FIG. 2. Dependence of $J_1(\omega_0)$ on $(\Delta\nu)^2 \nu_0^{-1/2}$ for the methylene deuterons in the octyl chain of 40.8. Different symbols denote data at 9.2 and 38.4 MHz for each methylene group as indicated in the accompanying nematic phase spectrum. The linear dependence of J_1 upon $(\Delta\nu)^2 \nu_0^{-1/2}$ for all methylenes at 64.5 (nematic) and 58.3 °C (high temperature end of the S_A phase) is indicated by heavy solid lines. At lower temperatures in the smectic A phase and throughout the smectic B phase, the 38.4 MHz data (stippled lines) fall above the 9.2 MHz data (light solid lines).

liquid crystals with underlying smectic phases.[16-20] The extent of the drop in J_2 for the chain deuterons varies with carbon number and may be a direct consequence of

the influence of static order on the spectral density functions[20] for rotational diffusion, but it is also possible that relatively large angle, coherent fluctuations of the director just below T_{IN} contribute to J_2. A more quantitative analysis of this problem and other aspects of the 40.8 relaxation data is in progress.

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Unimolecular reactions in condensed phases: Is the turnover in the viscosity dependence of the rate observable?

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Theoretical studies[1-5] of unimolecular rate processes in condensed phases predict an initial growth of the rate with solvent viscosity at very low viscosity, then a turnover and a decreasing rate with further increase of viscosity. On the experimental side, Hasha et al.[6] have observed this turnover in the rate of ring inversion in cyclohexane solutions. In contrast, such behavior is not observed in

the photochemical isomerization of diphenyl butadiene (DPB) even going in solvent viscosity down to 0.04 cp,[7] and the results may be fitted to the non-Markovian version[3,8] of Kramers intermediate and high viscosity regime. Courtney et al.[9] have recently observed that the rate of DPB photoisomerization is approximately the same in room temperature liquid ethane and in an

isolated (in supersonic jet) molecule having excess energy equal to the thermal energy. This implies rapid intramolecular energy transfer between reactive and nonreactive modes.

It has been argued[7] that failure to observe the turnover predicted by the one-dimensional Kramers theory may result from the rapid energy relaxation in large molecules. Here I quantify this idea within our non-Markovian theory of activated rate processes.[3] The final result is a generalization of the Kramers rate expression which contains the number N of strongly interacting modes as an additional parameter.

My starting point is a set of generalized Langevin equations for the atomic (mass weighted) coordinates[8]

$$\ddot{X}_a = -\frac{\partial U}{\partial X_a} - \int_0^t dt \sum_{b=1}^N Z_{ab}(t-\tau)\dot{X}_b(\tau) + R_a(t), \qquad (1)$$

U is the intramolecular potential and $R_a(t)$ and $Z_{ab}(t)$ are the medium induced random force and friction kernel related by $\langle R_a(t)R_b(t')\rangle = Z_{ab}(t-t')/\beta$ ($\beta = 1/k_B T$). In this multidimensional system the barrier B is a saddle point. I now investigate separately the dynamics near the barrier and in the well below it.

Barrier dynamics. Linearizing and diagonalizing the potential about B we can identify the (assumed single) reactive mode R of imaginary frequency $i\omega_R$. Following Ref. 8 we can obtain a single generalized Langevin equation for the R mode, with friction kernel $Z_R(t)$ and random force $\rho_R(t)$ given in terms of the atomic quantities $Z_{ab}(t)$ and $R_a(t)$. The one dimensional theory[3] now gives the nonequilibrium steady state distribution of the R mode position (x) and velocity (v) near the barrier

$$P^{(B)}(x,v) = \frac{Q_{N-1}^{(B)}}{Q_N} e^{-\beta E(x,v)} F\left[\sqrt{\frac{\pi}{2\bar{\alpha}\beta}} + \int_0^{v-|\Gamma|x} dz\, e^{-1/2\beta\bar{\alpha}z^2} \right]. \qquad (2)$$

The corresponding net flux is

$$j^{(B)} = \int_{-\infty}^{\infty} dv\, P^{(B)}(x,v)$$
$$= (Q_{N-1}^{(B)}/Q_N)F\beta^{-3/2}\sqrt{2\pi/(\bar{\alpha}+1)}e^{-\beta E_B}.$$

Here Q_N is the molecular partition function while $Q_{N-1}^{(B)}$ is the partition function for the $N-1$ nonreactive (NR) modes when the R mode is near B. $E(x,v)$ is the reactive mode energy and E_B is its value at the reaction threshold. $\bar{\alpha}$ and Γ are given in terms of ω_R and Z_R by Eqs. (3.11) and (1.20) of Ref. 3. F is determined below.

To obtain Eqs. (2) and (3) I assumed that near B the NR modes are in thermal equilibrium. This is reasonable because near B they are not coupled to the R mode and are therefore not affected by the reactive flux. The assumption[1] that equilibrium exists also deeper in the well determines F and the barrier dominated rate $k^{(B)}$,

$$k^{(B)} = \frac{Q_{N-1}^{(B)}}{2\pi\hbar\beta Q_N}\sqrt{\frac{\bar{\alpha}}{\bar{\alpha}+1}}e^{-\beta E_B} \qquad (3)$$

which was obtained previously.[8] I now consider the nonequilibrium well dynamics.

Well dynamics. I assume that the reactive mode maintains its identity and that its energy contents may be approximately defined also deeper below the barrier region. However the normal modes (defined to be uncoupled by the potential at the barrier) are now strongly mixed. I therefore assume fast energy transfer between them and take $P^{(W)}(E|E_T)$, the probability to find energy E in the reaction coordinate given a total molecular energy E_T, to be

$$P^{(W)}(E|E_T) = [\hbar\omega_R(E)]^{-1}\rho_{N-1}(E_T-E)/\rho_N(E).$$

ρ_{N-1} and ρ_N are density of states for the $N-1$ nonreactive mode species and for the entire molecule respectively. I also calculate the steady state distribution $P_M^{(W)}(E_T)$ for the total molecular energy by extending to many dimensions the formalism of Ref. 3. The probability $P^{(W)}(E)$ that the reactive mode contains energy E is then obtained from

$$P^{(W)}(E) = \int_0^{\infty} dE_T P_M^{(W)}(E_T)P^{(W)}(E|E_T).$$

This finally yields

$$P^{(W)}(E) \cong \frac{Q_{N-1}(E)e^{-\beta E}}{\hbar\omega_R(E)Q_N}\left[A_1 + A_2 \int_E^{E_1} dE' \right.$$
$$\left. \times e^{\beta(E'+\bar{\epsilon})}/D(E'+\bar{\epsilon}) \right] \qquad (4)$$

with the associated flux along the energy axis $j^{(W)} = A_2/(Q_N\beta)$. In Eq. (4) A_1, A_2, and E_1 (only two of which are independent) are parameters to be determined, $\bar{\epsilon} = (N-1)/\beta$ and $D(E) = \rho_N(E)k_{VR}(E)E$. $k_{VR}(E)$ is the relaxation rate for the total molecular vibrational energy and may be shown, using Eq. (1), to be given by

$$k_{VR}(E) = E^{-1}\int_0^{\infty} dt \sum_{a,b=1}^N Z_{ab}(t)[\overline{\dot{X}_a(t)\dot{X}_b(0)}]_E,$$

where the average is over initial conditions and where the time evolution of $X_a(t)$ is calculated for the free molecule at total energy E.

Next I follow the procedure of Ref. 3 to join together the barrier (2) and well (4) distributions. E_1 is chosen to be the joining energy, such that the distributions (2) and (4) and their energy derivatives are equal at the point ($E = E_1$, $v = 0$). These, together with flux conservation, $j^{(B)} = j^{(W)}$, and the normalization of the overall distribution in the reactant space determine the parameters A_1, A_2, E_1, and F and yield the rate k ($=j^{(B)} = j^{(W)}$) in the form

$$k = [(\eta k^{(B)})^{-1} + \tau]^{-1}. \qquad (5)$$

In the general case η and τ are given as integrals over energy of functions involving $D(E)$, $\rho_N(E)$, $e^{-\beta E}$, and $\omega_R(E)$. To simplify the present discussion I consider only

the limit of large molecules and deep wells (N, $\beta E_B \gg 1$). In this case I get $\eta = 1$ and $\tau \sim Q_N e^{\beta(E_B + \bar\epsilon)}/D(E_B + \bar\epsilon)$. Using the classical expressions $Q_N = (\beta\hbar\omega)^{-N}$ and $\rho_N(E) = (E/\hbar\omega)^{N-1}/[\hbar\omega(N-1)!]$ then leads to

$$\tau \simeq [k_{VR}(E_B + \bar\epsilon)]^{-1} \exp[\beta E_B - N \ln(1 + \beta E_B/N)]. \quad (6)$$

Equations (3), (5), and (6) give an explicit dependence of the reaction rate k on the number of strongly coupled modes N (assuming that the reaction coordinate is one of these modes. Other cases are possible, see Ref. 10). These results (and the more general expressions to be presented elsewhere) thus combine the Kramers theory which considers energy pumping and barrier crossing dynamics and the RRKM theory which assumes rapid intramolecular energy relaxation.

If $\tau > (k^{(B)})^{-1}$ the reaction rate k is dominated by the energy pumping associated with k_{VR} which increases with the solvent friction. As long as $\tau \ll (k^{(B)})^{-1}$ the rate is dominated by the barrier dynamics and increases toward its transition state value for decreasing solvent viscosity. Equation (6) indicates that for large N the second situation prevails and that the turnover region $[\tau \sim (k^{(B)})^{-1}]$ will be difficult to access even for very low viscosities. This results from both the explicit N dependence of Eq. (6) and from the larger k_{VR} associated with larger molecules. Thus either rapid intramolecular energy redistribution between many modes or efficient intermolecular energy relaxation makes the barrier dynamics dominant and the turnover region inaccesible.

Obviously well dynamics (energy pumping) becomes the rate limiting process for $k_{VR} \rightarrow 0$ which may be achieved in the gas phase. Experiments that go continuously from liquid to low pressure gas phase (above the solvent critical point) and follow the turnover behavior of different molecules are highly desirable.

After this paper was submitted for publication I learned of two other works by Borkovec and Berne [J. Chem. Phys. (in press)] and Zawadzki and Hynes [Chem. Phys. Lett. (in press)] which reach similar conclusions concerning the viscosity dependence of activated rate processes in polyatomic molecules.

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Entropy, Baierlein's theorem, and spin-polarized hydrogen[a)]

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At low temperature and density and even if statistics are ignored, bulk gaseous spin-polarized hydrogen is shown to invalidate the conjecture of Baierlein that the Gibbs entropy of an ideal gas when pair-wise, velocity-independent interactions are assumed to be extant.

Spin-polarized hydrogen, H↓, has been of great interest to condensed matter physicists for a number of years now because of its extreme quantal behavior.[1] Thus it is predicted to have a ground state which is a gas at zero temperature and it is expected to exhibit Bose–Einstein condensation to become a superfluid gas. In addition, there should be diffractive features in its transport coefficients[2] and recently collective oscillatory perturbations of the nuclear spin magnetization have been discovered in samples of stable H↓.[3]

In this brief report, I present another astounding property of this spin-polarized quantum system. I have used the phase shifts and second virial coefficients computed in Ref. 4 for H↓ and its admixtures with the isotopes of helium to derive the imperfection entropy per particle, and then to show that gaseous H↓, H↓–^{3}He, and H↓–^{4}He are three-dimensional systems which violate Baierlein's theorem on entropy even when quantum

statistics are "switched off," the first time that physical as opposed to model systems have been demonstrated to do so.[5-7]

I begin by recounting the theorem.[5] It states that the Gibbs entropy for a system of free particles at density ρ and absolute temperature T, $S(K, \rho, T)$, is greater than that for the same system with arbitrary velocity-independent interactions added, $S(K + V, \rho, T)$:

$$S(K + V, \rho, T) \le S(K, \rho, T).$$

In particular, for a gas of N particles with pair potentials, at low temperature and for small density, the theorem has been shown[6] to assume the form:

$$\partial(TB - TB_0)/\partial T \le 0 \text{ for identical particles,}$$

where B is the second virial coefficient of the particles while B_0 is the second virial coefficient of the ideal