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Collisional Relaxation of Non-Equilibrium Vibrational Energy Distributions in a Thermal Unimolecular System. Surface Collisions

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Measurements are made for the first time (on cyclopropane) of the dynamics of collisional relaxation of vibrational distributions of reacting molecules at high energies, and at high temperatures. This is the same as the determination of the mean first passage time τ of molecules with respect to an absorbing barrier. A simple technique, called the Variable Encounter Method has been devised for this purpose.

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Collisional Relaxation of Non-Equilibrium Vibrational Energy Distributions in a Thermal Unimolecular System.[a] Surface Collisions.

by D. F. Kelley, B. D. Barton, L. Zalotai[b] and B. S. Rabinovitch

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There have been no measurements to date of the dynamics of collisional relaxation of vibrational distributions characteristic of reacting polyatomic molecules at high energies. Formal theoretical treatments have been given.[1,2] The unknown desideratum has been the appropriate matrix of the collisional transition probabilities, $\underset{\sim}{P}$. The same matter appears in the form of the mean first passage time, $\bar{\tau}$, of molecules with respect to an absorbing barrier at energy, E_0. Kim[3] and Widom[4] have given expressions for $\bar{\tau}$ in terms of $\underset{\sim}{P}$. For a thermal unimolecular system, the concept of an absorbing barrier corresponds to the limiting low pressure behavior. For the trivial case of a constant temperature, steady-state system, $\bar{\tau} = 1/k_0$, where k_0 is the low pressure unimolecular rate constant. But $\bar{\tau}$ has not been measured for the dynamical case of transients wherein some initial input distribution, not necessarily Boltzmann, relaxes to a final distribution characteristic of the bath temperature, whether by homogeneous or heterogeneous collision processes. Based on a quasi-accommodation model for energy transfer,[5] as well as experimental results with bath molecules of increasing complexity,[6] one anticipates that the wall may be at least as efficient as any bath molecule.

A very simple technique for studying the dynamics of energy transfer at a surface has been developed.[7] The apparatus consisted simply of a large, degassed 5 ℓ. fused quartz bulb, modified with several attached, heated "reactor" zones of varying dimensions (cylindrically symmetric) distributed over the surface. The bulb was connected to a gas handling system and could also be heated to alter the input distribution. Entrance area to a reactor was restricted to $\simeq$ 1/100 of the bulb area. Dimensions of the reactors used so far provided mean wall collision numbers, $\bar{m}$, of 2, 4.5, 10.5 and 22.3, per encounter. For a given $\bar{m}$, the distribution of wall collisions was found by Monte Carlo calculation.[7,8] Molecules that returned to the bulb were cooled by collisions before another encounter with the reactor. Any value of $\bar{m}$ from 1 to 10^4 is readily attained; the technique is termed the Variable Encounter Method.

We have applied the method to the structural isomerization of 1,1-cyclopropane-d_2 activated by collisions at a seasoned surface ($E_0 \simeq 63$ kcal mole^{-1}). This system is notably free from complications. Brief pre-exposure of the oxidized silica wall to substrate provided adequate seasoning and reproducible results. To perform a run, one reactor was heated to a desired temperature, the bulb (at 375 K) was pumped to a stable residual pressure of $< 10^{-6}$ torr, and substrate was admitted at a pressure of $1\text{-}2\times10^{-4}$ torr and left for a suitable time. A flow mode was also possible. Analysis was by gas chromatography; percent reaction varied from 1 – 50%.

Figure 1 shows experimental temperature plots of the average reaction probability per collision, $\bar{P}_c$, for the four reactors. The data were compared to stochastic calculations using two forms of $\underset{\sim}{P}$, gaussian and exponential. Several models were computed in which the average downjump step size, $\langle \Delta E \rangle$, varied as E^x, x = 0, 1/2, 1. The gaussian form (with x = 0, 1/2) tentatively give the best fits (cf. refs. 6 and 9). Some numerical values of $\langle \Delta E \rangle$ for the case x = 0, are given in the figure (use of x = 1/2, 1 leads, of course, to larger values of $\langle \Delta E \rangle$ at the level of energy E_0). Once $\underset{\sim}{P}$ has been selected, $\bar{\tau}$ follows immediately.[3,4]

Figure 2a illustrates the variation of $\bar{P}_c$ with $\bar{m}$ at constant temperature. Figure 2b shows the sequential variation of P_c vs collision number, calculated from the flat gaussian model.

We find: a) For the temperatures covered, accommodation to a steady state with the wall takes place in a small number of collisions ∿ 8-15 (Fig. 2b), the number increasing with temperature; this accounts for the findings made in low pressure pyrolysis studies[10] that $\bar{m}$ values $\gtrsim$ 80-100 provide temperature accommodation; at lower temperatures, especially, wall efficiency approaches strong collider behavior and $\bar{\tau}$ is quasi-independent of the input distribution (bulb temperature). b) Wall collisions are more efficient than gas phase collisions; the surface seasoned with a film of "polycyclopropane" is characterized by down step sizes $\langle\Delta E\rangle$ of 4,000 and 3,400 cm^{-1}, $(x = 0)$, at 775 K and 975 K, respectively;[11] these compare with the lesser values, ∿ 3,500 and 1,900 cm^{-1}, measured previously[12] for binary gas phase cyclopropane-d_2 collisions; c) The present data thus support the previous finding that energy transfer collision efficiency declines at higher temperatures for this polyatomic unimolecular system. Dove and co-workers[13] have estimated an "incubation" period of ∿ 3,000 collisions for the shock-heated triatomic N_2O system above 2000K.

Features such as surface structure, substrate structure and level of E_0 are subjects for future investigation by this technique.

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b) UNIDO Fellow. University of Szeged, Szeged, Hungary.

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Figure Captions

1. Plots of experimental values of $\overline{P}_c$ _vs_ T for each of the four reactors. Solid curves are calculated fits for a gaussian model (x = 0) of the energy transfer probabilities for each value of m, and include the limiting case, $m = \infty$. The best-fit values of $\langle \Delta E \rangle$ (cm^{-1}) are given at several temperatures.

2. A) Illustrative plots of experimental values of $\overline{P}_c$ _vs_ m at 823K, 973K and 1123K. Solid curves are calculated for respective values of $\langle \Delta E \rangle$ of 3800, 3400 and 3050 cm^{-1}. The ordinate scales are arbitrary and are normalized to $\overline{P}_c = 1$ for $m = \infty$, at each temperature.

   B) Illustrative histograms of the calculated sequential probability $P_c(n)$ _vs_ n, the number of consecutive collisions, for the temperatures and values of $\langle \Delta E \rangle$ used in A).

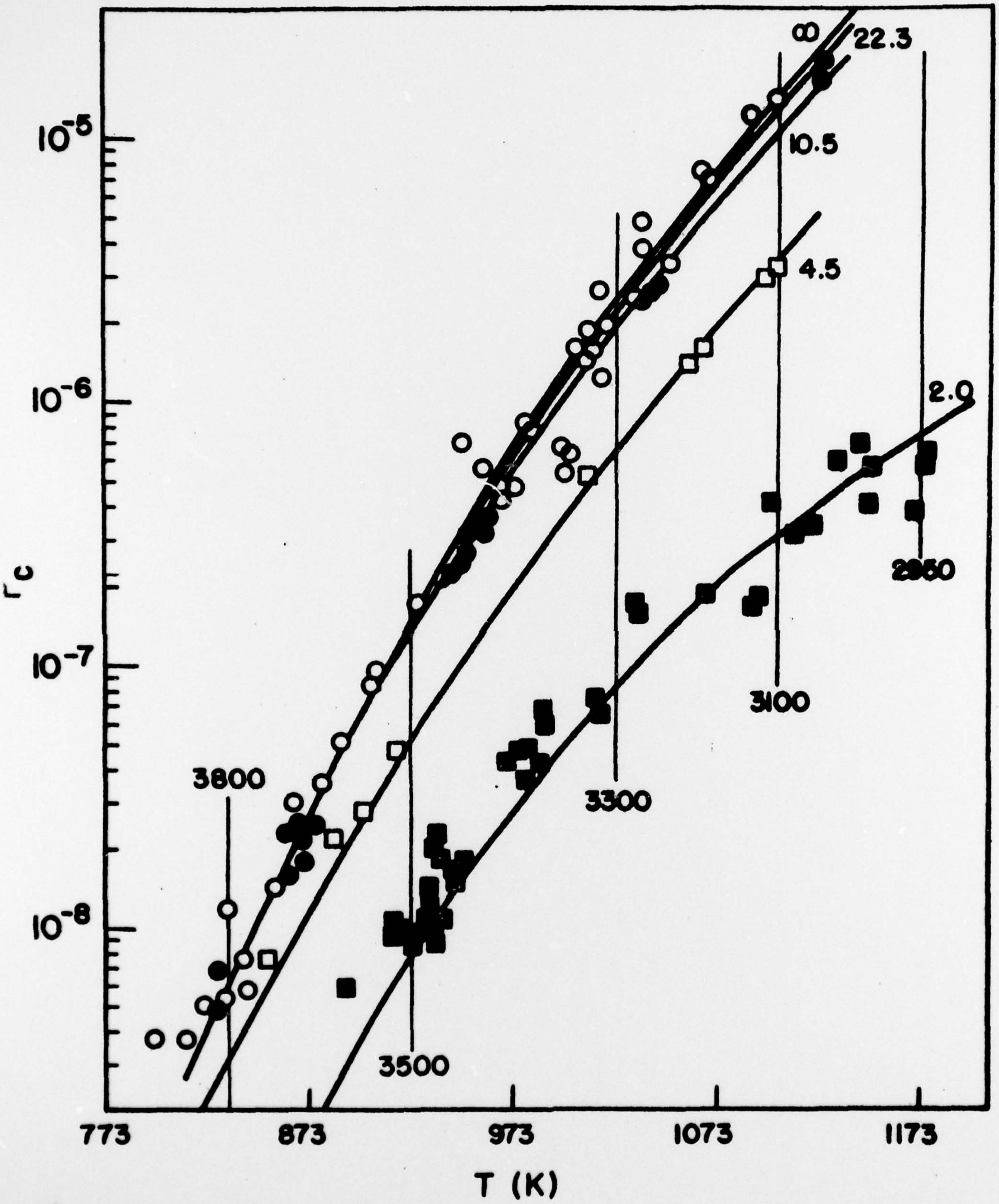

Fig1 Kelley et al

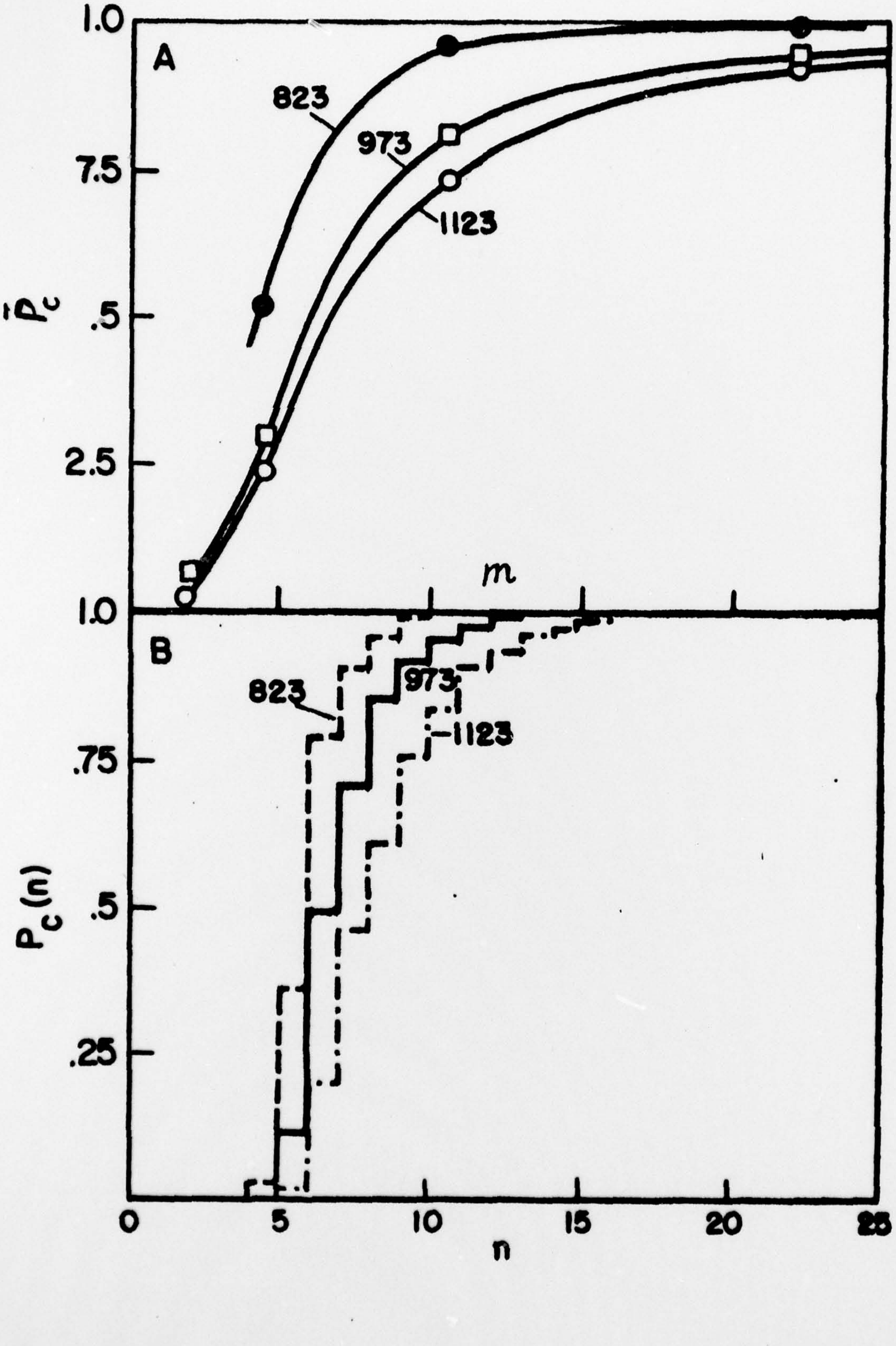

Fig 2. Kelley et al