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Reactive processes hindered by one or a series of intervening potential barriers play an ubiquitous role in chemical and physical sciences.[1] Over the last few years there has been a flurry of activity in order to incorporate quantum effects (at all temperatures) into the rate theory.[1(a),2] In absence of quantum tunneling one deals with generalized Kramers theory.[1,3] In this context, it should be emphasized that (position)-diffusion controlled Kramers theory is equivalent[1(a),4] to classical many-body transition state theory.[5] The inclusion of quantum tunneling into the Kramers theory is more sophisticated. In the high temperature regime, quantum effects of a reacting system coupled to an environment (i.e., dissipation) have been studied first by Wolynes[6]; his result has since been rederived via other high temperature methods by several authors.[7] In particular, Pollak[7(c)] has rederived the result of Wolynes by use of standard many-body quantum transition state theory (QTST) in which classical partition functions are simply substituted by their quantum counterparts and the classical transmission of "one" above the barrier threshold $E = E_b$ is substituted by a temperature averaged parabolic transmission coefficient $\kappa = \frac{1}{2}\hbar\beta\mu/\sin(1/2\hbar\beta\mu)$ (i.e., the Wigner correction[8]) wherein μ denotes the relaxation (angular) frequency along the reaction path at the saddle point. All of these high temperature quantum rate theories, however, exhibit a divergence at the crossover temperature $T_0 = \hbar\mu/(2\pi k)$,[9] above which activated events dominate over tunneling transitions. A quantum rate theory covering all temperatures has been put forward in terms of the "bounce" formalism for dissipative metastable systems.[1(a),2] In doing so, one uses path integral methods for the reduced dynamics and expresses the rate in terms of an imaginary part for the free energy F (i.e., Im F). Within this method, the many-body quantum rate Γ is given by the two expressions[1(a),2,10,11]

$$\Gamma = -\frac{2}{\hbar} \operatorname{Im} F \begin{cases} 1; & T \leqslant T_0 \quad (1a) \\ \dfrac{T_0}{T}; & T > T_0 \quad (1b) \end{cases}$$

which match smoothly at $T = T_0$.[11] It is rather unfortunate, however, that expression (1b) cannot be uniquely derived from the theory for temperatures $T \leqslant T_0$. The presence of the additional factor (T_0/T) has thus triggered some criticism within the scientific community which in some cases went so far as to question[12] the validity of the results. It is, therefore, highly desirable to have a *unique* approach covering both high temperatures and low temperatures on the same basis. Such an approach indeed can be given. Our starting point will be based on the nonseparable many-body QTST put forward by Miller in 1975.[13] By use of the semiclassical approximation the quantum reactive flux yields for the rate Γ the expression[13] $[E_T = E - \Sigma_{i=2}^N (n_i + 1/2)\hbar\omega_i(E_T)]$

$$\Gamma = Z_0^{-1} \frac{1}{2\pi\hbar} \int_0^\infty dE \exp(-\beta E)$$
$$\times \sum_{(n_2,\ldots,n_N)=0}^{\infty} \{1 + \exp[B(E_T)/\hbar]\}^{-1}. \quad (2)$$

Z_0 is the partition function of the metastable state and the sum in Eq. (2) is a cumulative reaction probability. $B(E_T)$ denotes the action along an unstable periodic orbit $q_1(\tau)$, $\tau = it$, with period $T(E_T)$ at energy E_T available for the reactive mode on the upside-down potential surface of N coupled degrees of freedom. The set $\{\omega_i(E_T)\}$ are dynamical stability frequencies.[13] We assume that the one-dimensional reaction coordinate $q_1 = q$ moves in a metastable potential $V(q)$ and obeys the classical, dissipative equation of motion:

$$\ddot{q} + \int_0^t ds\, \gamma(t-s)\dot{q}(s) + \frac{1}{M}\frac{\partial V}{\partial q} = 0. \quad (3)$$

These dynamics can be derived from the underlying total Hamiltonian of reactive system coupled bilinearly to a bath of harmonic oscillators [e.g., see Eq. (8) in Ref. 4]. The whole crux within the approach in Eq. (2) consists, of course, in the evaluation of the action $B(E_T)$, period $T(E_T)$, and stability frequencies $\omega_i(E_T)$. Guided by some results of recent work[14–16] we can now evaluate Eq. (2) further: For temperatures $T > T_0$ the integral in Eq. (2) is dominated by energies near the barrier top, $E_T \geqslant E_b$. In that regime we can use a harmonic, local adiabatic approximation:

$$\omega_i(E_T) \cong \lambda_i^*, \quad T(E_T) \cong 2\pi/\mu. \quad (4a)$$

Here the set $\{\lambda_i^*\}$ are the normal mode (angular) frequencies of the transverse coordinates at the saddle point $q_1 = q_b$ and μ is given by the positive solution of $\mu = [\frac{1}{4}\hat{\gamma}^2(\mu) + \omega_b^2]^{1/2} - \frac{1}{2}\hat{\gamma}(\mu)$, with $\omega_b^2 = 1/M|V''(q = q_b)|$, and $\hat{\gamma}(\omega)$ denotes the Laplace transform of $\gamma(t)$ [see Refs. 3(b) and 3(c)]. The action in full phase space will be approximated by the dissipation-modified action for a parabolic barrier,[17] i.e.,

$$B(E_T) \cong \left[E_b + \sum_{i=2}^N (n_i + 1/2)\hbar\lambda_i^* - E\right]2\pi/\mu. \quad (4b)$$

Note that $\{\lambda_i^*\}$ as well as μ change as a function of the coupling strength $\hat{\gamma}(\mu)$. Inserting Eqs. (4a) and (4b) into Eq. (2), and interchanging the integration in Eq. (2) with the sums then yields the known quantum rate result,[6,7] i.e., for $T > T_0$,

$$\Gamma = \left\{ \frac{\mu}{\omega_b} \frac{\omega_0}{2\pi} \exp(-\beta E_b) \right\}$$
$$\times \prod_{n=1}^{\infty} \frac{\omega_0^2 + n^2\nu^2 + n\nu\hat{\gamma}(n\nu)}{-\omega_b^2 + n^2\nu^2 + n\nu\hat{\gamma}(n\nu)}, \quad (5)$$

where $v = 2\pi/\hbar\beta$ and $\omega_0^2 = (1/M)V''(q = q_0)$ is the frequency in the well bottom. Equation (5) agrees with Eq. (1b).[2,11] For the last part in Eq. (5) we made use of an identity, derived originally by Pollak [see Eqs. (20) and (25) in Ref. 7(c)], that involves the partition function $Z_0^{-1} = \Pi_{i=1}^{N} [2\sinh(\tfrac{1}{2}\hbar\beta\lambda_i^0)]$ at the well bottom.

At temperatures $T \sim T_0$, the integral in Eq. (2) becomes dominated by energies $E_T \lesssim E_b$, where $B(E_T) > 0$. Expanding the action near $E_T = E_b$ we set more accurately for $E_T \lesssim E_b$, with $T' = -B''(E_b)$:

$$B(E_T) \cong (E_b - E_T)\frac{2\pi}{\mu} + \frac{1}{2}(E_b - E_T)^2|T'|. \quad (6)$$

By use of Eqs. (4a) and (6) we now evaluate the integral in Eq. (2) to arrive, at the explicit result[18] [$\mathrm{Erfc}(x) = 2\pi^{-1/2}\int_{-\infty}^{x} dy \exp - y^2$]

$$\Gamma = \frac{\sinh[(1/2)\hbar\beta\lambda_1^0]}{(2\pi\hbar|T'|)^{1/2}} \prod_{i=2}^{N} \frac{\{2\sinh[(1/2)\hbar\beta\lambda_i^0]\}}{\{2\sinh[(1/2)\hbar\beta\lambda_i^*]\}}$$

$$\times \mathrm{Erfc}\left\{\left(\frac{\hbar}{2|T'|}\right)^{1/2}(\beta - \beta_0)\right\}$$

$$\times \exp\left[-\beta E_b + \frac{\hbar}{2|T'|}(\beta_0 - \beta)^2\right], \quad T \sim T_0. \quad (7)$$

This rate is shown to *precisely equal* the result of the bounce-crossover theory[11] using Eq. (1a). Near $T \gtrsim T_0$ the expression in Eq. (7) matches the expression in Eq. (5). At lower temperatures, $T \ll T_0$, the action must be evaluated by taking the *full* nonlinearity into account.[16] In that regime, however, the integral in Eq. (2) can be evaluated by a steepest descent approximation.[16]

In conclusion, many-body QTST in Eq. (2) complemented by the set of equations (4) and (6) provides a *unified* approach to the quantum Kramers rate[1(a),2] that works at all temperatures.

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[16] P. Hänggi, Z. Phys. B **68**, 181 (1987); in particular see Eq. (4.9) where T' should read $|T'|$. For very weak dissipation, the error for the many-body QTST result in Eq. (2), induced by deviations from the Boltzmann distribution, becomes exponentially smaller with decreasing temperature.

[17] We address the WKB limit [i.e., $(\hbar\mu/E_b) \ll 1$] and weak noise $kT/E_b \ll 1$. Thus, corrections to the harmonic approximation for $\omega_i(E_T)$ and $B(E_T)$ yield for $T > T_0$ only small corrections of the order $kT_0/E_b \ll 1$ to the leading prefactor in Eq. (5).

[18] In doing the integration we neglect small WKB corrections [$\propto \sqrt{(\hbar\mu/2\pi E_b)}\exp - (2\pi E_b/\hbar\mu)$]. Anharmonic corrections for $\omega_i(E_T)$ again lead to negligible prefactor corrections of order kT_0/E_b. Note that near $T \sim T_0$, the prefactor is proportional to the inverse WKB parameter, i.e., $(2\pi\hbar|T'|)^{-1/2}/\mu \propto (E_b/\hbar\mu)^{1/2} \gg kT_0/E_b$.

Evidence of structural isomerism in small niobium clusters

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The electronic and geometrical structures of small metal clusters, and the variation of these with cluster size and composition, are topics or considerable interest in many branches of chemistry and physics. Recent experiments have demonstrated that the chemical reactivity of small metal clusters can vary dramatically as a function of cluster size,[1-22] and these (and other) experimental results have prompted several theoretical investigations of the electronic structure of small metal clusters.[23-28] Very recent experiments have demonstrated the presence of structural isomers of ionic species such as C_7^+,[21] Nb_{11}^+, and Nb_{19}^+.[22] In this

Communication we report the first evidence of structural isomers for neutral metal clusters: Nb_9, Nb_{11}, and Nb_{12}.[29]

As in previous work,[1-3,8-18] the reactivity of Nb_n ($n = 3$–25) with N_2 and D_2 was studied using a pulsed laser vaporization source coupled with a fast flow reactor. The clusters along with their reaction products were detected by photoionization time-of-flight mass spectrometry, using either the ArF (6.4 eV) or F_2 (7.9 eV) radiation from an excimer laser as the photoionization source. Details of the fast flow reactor and the TOFMS design are provided elsewhere.[2,30]