

of higher order are also ruled out for the same thermodynamic considerations and thus remain the  $C + NO \rightarrow CN + O$  ( $\Delta\epsilon_0 = -1.35$  eV) and  $C_2 + NO \rightarrow CN + CO$  ( $\Delta\epsilon_0 = -6.4$  eV) reactions. The former reaction with 0.28 eV of additional kinetic energy sets an excitation limit on  $CN(X^2\Sigma^+)$  at  $v'' = 6, K'' = 28$ . Observation of the (3-4) bandhead corresponding to an appreciable fraction of radicals with less than 0.5 eV available in kinetic energy of separation is consistent with that limit. Contrarily, the latter reaction is expected to result in a much higher vibrational excitation and to give rise to the  $CN(B-X)$  chemiluminescence.<sup>4</sup> Furthermore, in our conditions of expansion and cooling,  $C_2$  radicals are mainly found associated into clusters. These clusters, of van der Waals type:  $C_2-X$  ( $X = Ar$  or  $C_2$ ), observed by LIF on the  $\Delta v = 0$  sequence of the  $C_2$  Swan band system, are of quite different nature and, particularly, much smaller than the  $C_n$  and  $C_{2n}$  clusters observed by Rohlfling *et al.*<sup>5</sup> The reactivity of the  $C_2-X$  adducts with NO is unknown, but the chemiluminescence of  $CN(B^2\Sigma^+)$  is detected only when free  $C_2$  ( $a^3\Pi_u$ ) radicals are present. This can be obtained when degrading the cooling of the carbon beam by modifying the triggering delay between the excimer and the pulsed valve. However, in that case, no significant modification of the  $CN(X^2\Sigma^+)$  excitation spectrum is noticed. Moreover, the LIF signal intensity is not proportional to the  $CN(B^2\Sigma^+)$  chemiluminescent signal. These combined observations demonstrate that  $C_2$  reaction does not contribute significantly to the  $CN(X^2\Sigma^+)$  excitation spectrum.

Partial dynamical information on the  $C + NO$  reaction has been previously obtained by two other groups. Jackson *et al.*<sup>6</sup> produced C atoms by flash photolysis of  $C_3O_2$  in a static cell and detected  $CN v'' = 0$  and 1. A Boltzmann fit of approximately 800 K was deduced for the rotational distribution in  $v'' = 0$ . Krause,<sup>7</sup> in a beam-gas experiment with a

carbon beam produced by a graphite evaporation source operated up to 3500 K detected  $CN v'' = 0-3$ , with again a Boltzmann distribution of 800 K for the  $K'' > 7$  rotational levels of  $v'' = 0$ . The fact that we are able to detect the  $v'' = 4$  vibrational level at  $E = 0.28$  eV of kinetic energy, whereas this was not seen at  $\bar{E} = 0.7$  eV in the beam-cell experiment, is certainly due to a higher signal-to-noise ratio in our case. Even better signal-to-noise ratio is expected in future experiments by increasing the concentration of carbon atoms. Indeed, in this preliminary step, the energy deposited on the carbon rod by the vaporization laser was only 2-3 mJ.

To illustrate the possibilities of this pulsed crossed beam apparatus, we show on Fig. 1(b) a LIF spectrum of  $CN(X^2\Sigma^+)$  radicals produced by the reaction  $C + N_2O \rightarrow CN + NO$  ( $\Delta\epsilon_0 = -2.90$  eV) at 0.37 eV of relative kinetic energy of reactants. Although quantitative information is not derived from such data, it shows clearly a population inversion in the vibrational distribution with a maximum around  $v'' = 4$ , result which was previously found by our group with the  $C + N_2O$  reaction produced in bulk conditions at 300 K.<sup>8</sup>

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## Shortcomings of current theories of non-Markovian activated rate processes<sup>a)</sup>

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(Received 23 April 1985; accepted 10 July 1985)

The calculation of barrier crossing rate constants is an important problem in chemical physics. Recent work has focused on the non-Markovian effects where a particle (of unit mass) is described by a generalized Langevin equation<sup>1-7</sup>

$$\ddot{x} = -\frac{\partial U(x)}{\partial x} - \int_0^t dt' \zeta(t-t')\dot{x}(t') + R(t), \quad (1)$$

where the random force  $R(t)$  satisfies the fluctuation-dissipation theorem and  $U(x)$  is a symmetric double well potential

with energy barrier  $\beta Q$  in units of  $k_B T$ .

If the dynamics in the *intermediate and overdamped regime* is solely determined by the potential near the top of the barrier one can approximate the potential by an inverted parabola. As first shown by Grote and Hynes<sup>1,2</sup> the rate constant for this case is

$$k_{GH} \approx k_{TST} \frac{\lambda}{\omega_B}, \quad (2)$$

where  $\omega_B$  is the barrier frequency,  $k_{TST} = (\omega_0/2\pi)e^{-\beta Q}$  is

the transition state rate constant,  $\omega_0$  is the well frequency, and  $\lambda$  is the largest positive root of

$$\lambda^2 + \lambda \hat{\zeta}(\lambda) = \omega_B^2, \quad (3)$$

where  $\hat{\zeta}(s)$  is the Laplace transform of the time dependent friction kernel  $\zeta(t)$ .

In the *underdamped regime* the energy diffusion mechanism becomes rate limiting<sup>3-5</sup> and the rate constant is approximately given by

$$k_{ED} \simeq \text{Re} \hat{\zeta}(-i\omega_0) \frac{\beta Q}{2} e^{-\beta Q}. \quad (4)$$

It has been argued recently<sup>4,5</sup> that only these two mechanisms contribute so that the overall rate constant  $k$  should be well approximated by the stable states formula<sup>1,4</sup>

$$k^{-1} \simeq k_{GH}^{-1} + k_{ED}^{-1} \quad (5)$$

or similar relations.<sup>5</sup>

Given the importance of these ideas we have decided to test their validity against full stochastic simulations. In this study we focus on a simple exponential friction kernel with Laplace transform

$$\hat{\zeta}(s) = \frac{\gamma}{1 + \tau_c s}; \quad \tau_c = \alpha\gamma, \quad (6)$$

where  $\gamma$  is the static friction and  $\tau_c$  is the correlation time. This friction kernel resembles closely the frequency dependent part of the hydrodynamic friction studied in the theory of reaction rates<sup>6</sup> if  $\tau_c$  is proportional to the damping  $\gamma$ . We thus take  $\tau_c = \alpha\gamma$ .

We study this problem numerically by considering the system<sup>7</sup>

$$\begin{aligned} \dot{x} &= v, \\ \dot{v} &= -\frac{\partial U(x)}{\partial x} + z, \\ \dot{z} &= -\frac{1}{\alpha\gamma} z - \frac{1}{\alpha} v + \xi. \end{aligned} \quad (7)$$

Elimination of the variable  $z$  yields Eq. (1) with the friction kernel [Eq. (6)]. The spectral density of the white Gaussian noise  $\xi(t)$  is adjusted to reproduce the correct random force of Eq. (1). Numerical integration of Eq. (8) is achieved using an Adams-Moulton predictor-corrector algorithm<sup>8</sup> and the random force is approximated by a constant during one integration step.<sup>9</sup> The rate constant is determined using the rapid absorbing boundary method.<sup>9</sup>

In this Communication we report results for a symmetric piecewise harmonic double well potential<sup>5,10</sup> ( $\beta Q = 20$  and  $\omega_B/\omega_0 = 2$ ). The static friction coefficient  $\gamma$  is varied at fixed  $\omega_B^2\alpha = 4/3$ . The rate constant  $k_{GH}$  of Grote-Hynes theory, Eq. (2), [see Fig. 1 (---)] approaches a constant ( $k_{GH}/k_{TST} \rightarrow 1/2$ ) for large  $\gamma$  since the correlation time  $\tau_c = \alpha\gamma$  increases with  $\gamma$ . The energy diffusion rate constant  $k_{ED}$  was evaluated numerically from exact expressions presented elsewhere.<sup>3</sup> One finds that Eq. (5) is accurate to within a few percent in this particular case. As shown in Fig. 1 (—)  $k_{ED}$  increases initially with  $\gamma$  but since the correlation time also rises  $k_{ED}$  goes through a maximum (not shown in Fig. 1) and decreases like  $1/\gamma$  for large  $\gamma$ . Note that for our particular choice of parameters one remains in the weak to moderate friction regime for all  $\gamma$ . If the overall rate constant

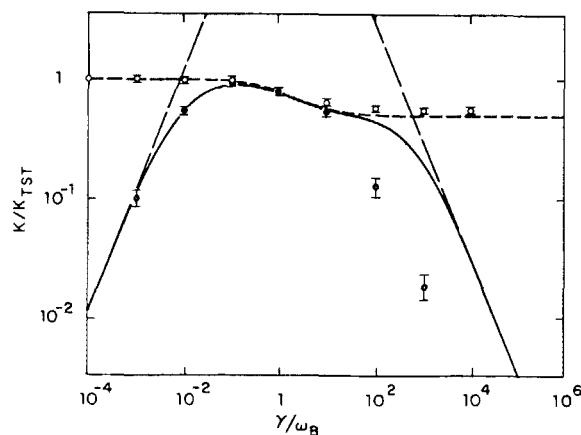


FIG. 1. Barrier crossing rate constants vs the static friction  $\gamma$  for a non-Markovian bath. The prediction of the Grote-Hynes theory [Eq. (2) (---)], the energy diffusion mechanism [Eq. (4) (—)], and the overall rate constant Eq. (5) (—) within this model. Dots are simulation data (with 95% confidence intervals) for the symmetric double well potential (●) and the inverted parabola (○).

$k$  is given by Eq. (6) [see Fig. 1 (—)] the Grote-Hynes theory should be rate limiting over a wide range of  $\gamma$ .

The simulation data (●) in Fig. 1 agree well with Eq. (6) at low  $\gamma$ . Surprisingly, however, for large  $\gamma$  the simulations show a much faster decrease (roughly as  $1/\gamma$ ) in complete disagreement with the Grote-Hynes theory.

As a check, another stochastic simulation was run using the inverted parabolic barrier instead of the double well potential. For this potential the Grote-Hynes theory should be correct and should give the same results as the simulation. Indeed, for this case our simulation data shown in Fig. 1 (○) agree well with the Grote-Hynes theory (---).

In conclusion we have demonstrated that a simple interpolation formula [Eq. (6)] which is based solely on the Grote-Hynes theory and energy diffusion mechanism can fail by orders of magnitude in the intermediate regime. In this regime the rate constant is very sensitive to anharmonicities in the potential. This can be most clearly seen by comparing the simulation data for the double well (●) with those for the corresponding parabola (○) in Fig. 1. The Grote-Hynes theory, while correct for the inverted parabola, cannot generally be applied to evaluate rate constants for double well potentials. For this reason we question earlier interpretations of weak viscosity dependence of isomerization rate data<sup>6</sup> which were based on the application of Grote-Hynes in the intermediate regime.

One of us (M. B.) would like to thank Peter Hänggi and Peter Talkner for a long and illuminating discussion.

<sup>1</sup>This research was supported by a grant from NIH.

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## COMMENTS

### Comment on "Torsional potential and intramolecular dynamics in the $C_2H_4^+$ photoelectron spectrum"

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(Received 11 March 1985; accepted 31 May 1985)

In a recent article,<sup>1</sup> Pollard *et al.* report the observation and analysis of the photoelectron spectrum of jet cooled ethylene. The quality of the spectrum obtained in this investigation is appreciably higher than previously reported, thus the vibrational progressions were more clearly resolved than before. Conventional assignments<sup>2,3</sup> were given to the observed vibrations. The main purpose of this comment is to indicate that the assignments given to the two higher frequency vibrational intervals observed in the  $\tilde{X}$  state of the ion are incorrect.

The conventional assignment of these two frequency intervals is made by nominal analogy with the 3s Rydberg state of ethylene.<sup>4</sup> However, only one  $\sim 1400\text{ cm}^{-1}$  frequency interval is observed in the 3s Rydberg state of ethylene. It is correlated with the most prominent photoelectron frequency interval,  $\sim 1250\text{ cm}^{-1}$ . The other photoelectron frequen-

cy interval is identified with the closest ground state frequency interval of the same symmetry species,  $\sim 1340\text{ cm}^{-1}$ . The latter is not active in the 3s Rydberg state. These correlations are displayed in Table I for both  $C_2H_4$  and  $C_2D_4$ . It is clear from this table that there are several problems with this assignment. At a minimum, both the noncrossing rule<sup>5</sup> and Rayleigh's rule<sup>6</sup> are violated in the ion and inconsistencies occur in the frequency changes observed on going from the 3s Rydberg state to the ion in the two isotopic molecules.

We propose that these problems can be resolved by interchanging the assignments of these two frequency intervals in the  $C_2H_4$  ion. This reassignment is supported both by the frequency intervals observed in the first photoelectron band of  $C_2H_nD_{4-n}$  series of isotopic molecules<sup>2</sup> and by the changes observed in frequency intervals through the 3s, 3p, 3d, 3d', 4d', and 5s Rydberg states of the  $C_2H_nD_{4-n}$  series of isotopic molecules.<sup>7</sup> In all cases except for  $C_2H_4$  itself, the higher frequency interval,  $\sim 1300\text{--}1450$ , is the more prominent. In  $C_2H_4$ , except for the 3s Rydberg state, a  $\sim 1210\text{--}1250\text{ cm}^{-1}$  frequency interval is the most prominent. A weaker, higher frequency interval is also present. These results indicate that in  $C_2H_4$ ,  $\nu_2$ , the nominal C=C stretching vibration, is sufficiently reduced in frequency in the excited and first ionic states to bring it into resonance with  $\nu_3$ , the nominal HCH angle deformation vibration. In the other  $C_2H_nD_{4-n}$  molecules,  $\nu_3$  is sufficiently lower than  $\nu_2$  that such a resonance does not occur in the excited and first ionic states. The abnormal intensity of  $\nu_3$  in  $C_2H_4$ <sup>8</sup> is another indication of this resonance.

The conclusions to be drawn from the above are that the traditional assignment of the  $\nu_2$  frequency of  $C_2H_4^+$  in the first ionic state is incorrect and, even more important, the resonance between  $\nu_2$  and  $\nu_3$  in  $C_2H_4$  excited and first ionic states negates attempts to determine C=C bond properties from even the reassigned direct experimental frequencies.

TABLE I. "Traditional" vibrational assignments of  $C_2H_4^+$  and  $C_2D_4^+$  (in  $\text{cm}^{-1}$ )<sup>a</sup>.

Mode <sup>b</sup>	$C_2H_4$			$C_2D_4$		
	<i>N</i>	3s	<i>I</i>	<i>N</i>	3s	<i>I</i>
$\nu_2$	1620	1340	1260 <sup>c</sup>	1520	1300	1340
$\nu_3$	1340	...	1460 <sup>c</sup>	980	...	1050 <sup>d</sup>

<sup>a</sup>Frequencies rounded to the nearest 10  $\text{cm}^{-1}$ . Ground state (*N*) frequencies: B. L. Crawford, Jr., J. E. Lancaster, and R. G. Inskeep, *J. Chem. Phys.* **21**, 678 (1953). 3s Rydberg state frequencies: Ref. 4. Ground ion state (*I*) frequencies: Refs. 1, 2, and 3.

<sup>b</sup> $\nu_2$ : C=C stretch,  $\nu_3$ : HCH angle bend.

<sup>c</sup>The vibrational intervals whose assignments are discussed in the text. These assignments are proposed to be inverted and the vibrations to be in Fermi resonance.

<sup>d</sup>This value may be incorrect. Even so, unless the correct frequency is higher than  $1340\text{ cm}^{-1}$ , the noncrossing rule is violated. Rayleigh's rule is violated for  $\nu_2$  irrespective of this value.