

may be due to a solvent reorganization about the newly formed proton causing some amount of charge separation in the ion pair. Similar processes occur in solution on the nanosecond timescale.<sup>3,10</sup> The geometry of the reorganized solvated proton should have a better Franck–Condon overlap with the cluster ion potential and therefore an increased cross-section ( $\sigma_s$ ) for detection of  $M_nH^+$  relative to the initially formed bound ion pair ( $\sigma_p$ ). Calculated traces indeed show that the formation curves for  $M_nH^+$  fit well to a biexponential function with the aforementioned long-time component of 0.5 ns and a ratio of cross sections of  $\sigma_s/\sigma_p = 1.6$  (cf. Fig. 1,  $n = 4$ , solid line).

In conclusion, a well-defined acid–base reaction was studied as a function of incremental solvation in molecular clusters and has provided new detail regarding the role of solvation on a single-molecule basis.

*Note added in proof:* Since this paper went to proof, a very relevant picosecond mass-selective study was published by Breen, *et al.*<sup>15</sup> for the system 1-naphthol\*-(NH<sub>3</sub>)<sub>n</sub>. Their results also show a distinct solvent size threshold effect for proton transfer.

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## NOTES

### The origin of small and large molecule behavior in the vibrational relaxation of highly excited molecules

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The internal energy dependence of the vibrational relaxation of highly excited molecules has been a subject of continuing interest for the last decade. A recent review<sup>1</sup> highlighted the qualitatively different behavior of diatomic and polyatomic molecules. In the former case the average amount of energy transferred per collision,  $\langle\Delta E\rangle$ , has been observed to vary as a power of the average vibrational energy of the excited molecule  $\langle E_v \rangle$ ,

$$\langle\Delta E\rangle = -C\langle E_v \rangle^n, \quad (1)$$

where  $n$  is a constant greater than one. In contrast, polyatomic molecules tend to follow an exponential (or possibly slower than exponential) decay law with  $n \approx 1$ .

The purpose of this note is to inquire into the underlying physical difference between diatomic and polyatomic mole-

cules producing these two types of behavior. An insightful paper published by Nesbitt and Hynes<sup>2</sup> points to a possible answer. Nesbitt and Hynes used classical trajectories to calculate the relaxation rate for collinear collisions between an atom and a Morse oscillator with a repulsive exponential potential. They demonstrated that for adiabatic collisions a modified power law is obeyed, whereas exponential decay ( $n \lesssim 1$ ) results in the impulsive limit. The modification to Eq. (1) is that  $\langle\Delta E\rangle$  scaled by the local oscillator frequency,  $\omega(E_v)$ , varies as a power of the vibrational quantum number  $v$ . Their findings have been confirmed in a number of theoretical studies with varying degrees of approximation.<sup>3–5</sup> The outcome of these studies is that a linear dependence of  $\langle\Delta E\rangle$  on  $\langle E_v \rangle$  is characteristic of hard sphere scattering,<sup>2,3</sup> whereas the adiabatic power law can be derived

from classical energy scaling.<sup>5</sup> The latter result is actually a power series in  $v$ , with the power law being only a rough numerical fit to a polynomial function.

The logical connection between the scaling rules of Nesbitt and Hynes and the experimental measurements of small and large molecule relaxation is that diatomic molecules relax adiabatically while polyatomic molecules relax impulsively. Why should this be so? The unique property of a large molecule is that it has many vibrational modes, some of which may have very low frequencies. If the vibrational modes are all strongly coupled together, the lowest frequency one can act as a doorway mode for all of the others. Because of its low frequency, this doorway mode relaxes impulsively. In contrast, the higher frequencies characteristic of most diatomic molecules result in adiabatic relaxation at room temperature.

The distinction between adiabatic and impulsive behavior is quantified by the adiabaticity parameter<sup>6</sup>

$$A = 2\pi L\omega/V, \quad (2)$$

where  $L$  is the range of the potential and  $V$  is the relative collision velocity. Eq. (2) shows that our explanation may be tested experimentally by varying either the isotopic frequency of the excited molecule or the relative collision velocity. Either reducing  $\omega$  or increasing  $V$  brings  $A$  closer to the impulsive limit and should therefore decrease the value of  $n$ .

Although the first test (reducing  $\omega$ ) is imperfect since other processes (e.g., rotational and intermolecular  $VV$  energy transfer) may also occur, it nevertheless is a useful indicator. Collected in Table I are examples taken from the database in Ref. 1 comparing the values of  $n$  for the relaxation of HF and DF by five common collision partners.<sup>7-12</sup> With  $N_2$ ,  $H_2$ , and  $CO_2$  baths  $n$  is clearly smaller for DF relaxation, whereas for HF and DF baths the effect is only marginally in the expected direction. A possible reason for the small effect in the last two cases may be that rotational interactions, which are known to be important in the self-relaxation of HF, mask the effect of vibrational adiabaticity.

A more stringent test is to vary the collision velocity, by either increasing  $V$  to bring diatomic molecules into the impulsive regime or decreasing  $V$  to bring polyatomic molecules into the adiabatic regime. The former could be accomplished by using seeded crossed molecular beams,<sup>13</sup> while

the latter could be achieved in a single molecular beam, using isentropic expansion to produce low transverse velocities.<sup>14</sup> Abundant evidence for impulsive excitation of ground state  $I_2$  by energetic He atoms is seen in the product vibrational state distribution reported by Gentry and co-workers.<sup>13</sup> Evidence of impulsive deexcitation of  $I_2(B, v = 15, 25, 35)$  by He may be found in the crossed beam study of Parmenter and co-workers.<sup>15</sup> The low reduced mass, high collision energy ( $720 \text{ cm}^{-1}$ ), and low vibrational frequency of  $I_2(B)$  ( $126 \text{ cm}^{-1}$ ) all contribute to reducing the value of  $A$ .<sup>16</sup> Using depletion of the parent beam to normalize their relative cross sections, they find that  $\langle \Delta E \rangle / \hbar\omega$  is insensitive to  $E_v$ , and that  $n$  is definitely not greater than one.<sup>17</sup>

A necessary condition for large molecule behavior is strong coupling for all the vibrational modes. Three instances where this condition does not appear to be met are the relaxation of  $SF_6$ ,<sup>18</sup>  $SiF_4$ ,<sup>19</sup> and  $CF_3I$ <sup>20</sup> by Ar at low vibrational energy. In all three cases  $n = 3/2$  was observed below the onset of the quasicontinuum, with exponential decay occurring at higher energy. Each of the molecules has a low-lying bottleneck and displays a bimodal vibrational state distribution produced by IR multiphoton excitation.<sup>21-24</sup> Both effects are indicative of weak mode coupling at low energies. The nonexponential decay observed at low energy may therefore be due to weak coupling of the low and high frequency modes.<sup>25</sup>

The complexity of the mechanism for intermediate sized molecules is seen in the observation of Abel *et al.*<sup>20</sup> that  $CF_3I$  relaxation by propane and octane is exponential at all energies. An explanation consistent with our approach is that for the hydrocarbons long range attractive forces increase the steepness of the potential energy curve in the region of the classical turning point.<sup>26</sup> Collisions in this case are more impulsive than with Ar, resulting in more efficient internal coupling of the vibrational modes.

In conclusion, we propose that the power law behavior observed for diatomic molecules is caused by an adiabatic mechanism, whereas the exponential decay found for polyatomic molecules is due to impulsive interactions. Polyatomic molecules relax impulsively because low frequency modes act as doorway states for the rest of the molecules. In contrast, all of the diatomic molecules that have been studied in bulk experiments have high frequencies and therefore relax adiabatically at room temperature. An experimental test

TABLE I. Power law behavior for HF and DF relaxation.

Collision pair <sup>a</sup>	$n^b$	Ref.	Collision pair	$n$	Ref.
HF(1-7) + HF	$2.7 \pm 0.1$	7	DF(1-3) + HF	$1.9 \pm 0.1$	8
HF(5-7) + DF	$2.76 \pm 0.02$	9	DF(1-3, 9-12) + HF	$2.6 \pm 0.1$	8, 9
HF(5-7) + $N_2$	$8.3 \pm 0.3$	10	DF(9-12) + DF	$2.7 \pm 0.3$	9
HF(1, 3, 4, 6) + $N_2$	$3.1 \pm 0.3$	12	DF(9-12) + $N_2$	$6.6 \pm 0.6$	11
HF(1, 3-7) + $N_2$	$3.7 \pm 0.5$	10, 12	DF(1-4) + $N_2$	$1.87 \pm 0.05$	8
HF(5-7) + $H_2$	$5.0 \pm 0.6$	10	DF(1-4, 9-12) + $N_2$	$3.1 \pm 0.3$	8, 11
HF(5-7) + $CO_2$	$2.8 \pm 0.3$	10	DF(1-4) + $H_2$	$2.0 \pm 0.1$	8
			DF(1-3) + $CO_2$	$2.1 \pm 0.1$	8
			DF(9-12) + $CO_2$	$1.1 \pm 0.1$	11
			DF(1-3, 9-12) + $CO_2$	$1.6 \pm 0.1$	8, 11

<sup>a</sup> Vibrational quantum numbers are listed in parentheses.

<sup>b</sup> Calculated from a least square log-log fit of the rate constant vs quantum number.

of the transition between these two extreme types of behavior is presently feasible.

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## The ice/water interface: A molecular dynamics simulation using the simple point charge model

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Previously<sup>1,2</sup> we have simulated the basal plane of the ice/water interface. Measured properties of the interface include the density profile, diffusion constants, and molecular orientation as a function of a coordinate normal to the interfacial plane. These studies of the TIP4P model<sup>3,4</sup> provide a detailed picture of the change in microscopic properties as the interface is traversed from the bulk crystal to the bulk melt. Finite size effects were also investigated (in part) by increasing the interfacial surface by a factor of four (and the number of water molecules from 1440 to 8064): no measurable differences were observed.

In this note the ice/water interface is investigated using the simple point charge (SPC) model<sup>5</sup> for water. Molecular dynamics (NVE) simulations demonstrate that the model interface is stable on the time scale of at least 300 ps. The density profile and mean square displacement of molecules are measured, and the results are nearly identical to those obtained earlier using the TIP4P model for water. The model dependence of the observed interfacial properties is studied to increase confidence in the results as representative of the true physical interface, rather than artifacts of a particular water model. The lack of change is additional evidence

that the properties measured in the simulation are intrinsic to the ice/water interface, and do not depend sensitively on the particular model potentials employed.

A byproduct of this simulation is the recognition that the apparent melting point of the model ice  $1h$  differs between the TIP4P and SPC models.<sup>3</sup> The SPC model is a three-center model of water which models bulk water well. At  $25^\circ\text{C}$  and  $1 \text{ g/cm}^3$ , the pressure of SPC water is not as accurate as TIP4P water. The principal difference between the SPC and the (four center) TIP4P model is that the negative charge in the TIP4P model is located on the H-O-H bisector but *not* at the oxygen center. Details of the NVE molecular dynamics are identical to previous work<sup>1,2</sup> and only essential items are included.

We simulate 1440 water molecules in a rectangular parallelepiped  $23.2 \times 17.9 \times 106.3 \text{ \AA}^3$ . To construct the ice/water interface, the final configuration from a previous<sup>1</sup> simulation was taken as the starting point. To obtain a starting coordinate file for the SPC model, the coordinates for the TIP4P atoms were changed: The O-H bond lengths were adjusted along the existing directions and the bond angle was adjusted symmetrically about the H-O-H bisector. This dis-