. Some calculations were also made at $T_T = 1000$ K. The initial orientation of the molecule-bath colliding pair was randomly chosen by rotation through Euler's angles. The initial rotational energy about each axis was $RT_R/2$.

Typically 2000 trajectories were computed for each initial condition so that the final results of the present study are based on a total number of more than 42 000 trajectories.

For each group of 2000 trajectories the average energy transferred, $\langle \Delta E \rangle_d$, $\langle \Delta E \rangle_{up}$, $\langle \Delta E \rangle_{all}$, and $\langle \Delta E^2 \rangle$, were computed. The change in internal energy of the H_2O molecule was not separated into the vibrational and rotational components. Since H_2O is an asymmetric top, only an approximate calculation of the rotational energy can be made. This fact, together with the small changes of internal energy, introduces a large uncertainty in the values of $\langle \Delta E \rangle$ for vibrational and rotational energy transfer, and for this reason they were not analyzed.

C. Methodology of Analysis of $P(E',E)$. Usually, the analysis of the results of trajectory calculations is made using histograms of vibrational energy transfer, which requires the use of an energy bin. The transition probability function $P(E',E)$ for energy transfer from energy E to E' is then obtained by fitting the histogram to some adequate, but otherwise arbitrary, function. However, the fit to the transition probabilities is dependent on the bin size used to remove the elastic peak, which then determines the values of $\langle \Delta E \rangle$ derived from the fitting function. To reduce the effect of this arbitrariness different fits must be made to obtain a satisfactory convergence of the results.

In the present work, instead of the histograms, we use a transition probability distribution of the amount of energy transferred per deactivating collision, that is, a cumulative transition probability. This function is obtained by direct count of the number of individual trajectories which transfer an amount of energy equal to or greater than a certain value of ΔE, and it is an always increasing function, which is formally defined as

$$Q(\Delta E) = \int_{\Delta E}^{\infty} P(E',E)\, dE' = \int_{\Delta E}^{\infty} P(\Delta E)\, d\Delta E \qquad (4)$$

with $\Delta E = E' - E$ and $E' < E$.

From eq 4 the transition probability density $P(E',E)$ can be obtained by differentiating $Q(\Delta E)$:

$$-\frac{dQ(\Delta E)}{d(\Delta E)} = P(E',E) \qquad (5)$$

Since the calculation of $Q(\Delta E)$ is made directly from the trajectory results, it does not require a previous knowledge of the probability density $P(E',E)$.

III. Results and Discussion

In this section we present the results of trajectory calculations for the first and second moments corresponding to the change in relative energy transferred per collision, at different initial vibrational and rotational energies of the water molecule. The results for the first moments for down and up collisions, $\langle \Delta E \rangle_d$ and $\langle \Delta E \rangle_{up}$, are given together with the overall values, $\langle \Delta E \rangle$. The spread of the collisional transition probability function $P(E',E)$, given by

$$\sigma = (\langle \Delta E^2 \rangle - \langle \Delta E \rangle^2)^{1/2} \qquad (6)$$

is also analyzed.

A. The Effect of Internal Energy on the Energy Transfer Moments. Rotational energy plays a very important role in collisional energy transfer. In a previous work, we have shown that the relaxation of highly vibrational excited HgBr strongly depends on the rotational energy of the diatomic molecule.[32] It has also been shown that for highly vibrationally excited polyatomic molecules at zero rotational energy, up collisions dominate because of T−R transfer.[33] For SO_2 + Ar, rotational excitation initially facilitates the deactivation process, but at higher values it becomes detrimental to energy transfer.

To analyze the effect of internal energy on the energy transfer process, trajectories were performed at a fixed initial vibrational energy of 50, 75, and 100 kcal/mol. The influence of rotational excitation was taken into account by varying the initial rotational temperature, in the range 0−10 000 K. In addition, two translational temperatures, 298 and 1000 K, were studied.

The results obtained for the first moment at different initial vibrational energies for the overall energy change are displayed in Figure 1. They show that the strong and complex influence of rotational energy on energy transfer processes is characterized by three different regimes.

(a) At $T_R = 0$ K, molecules are rotationally frozen and collisions with Ar result in an energy gain by water, when the

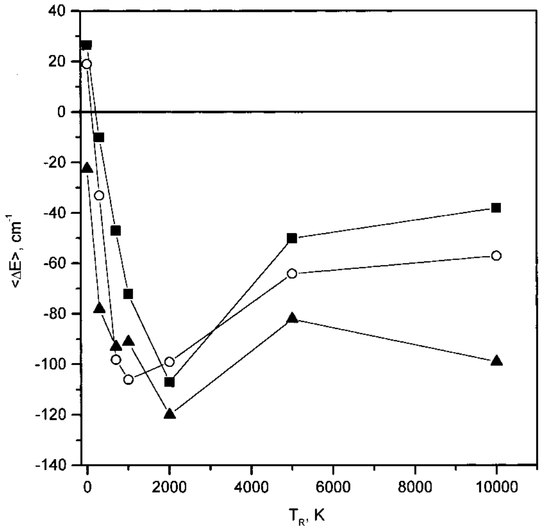

Figure 1. Average energy transferred per collision as a function of the rotational temperature at three different initial vibrational energies: (■) 50 kcal/mol, (○) 75 kcal/mol, and (▲) 100 kcal/mol. The lines through the points are only to guide the eye.

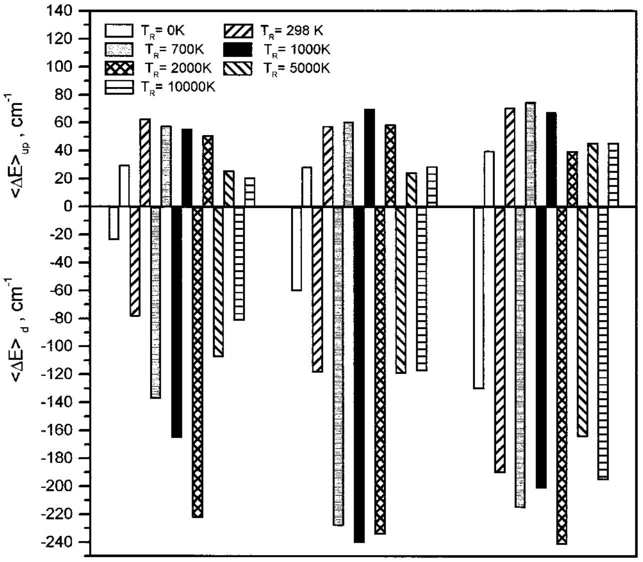

Figure 2. Average up and down energy transferred per collision with an initial vibrational energy of 50, 75, and 100 kcal/mol and different rotational temperatures, as indicated in the graph.

initial vibrational energy is 50 or 75 kcal/mol. However, at higher vibrational excitation (100 kcal/mol) deactivation prevails. These results indicate the strong tendency of molecules to reach rotational equilibrium, despite high vibrationally energy content. Thus at $T_R = 0$ K and E_V values of 50 and 75 kcal/mol, the T−R process prevails over the V−T process and causes $\langle \Delta E \rangle$ to be positive. However, at $E_V = 100$ kcal/mol, the situation reverts and, on average, deactivation takes place at all rotational energies studied.

(b) For initial rotational temperatures $0 < T_R \leq 2000$ K, increasing the rotational excitation enhances the collisional deactivation of H_2O. The nature of this effect cannot be analyzed from the present results, since rotational and vibrational energies are not properly separable. However, a plausible explanation is that the enhancement arises from an increment of the impact velocity of molecules undergoing noncollinear collisions.[34]

(c) At higher initial rotational energies ($T_R > 2000$ K), the values of average energy transferred per collision begin to decrease, at all the vibrational energies studied. This is the expected result according to the Landau−Teller theory for energy transfer, since as the rotation period becomes progressively shorter than the collision time, the inefficient adiabatic limit is reached.[35,36] A similar effect was also observed in other systems, such as SO_2 + Ar.[27]

The strong and complex dependence of $\langle \Delta E \rangle$ on rotational temperature has to be considered when comparing the results of trajectory calculations with experiments, even though that is not the aim of the present study. Trajectory calculations provide average values of energy transfer in isolated, single collisions, with the colliding pair in initially selected conditions. However, in experiments, an alteration of the rotational temperature will result in a change of the value of $\langle \Delta E \rangle$ in a subsequent collision, the sign and magnitude of which will depend on the rotational temperature regime, as our results show. This effect should be more evident in trajectory computations using the successive collisions modeling.[37] Recent calculations of energy transfer in benzene−Ar collisions have clearly shown the importance of properly considering the influence of rotational temperature.[23,26] An increase in the rotational temperature during the deactivation of highly vibrationally excited molecules is expected to occur through a collisionally assisted V−R process, as shown in SO_2 + M[38] and HgBr + M.[32]

Although the above considerations clearly indicate the role of rotational temperature, a description of the energy transfer process is better achieved by considering the up and down values. The results are presented in Figure 2 and show that rotational excitation affects both activating and deactivating collisions, but in a different way. At $E_V = 50$ kcal/mol, the values of $\langle \Delta E \rangle_{up}$ at rotational temperatures of 0 and 298 K are larger than the corresponding values of $\langle \Delta E \rangle_d$, with a maximum at $T_R = 298$ K. At higher initial vibrational excitation, $\langle \Delta E \rangle_{up}$ increases but to a smaller extent than $\langle \Delta E \rangle_d$, which is always larger. However, at the highest T_R studied, $\langle \Delta E \rangle_d$ decreases while $\langle \Delta E \rangle_{up}$ remains approximately constant. At all the initial conditions calculated, with the exception of $T_R = 0$ K, the ratio between the number of up and down collisions is approximately constant, as shown in Table 2. Then, larger values of $\langle \Delta E \rangle_d$ are not due to an increment in the number of deactivating events but to the spread of $P(E',E)$. It seems then appropriate to analyze the dependence of this spread on internal energy.

The spread of the collision transition probability function $P(E',E)$ was calculated from the second moment, according to eq 6. The results obtained for σ at the different vibrational energies and rotational temperatures computed are presented in Figure 3. In general, the spread of $P(E',E)$ increases with initial vibrational excitation, at all the rotational temperatures. However, the effect of T_R on σ is more complex. Thus σ increases in the range 0−2000 K but then decreases to reach a plateau at temperatures higher than 5000 K. Note that even though σ is calculated from the first and second moments for overall energy transferred, it follows the same behavior as $\langle \Delta E \rangle_d$. This feature is further analyzed in Section II.B.

The value obtained for $\langle \Delta E \rangle$ from the present calculations at $E_V = 100$ kcal/mol and $T_R = 0$ K are smaller than that reported in ref 20 at the same rotational and vibrational energies but with a relative translational energy three times larger than in our computations. They are also smaller than those reported by Stace and Murrel with temperature in the range 2500−10 000 K and equipartition of energy, even though on a different potential energy surface. They found that the absolute value of $\langle \Delta E \rangle$ increases with temperature in the range studied (2500−10 000 K).[21] According to our results (Figure 1), in that temperature region rotational excitation has little effect on energy relaxation, so the main influence seems to be associated

TABLE 2: Average Up, Down, and Overall Energy Transferred, $\langle\Delta E\rangle_{up}$, $\langle\Delta E\rangle_{d}$, and $\langle\Delta E\rangle$, and Fraction of Down Transitions, P_d, in Collisions of H_2O with Ar at Different Vibrational Energies, E_V, and Rotational Temperatures, T_R[a]

E_V/ kcal/mol	T_T/K	T_R/K	$\langle\Delta E\rangle_{up}$/ cm^{-1}	$\langle\Delta E\rangle_{d}$/ cm^{-1}	$\langle\Delta E\rangle$/ cm^{-1}	P_d
50	298	0	30	−24	27	0.04
75	298	0	29	−60	19	0.11
100	298	0	40	−130	−22	0.37
50	298	298	63	−78	−10	0. 52
75	298	298	58	−118	−33	0. 52
100	298	298	71	−190	−78	0. 57
50	298	700	58	−137	−47	0. 54
75	298	700	61	−228	−98	0.55
100	298	700	75	−215	−93	0. 58
50	298	1000	56	−165	−72	0. 58
75	298	1000	70	−240	−106	0. 57
100	298	1000	68	−201	−91	0. 59
50	298	2000	51	−222	−107	0. 58
75	298	2000	59	−234	−99	0. 54
100	298	2000	40	−241	−120	0. 57
50	298	5000	26	−107	−50	0.57
75	298	5000	25	−119	−64	0. 62
100	298	5000	46	−164	−82	0. 61
50	298	10000	21	−81	−38	0.58
75	298	10000	29	−117	−57	0. 59
100	298	10000	46	−195	−99	0. 60
75	1000	298	60	−144	−42	0.50
50	1000	1000	66	−162	−78	0.63
75	1000	1000	58	−227	−92	0.55
100	1000	1000	73	−242	−97	0.54

[a] $\langle\Delta E\rangle = P_{up}\langle\Delta E\rangle_{up} + P_d\langle\Delta E\rangle_d$; $P_d + P_{up} = 1$.

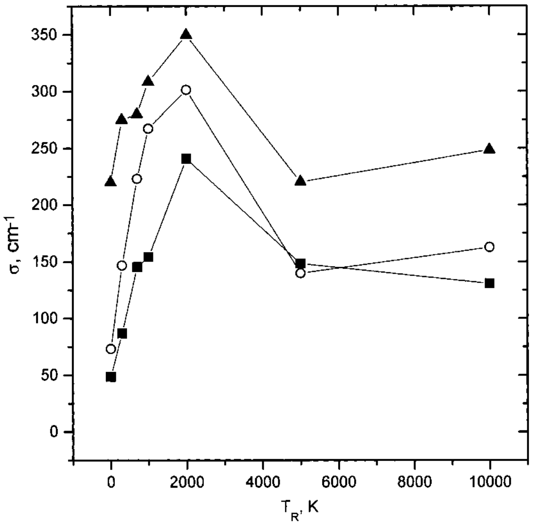

Figure 3. **3.** Spread of the distribution function for energy transfer σ as a function of the rotational temperature at three different initial vibrational energies: (■) 50 kcal/mol, (○) 75 kcal/mol, and (▲) 100 kcal/mol. The lines through the points are only to guide the eye.

with translational energy. Thus, the comparison of the values of $\langle\Delta E\rangle_d$ obtained in the calculations at $T_T = 298$ K with those at $T_T = 1000$ K, while the rotational temperature is kept at 298 K, shows an increase in the amount of energy transferred from -118 to $-$ 144 kcal/mol.

B. The Collisional Transition Probability. The cumulative distribution of ΔE was computed for each set of initial conditions, by direct count of the trajectories calculated. The results are almost continuos functions, with larger values found as the initial vibrational energy and rotational temperature increases. Some representative results are shown in Figure 4.

For the present calculations we have found that instead of using $Q(\Delta E)$ it is more convenient to compare the different results by scaling ΔE to a reduced variable, ϵ,

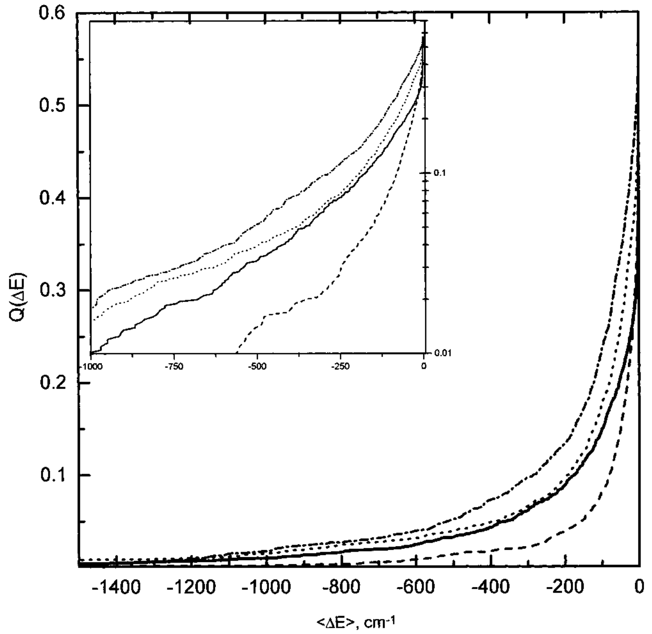

Figure 4. Cumulative down transition probability, $Q(\Delta E)$, resulting from direct counting of individual trajectories in collisions of H_2O with Ar for four representative initial conditions: (—) $E_V = 75$ kcal/mol, $T_R = 700$ K; (• • •) $E_V = 100$ kcal/mol, $T_R = 298$ K; (− −) $E_V = 50$ kcal/mol, $T_R = 10\,000$ K; (− • −) $E_V = 100$ kcal mol^{-1}, $T_R = 10\,000$ K. In the insert the same results are shown in a logarithm scale for $Q(\Delta E)$.

$$\epsilon = \frac{\Delta E}{\langle\Delta E\rangle_d} \tag{7}$$

where $\langle\Delta E\rangle_d$ is a constant for each set of trajectory calculations.

Then, from eq 4, the scaled cumulative function, $Q(\epsilon)$, results

$$Q(\epsilon) = \int_\epsilon^\infty P(\epsilon)\,d\epsilon \quad \text{for} \quad 0 \le \epsilon \le \infty \tag{8}$$

and

$$-\frac{dQ(\epsilon)}{d\epsilon} = P(\epsilon) = P(\Delta E/\langle\Delta E\rangle_d) \tag{9}$$

The value of $\langle\Delta E\rangle_d$ obtained for each of the 18 groups of 2000 trajectories computed at different initial conditions was used to calculate ϵ. Then $Q(\epsilon)$ was evaluated by counting the number of trajectories which transfer an amount of energy equal to or greater than ϵ and normalizing this count to the total number of trajectories. The trajectories computed at $T_R = 0$ K were not included in this treatment because up collisions predominate, and hence, the number of deactivating event is too sparse. Representative results obtained at $T_T = 298$ K are presented in Figure 5 and show that all the $Q(\epsilon)$ can be satisfactorily adjusted to the same biexponential function:

$$Q(\epsilon) = A\exp(-\epsilon/a) + B\exp(-\epsilon/b) \tag{10}$$

The parameters corresponding to the fit for each set of trajectories are given in Table 3. The same values are obtained, within the fitting error. Then, for the system H_2O + Ar, at $T_T = 298$ K, $Q(\epsilon)$ is a unique function that describes the behavior of all the trajectories, independently of the initial conditions,

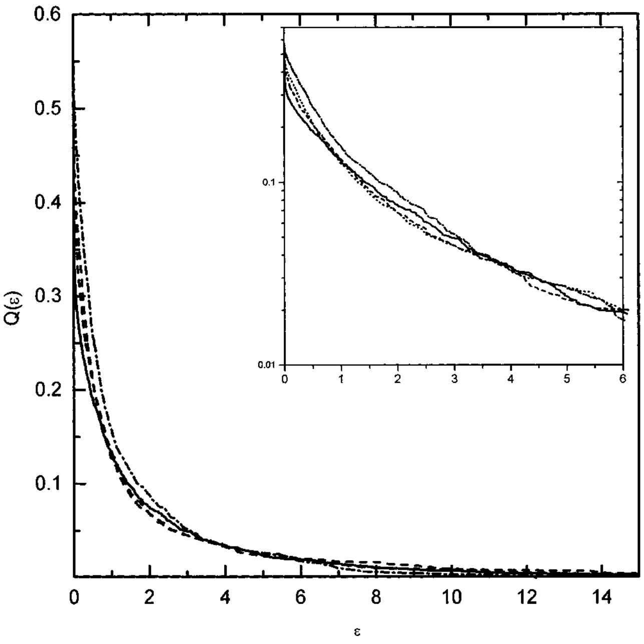

Figure 5. Parametrized cumulative down energy transfer probability $Q(\epsilon)$ for the same conditions of Figure 4.

so that a single $P(\epsilon)$ can also be obtained, using eq 9:

$$P(\epsilon) = \frac{A}{a}\exp(-\epsilon/a) + \frac{B}{b}\exp(-\epsilon/b) \tag{11}$$

From this expression, $P(E',E)$ for a single set of trajectory calculations with a specific value of $\langle \Delta E\rangle_d$ can be directly obtained, according to the following considerations:

$$P(E',E) = -\frac{dQ(\Delta E)}{d(\Delta E)} = -\frac{dQ(\epsilon)}{d(\epsilon)}\frac{d(\epsilon)}{d(\Delta E)} = \frac{P(\epsilon)}{\langle \Delta E\rangle_d} \tag{12}$$

Since the mean down energy lost in deactivating collisions is

$$\langle \Delta E\rangle_d = \frac{\int_0^\infty (E'-E)P(E',E)\,dE'}{\int_0^\infty P(E',E)} \tag{13}$$

and considering that $\langle \Delta E\rangle_d$ for a set of trajectories is a constant, substitution of eq 12 into eq 13, yields the following relation

$$\langle \Delta E\rangle_d = \frac{aA + bB}{A+B}\langle \Delta E\rangle_d \tag{14}$$

which means that

$$\frac{aA + bB}{A+B} = 1 \tag{15}$$

and also

$$A + B = \int_0^\infty P(E',E)\,dE' \tag{16}$$

From eqs 7, 11, and 12, the expression of $P(E',E)$ in terms of $\langle \Delta E\rangle_d$ is

$$P(E',E) = \frac{A}{a\langle \Delta E\rangle_d}\exp(-\langle \Delta E\rangle/a\langle \Delta E\rangle_d) + \frac{B}{b\langle \Delta E\rangle_d}\exp(-\langle \Delta E\rangle/b\langle \Delta E\rangle_d) \tag{17}$$

For the present trajectory calculations the average values of the coefficients of $Q(\epsilon)$ (Table 3) which simultaneously fit the curves shown in Figure 5 are $A = 0.37 \pm 0.09$, $B = 0.18 \pm 0.08$, $a = 0.41 \pm 0.12$, and $b = 2.5 \pm 0.8$, from which the following expression for $P(E',E)$ is obtained:

$$P(E'-E) = \frac{(0.9 \pm 0.2)}{\langle \Delta E\rangle_d}\exp\left(-\frac{\Delta E}{(0.37 \pm 0.09)\langle \Delta E\rangle_d}\right) + \frac{(0.071 \pm 0.007)}{\langle \Delta E\rangle_d}\exp\left(-\frac{\Delta E}{(2.5 \pm 0.4)\langle \Delta E\rangle_d}\right) \tag{18}$$

This universal function resumes the results of 36 000 deactivating collisional events, computed at $T_T = 298$ K. It should be noted that the existence of a unique $P(\Delta E)$ is not apparent from an analysis of the histograms, since each set of trajectories yields different functions with seemingly unrelated parameters.

As mentioned above, an important point of the present results relates to the dependence of σ on $\langle \Delta E\rangle$ and, more specifically, on $\langle \Delta E\rangle_d$.

For $P(E',E)$ given by eq 17, $\langle \Delta E^2\rangle_d$ results:

$$\langle \Delta E^2\rangle_d = \frac{\int_0^\infty (E'-E)^2 P(E',E)\,dE'}{\int_0^\infty P(E',E)} = \left(\frac{Aa^2 + Bb^2}{A+B}\right)\langle \Delta E\rangle_d^{\,2} \tag{19}$$

Then, for down collisions

$$\sigma_d = (\langle \Delta E^2\rangle_d - \langle \Delta E\rangle_d^{\,2})^{1/2} \tag{20}$$

and replacing eq 19 in eq 20, for the present results we obtain:

$$\sigma = \left(\frac{Aa^2 + Bb^2}{A+B} - 1\right)^{1/2}\langle \Delta E\rangle_d = 1.34\langle \Delta E\rangle_d \tag{21}$$

Then the spread of the down wing of $P(E',E)$ is linearly dependent on the first moment $\langle \Delta E\rangle_d$.

Regarding the calculations at $T_T = 1000$ K, the results obtained required the use of a three-exponential function to properly reproduce $Q(\epsilon)$. The calculated coefficients of the fits are presented in Table 4. The main characteristic is the appearance of a very weak component that could not be assigned to any elastic contribution. However, the reason for this effect is not clear, since the cumulative functions obtained at 298 and 1000 K, are approximately the same. More detailed studies of the influence of the translational temperature and the shape of $P(E',E)$ are required to further clarify these points and are presently being carried out.

The transition probabilities obtained must be normalized and fulfill detailed balance, which relates down and up transition probabilities, to ensure that the thermal equilibrium energy transfer processes do not alter the Boltzmann distribution, i.e.,

$$f(E)\,P(E',E) = f(E')\,P(E,E') \tag{22}$$

The normalization condition is imposed by eqs 15 and 16, but detailed balance is a more difficult problem, since in most of the calculations the rotational and the translational temper-

TABLE 3: Parameters Corresponding to the Fit of $Q(\epsilon)$ to a Double Exponential Function[a] for Different Initial Vibrational Energies and Rotational Temperatures

E_V/kcal/mol	T_T/K	T_R/K	A	a	B	b
50	298	298	0.35 ± 0.03	0.60 ± 0.02	0.173 ± 0.006	1.84 ± 0.02
75	298	298	0.42 ± 0.04	0.60 ± 0.01	0.10 ± 0.004	2.6 + 0.1
100	298	298	0.43 ± 0.03	0.38 ± 0.08	0.14 ± 0.002	2.75 ± 0.08
50	298	700	0.13 ± 0.06	0.11 ± 0.02	0.43 ± 0.007	1.2 + 0.1
75	298	700	0.33 ± 0.03	0.37 ± 0.01	0.21 ± 0.003	1.78 ± 0.07
100	298	700	0.39 ± 0.02	0.33 ± 0.01	0.19 ± 0.002	2.21 ± 0.05
50	298	1000	0.15 ± 0.7	0.18 ± 0.03	0.32 ± 0.03	1.2 + 0.2
75	298	1000	0.36 ± 0.04	0.39 ± 0.01	0.201 ± 0.004	2.1 + 0.1
100	298	1000	0.39 ± 0.05	0.30 ± 0.01	0.199 ± 0.003	2.21 ± 0.02
50	298	2000	0.41 ± 0.03	0.50 ± 0.01	0.123 ± 0.004	3.60 ± 0.09
75	298	2000	0.37 ± 0.04	0.45 ± 0.02	0.128 ± 0.004	3.6 + 0.1
100	298	2000	0.43 ± 0.05	0.40 ± 0.01	0.134 ± 0.004	3.5 + 0.1
50	298	5000	0. 41 ± 0.05	0.47 ± 0.03	0.147 ± 0.005	3.0 + 0.3
75	298	5000	0.448 ± 0.002	0.46 ± 0.01	0.160 ± 0.002	2.47 ± 0.03
100	298	5000	0.357 ± 0.001	0.50 ± 0.03	0.144 ± 0.002	2.90 ± 0.03
50	298	10000	0.46 ± 0.05	0.53 ± 0.01	0.109 ± 0.002	3.34 ± 0.07
75	298	10000	0.437 ± 0.002	0.42 ± 0.01	0.172 ± 0.002	3.00 ± 0.03
100	298	10000	0. 34 ± 0.04	0.47 ± 0.02	0.170 ± 0.002	2.57 ± 0.05
75	1000	298	0. 40 ± 0.03	0.57 ± 0.03	0.090 ± 0.003	2.95 ± 0.08

[a] $Q(\epsilon) = A \exp(-\epsilon/a) + B \exp(-\epsilon/b)$.

TABLE 4: Parameters Corresponding to the Fit of $Q(\epsilon)$ to a Triple Exponential Function[a] for Different Initial Vibrational Energies at 1000 K

E_V/kcal/mol	T_T/K	T_R/K	A	a	B	b	C	c
50	1000	1000	0.16 ± 0.02	0.02 ± 0.01	0.30 ± 0.03	0.91 ± 0.02	0.201 ± 0.006	1.75 ± 0.02
75	1000	1000	0.16 ± 0.01	0.070 ± 0.002	0.38 ± 0.01	1.01 ± 0.01	0.022 ± 0.004	7.8 + 0.5
100	1000	1000	0.26 ± 0.01	0.19 ± 0.02	0.25 ± 0.02	1.12 ± 0.01	0.054 ± 0.002	4.2 + 0.3

[a] $Q(\epsilon) = A \exp(-\epsilon/a) + B \exp(-\epsilon/b) + B \exp(-\epsilon/c)$.

atures are different. For these reason, we have verified the detailed balance condition (eq 22) for those computations with $T_R = T_T$ at 298 and 1000 K. At these two temperatures the probabilities of up transitions obtained from the trajectory calculations were compared with the values that resulted from eq 22. The ratio of both probabilities was always between 0.8 and 1.3, so the agreement can be considered satisfactory.

IV. Conclusions

The energy transfer process in the system $H_2O + Ar$ was simulated by classical trajectory calculations. The initial state was characterized by vibrational energies of 50, 75, and 100 kcal/mol, rotational temperatures in the range 0−10 000 K, and translational temperature of 298 and 1000 K. The absolute value of $\langle \Delta E \rangle$ increases with vibrational excitation at all the rotational temperatures studied, with the exception of the trajectories computed at $T_R = 0$ K. In addition, both $\langle \Delta E \rangle_{up}$ and $\langle \Delta E \rangle_d$ increase with vibrational excitation. The effect of rotational temperature is more complex, and three different T_R regimes are observed: 0 K, 298−2000 K, and above 2000 K. At $T_R = 0$ K, collisions at 50 and 75 kcal/mol result in activation of the water molecule. However, at 100 kcal/mol, deactivation takes place.

In the intermediate rotational temperature range the magnitude of the average energy transferred increases with T_R and decreases to nearly constant values at higher temperatures. This effect is in agreement with Landau−Teller theory.

The spread of $P(E', E)$ increases with vibrational energy and depends in a complex way on T_R. However, it is shown that σ varies linearly with $\langle \Delta E \rangle_d$.

Instead of using the histogram method, $P(E', E)$ is obtained from the cumulative count of trajectories that transfer an amount of energy equal to or greater than a certain value, ΔE. This cumulative function, $Q(\Delta E)$, is then scaled with $\langle \Delta E \rangle_d$ to a new function, $Q(\epsilon)$, with $\epsilon = \Delta E/\langle \Delta E \rangle_d$. A single $Q(\epsilon)$ fits all the trajectories computed with different initial conditions. Then $P(E', E)$ is calculated by differentiating $Q(\epsilon)$ to yield a function that depends only on $\langle \Delta E \rangle_d$.

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