Anomalous lifetimes of ultracold complexes decaying into a single channel

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We investigate the lifetimes of complexes formed in ultracold molecule collisions. Employing both transition-state theory and a non-Hermitian microscopic model, we examine processes that can extend the lifetime of complexes beyond that predicted by Rice-Ramsperger-Kassel-Marcus (RRKM) theory. We focus on complexes that possess only one open channel, and find that the extreme distribution of widths for this case favors low decay rates. Thus, decay from a complex into a single energetically available channel can be anomalously slow, even orders of magnitude slower than the RRKM rate, and moreover the decay may be nonexponential in time.

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I. INTRODUCTION

Ultracold molecules live at the fascinating intersection of simplicity and complexity. While molecules can be produced in their absolute ground state [1,2] and their long-range collisional dynamics described by a single partial wave, their short-range collisional dynamics is highly intricate [3]. It is this combination of simplicity and complexity which makes ultracold molecules such a powerful tool for the study of fundamental collisional mechanisms [4].

However, there is currently a specter haunting the field, the specter of sticky collisions [5]. Diatomic molecules are observed to collide and *go away*, as if perishing in a chemical reaction, even those that are not chemically reactive at zero temperature [6–15]. Rather, it is believed that these diatomic molecules enter into a a four-atom collision complex, where they dwell for an observable amount of time before completing their collision. The molecules have been observed to dwell inside these complexes for extraordinarily long time scales approaching milliseconds [12–14]. In at least one case, the same millisecond time scale holds for molecules colliding with individual atoms [16]. Such collisions are colloquially referred to as "sticky," following the terminology of Bethe from nuclear physics [17].

The *idea* of long-lived, sticky collision complexes is an appealing one. Owing to their deep, barrierless potential energy surfaces and rather large masses, four-body complexes of alkali atoms might be expected to possess a high density of states ρ in which the atoms are unable to dissociate and can get randomly stuck. The added feature of ultracold temperatures ensures that molecules which originate in their ground states can only dissociate into a single open channel, denoted $N_o = 1$. In this circumstance, it might be expected that the lifetime of the complex is proportional to ρ and inversely proportional to N_o, expressed in the simplest way by the Rice-Ramsperger-Kassel-Marcus (RRKM) expression [18]

$$\tau \approx \tau_{\mathrm{RRKM}} = \frac{2\pi\hbar\rho}{N_o}. \tag{1}$$

Considerations such as these led to early speculations of sticking in ultracold molecules [19–21].

This naive expectation, however, proves inadequate. High-quality estimates of the relevant densities of states reveal that realistic RRKM lifetimes are shorter than those observed. The longest predicted lifetime is 0.25 ms for the heaviest species RbCs [22]. While this particular estimate does nearly agree with the measured 0.53 ms lifetime of $(\mathrm{RbCs})_2^*$ [12], other experiments that have measured the lifetime find results orders of magnitude larger than the RRKM lifetime [13,14,16]. A caveat is relevant here: We are discussing the lifetimes of the complex *in the dark*, that is, in transient intervals where light from the optical dipole trap that confines the molecules is temporarily turned off. It is established that the complex's lifetimes are significantly reduced by scattering photons of the trapping light [23,24], but that is not our concern here.

We are instead interested in the natural, light-free lifetimes of the complexes, and how they can come to be far longer than the RRKM lifetimes. To understand this situation, we consider the time dependence of a complex assumed to consist of many resonances, each with its own characteristic decay rate, following an approach by Peskin *et al.* [25]. This approach gives an effective decay rate that agrees with the RRKM rate in certain limits, yet can deviate under other circumstances. In particular, we find that in the limit of a very small number of open channels, especially the $N_o = 1$ case of particular

interest to ultracold molecule applications, the distribution of decay rates can strongly favor decays slower than the RRKM result. In this context, we note that for decay of the chemically reactive species KRb, the collision complexes do appear to decay on timescales consistent with the RRKM result [24], a comforting fact, since the number of open channels N_o, due to products of the reaction, is much larger than one in this case.

In this article, we focus specifically on the role of the number of open channels in the statistical model. In Sec. II we will present general remarks on the statistical model in the present context, pointing out its limitations, yet arguing why it is relevant to pursue anyway. In Sec. III we review the transition-state theory and how it establishes a baseline RRKM rate with which to compare all results. Section IV will tackle the statistical theory by presenting a non-Hermitian model Hamiltonian, capable of identifying a mean decay rate of the complex in all regimes of coupling, from weak to strong. Section V follows by detailing the distribution of decay rates in the model, emphasizing that this distribution heavily favors slow decays for $N_o = 1$. It also presents numerical simulations to illustrate these distributions.

As a final introductory note, it may be worth considering the influence of nuclear spins in the complexes. If the nuclear spins of different hyperfine manifolds are coupled, then these additional degrees of freedom would increase the effective density of states, and hence also increase the RRKM lifetime. The role of nuclear spins has been discussed recently by several authors [20,26–29]. For ultracold exothermic processes such as for KRb molecules, experimental results are consistent with the fact that nuclear spins play a spectator role in the complex [28,29]. As N_o is large for this type of process, the lifetime of the complex in Eq. (1) might be short enough so that spin changing processes do not have time to occur [27]. In contrast, for ultracold endothermic processes, $N_o = 1$, lifetimes become longer and the role of nuclear spins might play an important role [20,26,27]. In any event, we do not explicitly consider such an influence in what follows.

II. THE STATISTICAL ASSUMPTION

The physics of the complexes is divided conceptually into two arenas, the formation of the complex and its subsequent decay, regarded as independent events. Central to the theory of complex formation in ultracold molecules is a statistical approach, which has been adopted from the literature of nuclear physics [30–37] and unimolecular dissociation [25,38]. This approach assumes that many resonances occur in the range of collision energies considered, so that quantities such as the scattering matrix can be averaged over these resonances. In this way, the averaged scattering matrix becomes subunitary, and in the theory it can account for the apparent loss of molecules due to complex formation [39,40].

And here is where the problems begin, because the density of states ρ appears to not be strictly large enough for this critical assumption of the model to hold. The mean spacing between energy levels in the complex, $d = 1/\rho$, tends to be large on ultracold scales, ranging from $\sim 200\,\mu$K in LiNa to $\sim 0.2\,\mu$K for RbCs [22]. Thus, in a gas of temperature $T \approx 0.5\,\mu$K, the number of resonances directly relevant would be of order unity at best, and far below this in general. Additional resonances could be relevant if they are very broad, but this remains uncertain at present [41].

Nevertheless, molecules in experiments certainly behave *as if* they are governed by a statistical theory. Molecular loss is convincingly modeled by theories in which the molecules, upon approaching a certain relative distance, vanish with a probability that usually sits somewhere between 0.5 and 1 [42]. It is assumed that these molecules vanish into complexes, as there is no place else for them to go. Indeed, in at least one case, KRb+KRb collisions (where there actually is somewhere else to go), the resulting complexes have been directly observed by photoionization followed by mass spectrometry [43], as have the products of reaction, which are distributed according to statistical laws [44].

Moreover, in the case of complexes destroyed by light scattering, this destruction appears to be adequately described by a model that assumes photoabsorption by complexes [23]. Finally, the observed ability of an applied electric field to increase the rate of loss due to complex formation [9,14], is explained using statistical analyses of the complex. Specifically, the effective density of states rises when the total angular momentum of the complex is no longer conserved and states of alternative total angular momentum contribute [45].

Further evidence of statistical behavior comes from calculations. For example, classical trajectory calculations certainly seem to indicate that the atoms in the complex explore phase space ergodically [46,47] Moreover, quantum scattering calculations, in cases where this can be done, confirm that ultracold molecular collisions agree with the statistical predictions of quantum chaos [3,48,49].

One further argument may be lobbied in favor of the statistical approach. In quantum statistical mechanics, it is known that an isolated system, evolving according to unitary time evolution, can exhibit apparent thermalization, if the system is chaotic and if only a few degrees of freedom are sampled. In such a case, thermodynamic variables that should be computed by averaging over *many* quantum states are actually well represented by an average over a *single* representative state, since either way the chaotic states explore large portions of the available phase space. This is a consequence of the eigenstate thermalization hypothesis [50]. For the theory of collision complexes, one may run this argument in reverse. If only approximately a single resonant state is populated in a collision, no matter; we replace averages over this state by an ensemble average over convenient nearby resonant states.

In any event, motivated by these encouraging examples, and in the interest of developing the statistical analysis as far as possible, we freely incorporate a statistical approach here and intend to average decay rates over many resonances.

III. RATES IN TRANSITION STATE THEORY

We therefore begin by positing that a complex has been formed, and that it has access to considerable phase space, as measured in the model by incorporating many resonant states. The complex has total energy E, assumed to lie in the vicinity of the original entrance channel. The density of states $\rho(E)$ at this energy defines a characteristic frequency $(2\pi\hbar\rho)^{-1} = d/(2\pi\hbar)$, identified by Weisskopf as the frequency with which a wave packet composed of stationary states of the complex can reach the complex's periphery and try to escape [32,34].

On each attempt at escape, let the probability of actually escaping to infinity in open channel i be denoted p_i. If there are N_o open channels, $i = 1, 2, \ldots, N_o$, then the escape rate is that given by transition state theory (TST) [25,38],

$$k_{\rm TST} = \frac{d}{2\pi\hbar}\sum_{i=1}^{N_o} p_i. \tag{2}$$

In the very simplest approximation, one assumes that the probability is unity in each open channel, $p_i = 1$, whereby

$$k_{\rm TST} \to \frac{d}{2\pi\hbar}\sum_{i=1}^{N_o} 1 = \frac{dN_o}{2\pi\hbar} = k_{\rm RRKM}. \tag{3}$$

This gives the RRKM rate, whose reciprocal is of course the RRKM lifetime in Eq. (1). Thus, in general, $k_{\rm RRKM}$ represents a fastest decay rate, that is, a lower limit on the lifetime, at least within transition state theory. From this standpoint already, it is reasonable to assert that observed lifetime may be longer than $\tau_{\rm RRKM}$.

If we consider the case with only one open channel such that there are no inelastic losses possible and note that the complex cannot decay before one full period of oscillation, we obtain a lower limit on the lifetime

$$\tau \geqslant \frac{2\pi\hbar}{d}. \tag{4}$$

Noting the lifetime is also given by $\tau = \hbar/\gamma$, we find the ratio of the mean width γ to the mean spacing d to be

$$\frac{\gamma}{d} \leqslant \frac{1}{2\pi}, \tag{5}$$

known as the Weisskopf estimate.

IV. MEAN DECAY RATES

Transition state theory provides approximate rate constants, based on a key parameter, the attempt frequency $d/(2\pi\hbar)$ for the complex to decay, which is a scale, not a specific frequency of particular events. More concretely, time evolution in quantum mechanics is governed by the relative energies of the stationary states, or of quasi-stationary states in the event that those states can decay. We here develop this picture, based on a microscopic model in which a non-Hermitian Hamiltonian is employed to describe the effects of decay of the resonances. Following common practice in the nuclear physics literature from which we draw the model, we refer to this as an "optical model," although we do not consider any influence due to light [35–37].

A. Optical model

We begin with a model of the resonant spectrum. This is described by the Hamiltonian

$$H^{\rm eff}_{\mu\nu} = E_\mu\delta_{\mu\nu} - i\pi\sum_i W_{\mu i}W_{i\nu}. \tag{6}$$

The bare energies E_μ are assumed to be the eigenvalues of a model Hamiltonian $H^{\rm GOE}$ drawn from a Gaussian orthogonal ensemble with mean spacing $d = 1/\rho$; and the coupling constants $W_{\mu i}$ are Gaussian distributed variables with mean values

$$\langle W_{\mu i}W_{\nu j}\rangle = \delta_{\mu\nu}\delta_{ij}v_i^2, \tag{7}$$

that is, v_i^2 is the variance of the matrix elements. Each matrix element $W_{\mu i}$ is regarded as the integral of the interaction potential between a bound state $|\mu\rangle$ and an energy-normalized continuum state $|i\rangle$ into which it might decay. Thus, v_i^2 has units of energy. The nuclear physics literature typically normalizes the bound-continuum coupling in units of the mean level spacing, defining a dimensionless parameter in each open channel,

$$x_i = \pi^2\frac{v_i^2}{d}. \tag{8}$$

This quantity x_i plays a role in determining the sticking probability in channel i (see Ref. [39] and Sec. IV D below). In this regard it plays the role of the absorption coefficient y in the universal theory of Idziaszek and Julienne [51], but adapted to a specific model of loss due to complex formation. This coefficient can be extracted from experimental data as a fit parameter in a generic theory of loss [52–54].

The time evolution of the resonant states is given by the complex eigenvalues of $H^{\rm GOE}$, denoted

$$E_\lambda - \frac{i}{2}\gamma_\lambda. \tag{9}$$

A state of the collision complex is assumed to be a coherent superposition with initial probability amplitude c_λ in resonant state $|\lambda\rangle$. In accord with the statistical approximations of the model, the coefficients c_λ are randomly chosen, subject to normalization $\sum_\lambda |c_\lambda|^2 = 1$ [25]. The *distribution* from which these coefficients are chosen reflects assumptions made about the formation of the complexes in the first place, a topic we do not address here. The time evolution of such a state is

$$|\psi(t)\rangle = \sum_\lambda c_\lambda|\lambda\rangle\exp\left\{-\frac{i}{\hbar}[E_\lambda - (i/2)\gamma_\lambda]\,t\right\}. \tag{10}$$

The time evolution of the diminishing population is therefore multiexponential,

$$P(t) = \langle\psi(t)|\psi(t)\rangle = \sum_\lambda |c_\lambda|^2\,\exp(-\gamma_\lambda t/\hbar). \tag{11}$$

This is arbitrarily normalized to $P(0) = \sum_\lambda |c_\lambda|^2 = 1$, hence represents the time-evolving population of complexes relative to the initial population. Thus, the resonance widths γ_λ represent decay arising from the nonhermiticity of the short-range Hamiltonian Eq. (6), and each resonance has its characteristic decay rate $k_\lambda = \gamma_\lambda/\hbar$.

We can reveal how the value of x_i controls the decay by looking into several limits. These are regarded as weak, strong, and intermediate couplings, insofar as $x_i \ll 1$, $x_i \gg 1$, or $x_i \approx 1$, respectively.

B. Weak coupling limit

In the perturbative limit, $x_i \ll 1$, the decay rate from $|\mu\rangle$ into $|i\rangle$ is given by Fermi's golden rule as

$$k_{{\rm pert},i} = \frac{2\pi}{\hbar}|W_{\mu i}|^2. \tag{12}$$

In this perturbative limit, the resonances are isolated, and the mean decay rate into channel i, averaged over many such

resonances, is

$$\langle k_{\rm pert}\rangle_i = \frac{2\pi}{\hbar}\nu_i^2 = \frac{d}{2\pi\hbar}(4x_i). \tag{13}$$

This rate corresponds to the transition-state theory rate (2), where in each channel the probability is $p_i = 4x_i$. Then, the total decay rate to the $N_{\rm o}$ open channels, averaged over many resonances, is

$$\langle k_{\rm pert}\rangle = \sum_{i=1}^{N_{\rm o}}\langle k_{\rm pert}\rangle_i = \frac{d}{2\pi\hbar}N_{\rm o}\bar{p}, \tag{14}$$

with

$$\bar{p} = \frac{1}{N_{\rm o}}\sum_{i=1}^{N_{\rm o}} p_i = \frac{1}{N_{\rm o}}\sum_{i=1}^{N_{\rm o}} 4x_i = 4\bar{x} \tag{15}$$

defining $\bar{p}$ and $\bar{x}$ is the arithmetic mean of the p_i's and x_i's.

Thus interpreted, the mean rate can also be viewed in transition state theory. The decay probability p_i in each exit channel can be expressed in terms of the mean coupling ν_i^2 [this quantity is already averaged over resonant states, Eq. (7)]. Thus,

$$p_i = 4x_i \approx \frac{4\pi^2\nu_i^2}{d}, \tag{16}$$

and the transition state rate, averaged over exit channels, is

$$k_{\rm TST} = \frac{d}{2\pi\hbar}\sum_{i=1}^{N_{\rm o}} 4x_i = \frac{d}{2\pi\hbar}\sum_{i=1}^{N_{\rm o}}\frac{4\pi^2\nu_i^2}{d} = N_{\rm o}\frac{\bar{\gamma}}{\hbar}, \tag{17}$$

in terms of the mean resonance width

$$\bar{\gamma} = \frac{1}{N_{\rm o}}\sum_i 2\pi\nu_i^2 = \frac{2}{\pi}d\bar{x}. \tag{18}$$

From this point of view, the Weisskopf limit (5), $\bar{\gamma}/d \leqslant 1/2\pi$, implies an upper limit to the dimensionless parameter, $\bar{x} \leqslant 1/4$. This value $\bar{x} \approx 1/4$ is beguilingly close to the measured value for RbCs of $x = 0.26(3)$ [11]. Nevertheless, values of x extracted from collision data sometimes exceed this limit, and indeed values of $x > 1$ describe the potentially physically relevant limit of overlapping resonances, the Ericsson fluctuation regime [39]. We conclude that the perturbative limit is not the whole story.

C. Strong coupling limit

The parameters x_i arise of course from the optical Hamiltonian in the model. Depending on the situation, the variance of the coupling can be small or large compared to the mean level spacing. That is, the dimensionless parameter x_i can run from very small values (isolated resonances) to very large values (overlapping resonances, in the Ericson fluctuation regime). In any of these cases, the effective Hamiltonian can be diagonalized to give complex eigenvalues Eq. (9).

In the very-strong-coupling limit, $x_i \gg 1$, the energy eigenvalues are dominated by those of the coupling matrix,

$$-i\frac{\gamma_\lambda}{2} \approx {\rm eig}(-i\pi WW^T), \tag{19}$$

where W is an $N \times N_{\rm o}$ matrix, with N the total number of channels in the model. This matrix has rank $N_{\rm o}$, whereby it has $N - N_{\rm o}$ eigenvalues that are all zero, and $N_{\rm o}$ that are of order $\gamma \sim 2\pi N\nu^2$. These latter resonances, decaying with rates $k \sim 2\pi N\nu^2/\hbar$, are denoted "prompt" resonances, and describe extremely rapid decay of the complex, faster than is relevant to our present purposes.

The true eigenvalues of the full $H^{\rm eff}$, including the real parts, still have $N_{\rm o}$ prompt resonances. The rest will have small nonzero width, however. In fact, for a given value of $x \gg 1$, the imaginary parts of the nonprompt resonances give decay rates distributed exactly as are those for $1/x$ in the weak-coupling limit. That is to say, for example, $x = 0.1$ and $x = 10$ will have decay rates with the same statistics, provided we ignore the prompt resonances. We will see this in the numerical examples below.

D. Intermediate coupling regime

For the intermediate range, $x_i \approx 1$, the distribution of decay rates is not quite so simple. Still, a simple argument suggests a way to interpolate between the two limits. This argument exploits detailed balance, and asserts that the probability p_i to exit in channel i is the same as the probability of the molecules sticking in a collision event when they are incident in channel i.

Specifically, within the statistical model, the scattering that results in sticking is described formally by the average scattering matrix S, averaged over an energy interval containing many resonances. The result, derived elsewhere [40], is

$$\langle S_{ij}\rangle = \frac{1-x_i}{1+x_i}\delta_{ij}, \tag{20}$$

in terms of the same dimensionless x_i described above. By virtue of detailed balance, the probability p_i for flux to leave the complex and exit via channel i is the same as the flux to enter the complex via the incident channel i, that is, equal to the sticking probability extracted from the lack of unitarity of $\langle S\rangle$:

$$p_i = 1 - |\langle S_{ii}\rangle|^2 = \frac{4x_i}{(1+x_i)^2}. \tag{21}$$

This expression has the advantage of getting the right answer in the two limits: $p_i \approx 4x_i$ for $x_i \ll 1$ and $p_i \approx 4/x_i$ for $x_i \gg 1$.

The simplest version of the decay rate in transition state theory is therefore given by setting p_i to the same value in all channels, for a suitable mean value $\langle x\rangle$ of x_i:

$$\langle \bar{k}_{\rm TST}\rangle = \frac{dN_{\rm o}}{2\pi\hbar}\frac{4\bar{x}}{(1+\bar{x})^2} \tag{22}$$

$$= k_{\rm RRKM}\frac{4\bar{x}}{(1+\bar{x})^2}. \tag{23}$$

That is, this rate is averaged both over a set of resonances and over the open channels.

V. DISTRIBUTION OF DECAY RATES

Thus, the mean expected rate of complex decay, according to transition state theory, modified by the optical model, is governed by the mean coupling parameter $\bar{x}$, as given in (23). However, the distribution of rates about this mean depends strongly on the number of open channels, as we show in this section.

A. The chi-squared distribution

As a preliminary, we note that the distribution of widths that results from the optical model is a known quantity, at least in the limit of small x. For a given number N_o of open channels, the distribution of widths γ is given by the chi-squared distribution [40,52–56]. We recast this as a distribution of decay rates $k = \gamma/\hbar$,

$$P_{\chi^2}(k) = \left(\frac{N_o}{2\bar{k}}\right)^{\frac{N_o}{2}} \frac{k^{N_o/2-1}}{\Gamma(N_o/2)} \exp\left(-\frac{N_o k}{2\bar{k}}\right). \tag{24}$$

Here $\Gamma(N_o/2)$ is the ordinary gamma function, evaluated at $N_o/2$. In the perturbative limit, the mean of this distribution is given by the mean coupling v^2 as (14)

$$\bar{k} = \frac{2\pi v^2 N_o}{\hbar} = \frac{dN_o}{2\pi\hbar}(4\bar{x}). \tag{25}$$

Thus, the *mean* decay rate would simply scale linearly in the number of open channels, just as in the RRKM theory. As argued above, and as will be seen in numerical examples below, the mean rate can be approximated by the transition-state theory result (23), thus

$$\bar{k} \approx \langle \bar{k}_{\rm TST} \rangle = \frac{dN_o}{2\pi\hbar} \frac{4\bar{x}}{(1+\bar{x})^2}. \tag{26}$$

It will be recalled that the bar denotes the arithmetic average over the rates to decay into the open channels i.

The difference between large and small N_o in deciding the width distribution is critical to the theory of the decay, and forms the key observation of the paper. In the limit of large N_o, the distribution (24) becomes strongly peaked around $k = \bar{k}$, in which case the mean decay rate becomes a good guide as to what to expect in the decay from a given resonance.

Vice versa, in the limit of a *single* open channel, $N_o = 1$, the chi-squared distribution strongly favors low values of k, that is, slow decays. We may think of this situation somewhat intuitively by considering the perturbative limit. In the case of a single open channel, $i = 1$, the coupling matrix elements $W_{\mu i}$ are drawn from a normal distribution with zero mean and variance v^2. Denoting the random variable as $w = W_{\mu i}$, the distribution of coupling matrix elements is normal by definition,

$$P_{\rm couplings}(w) \propto \exp\left(-\frac{w^2}{2v^2}\right), \tag{27}$$

where we do not require the normalization for our present purposes.

Each resonance with coupling w decays at a rate $k = 2\pi w^2/\hbar$. The distribution of rates is therefore given by the distribution of the squares of the random variable w. By the usual change of variable rules, this gives the distribution

$$\begin{aligned} P_{\rm rates}(k) &= P_{\rm couplings}(w)\left(\frac{dk}{dw}\right)^{-1} \\ &\propto \exp\left(-\frac{w^2}{2v^2}\right)\frac{\hbar}{4\pi w} \\ &\propto \exp\left(-\frac{\hbar k}{4\pi v^2}\right)\frac{1}{\sqrt{k}}, \end{aligned} \tag{28}$$

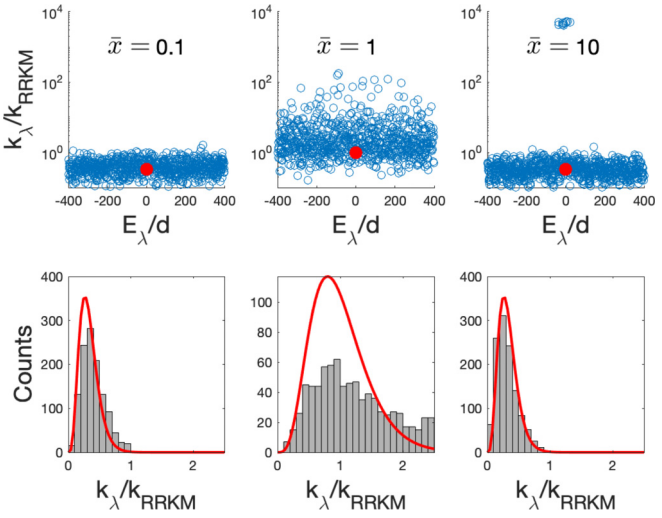

FIG. 1. Simulated spectra for $N_c = 1200$ closed channels and $N_o = 10$ open channels. The top row shows the spectrum from Eq. (9). This representation presents the real parts of the eigenenergies E_λ, normalized by the mean spacing d, on the horizontal axis, and the decay rate $k_\lambda = \gamma_\lambda/\hbar$, normalized by the RRKM rate, on the vertical axis. Bottom row: Histograms of the rates k_λ compared to the chi-squared distribution (red line). The three columns are computed for the dimensionless couplings $x = 0.1$, 1, and 10, from left to right.

which is of course the functional form when $N_o = 1$ in Eq. (24). The point is that the coupling matrix elements are clustered around zero. Since the values of w/v are predominantly less than unity, their squares must be clustered even closer around zero. This is expressed in the $1/\sqrt{k}$ divergence in the width distribution. From this perspective, it is perfectly natural that the single-channel case is dominated by short widths and long lifetimes.

Within the transition state theory, it is assumed that the mean rate is representative of the distribution of rates. However, the chi-squared distribution shows that this is not the case. In particular, when there is only one open channel, the most likely rate is in fact zero. This effect was ignored in early work that attempted to describe complex lifetimes using the simpler RRKM theory [20,21].

B. Numerical examples

To illustrate this effect we employ a generic numerical model. We compute a bound state spectrum consisting of $N_c = 1200$ bound states, where N_c denotes number of closed channels. These energies are chosen from a Gaussian orthogonal ensemble, in the spirit of the optical model above. The mean energy spacing d is taken to define the unit of energy. This schema is justified, as we intend to compare ratios of decay rates rather than absolute rates. Further, we define a sticking coefficient $\bar{x}$ that defines the mean coupling strength $v^2 = (d/\pi^2)\bar{x}$. Finally—and crucially—we define the number of open channels N_o. We then construct the optical model Hamiltonian Eq. (6) and find its eigenvalues Eq. (9). This process defines an ensemble of resonance widths γ_λ and decay rates $k_\lambda = \gamma_\lambda/\hbar$.

We explore the adequacy of this distribution in the following two figures. Figure 1 shows illustrative results for a modest

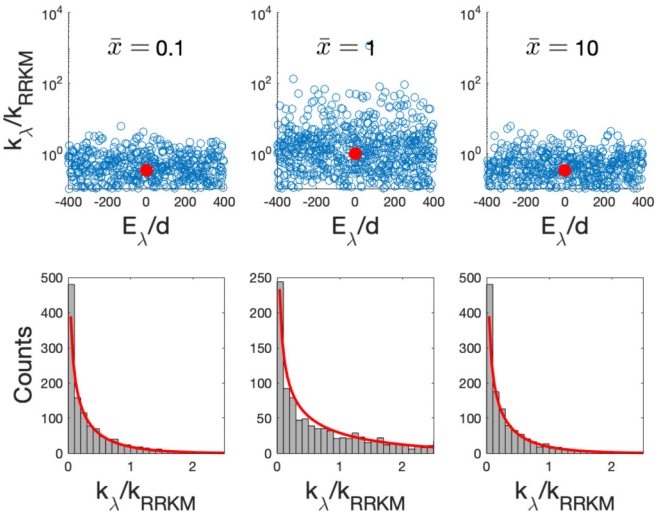

FIG. 2. Same as Fig. 1, but for a single open channel, $N_o = 1$.

number of open channels, $N_o = 10$. The columns correspond to different values of the mean coupling constant, $\bar{x} = 0.1$, 1, and 10 from left to right, representing the weak, intermediate, and strong coupling regimes. In each case the upper panel shows the eigenspectrum, plotting E_λ in units of mean spacing d on the horizontal axis and the decay rate k_λ in units of the RRKM rate on the vertical axis. In each panel the red dot is set at a height corresponding to k_{TST}. It is therefore at $4\bar{x}/(1+\bar{x})^2 \sim 0.33$ for $\bar{x} = 0.1$ or $\bar{x} = 10$, and $= 1$ for $\bar{x} = 1$.

For $\bar{x} = 0.1$ (upper left), k_{TST} seems, by eye, to represent the mean rate quite well. The same is true for $\bar{x} = 10$ (upper right), disregarding the prompt resonances which are clustered near the top of the figure. As for the optimal coupling case $\bar{x} = 1$ (upper middle), the decay rates seem more diffusely distributed.

The lower row of the figure plots histograms of the rates in the three cases, also in units of k_{RRKM}. (For $\bar{x} = 10$, this histogram disregards the prompt rates.) The distributions are compared to the chi-squared distribution (red lines), where in each case the mean is set to $\bar{k} = k_{TST}$. We note that the chi-squared distribution is a good fit to the weak and strong coupling cases, somewhat less so for the optimal coupling $\bar{x} = 1$. The point, though, is that even in the effective, non-Hermitian Hamiltonian model, the mean rate is adequately represented by the simple formula of transition state theory, $k_{RRKM}(4\bar{x})/(1+\bar{x})^2$. And because of this, in general the mean decay rate is less than the RRKM rate.

A second point is that the situation changes dramatically when there is only a single open channel. This is shown in Fig. 2, which plots the same information as in Fig. 1, but with $N_o = 1$. As before, the transition-state rate (red dot) is a reasonable stand-in for the mean value of the rates. The novelty lies in the distribution of these widths (lower panels), which are now sharply peaked at small rates. This qualitative difference is because the chi-squared distribution, for $N_0 = 1$, becomes

$$P_{\chi^2} = \frac{\pi}{2}\left(\frac{1}{2\bar{k}k}\right)^{1/2} e^{-k/(2\bar{k})}, \tag{29}$$

which diverges as $k^{-1/2}$ for small k. Thus, a decay rate chosen at random is likely to be far less than the mean decay rate, slowing down the whole process.

C. Rates versus coupling strength

The preponderance of small k's in the $N_o = 1$ limit has serious consequences for the time-dependent decay. To see this, we evaluate the sum in Eq. (11). The details of this decay depend of course on the presumed distribution of coefficients c_λ at some putative time $t = 0$, and therefore would require a detailed time-dependent model of complex formation, which we do not attempt here. Rather, we simply assume that the population $|c_\lambda|$ of each resonance is proportional to the probability $P_{\chi 2}(k_\lambda)$ that the corresponding rate k_λ occurs. In this case, Eq. (11) can be reinterpreted as the integral

$$P(t) \approx \int_0^\infty dk P_{\chi 2}(k) \exp(-kt) = \left(1 + \frac{2\bar{k}t}{N_o}\right)^{-\frac{N_o}{2}}. \tag{30}$$

In the limit $N_o \to \infty$, this expression gives the exponential decay law at the mean rate $\bar{\gamma}$,

$$P(t) \to \mathrm{e}^{-\bar{k}t}, \tag{31}$$

which corresponds to the case of reactive molecules such as KRb which should therefore exhibit an exponential decay.

However, in the single-channel case the expression becomes

$$P(t) = \frac{1}{\sqrt{2\bar{k}t + 1}}, \tag{32}$$

representing an algebraic, rather than exponential, decay. It agrees with the exponential decay at short times, but at time scales $\approx 1/\bar{k}$ the decay begins to slow down.

Using this result, we can illustrate decay rates as a function of the mean coupling $\bar{x}$. To do so, we would like to plot a decay rate versus x. This is somewhat problematic, since by its very nature the decay is nonexponential, hence not easily characterized by a number k_{eff} in an expression $\exp(-k_{eff}t)$. To circumvent this difficulty, we somewhat arbitrarily fit the population $P(t)$ to a single decay rate over the time interval over which P drops to $1/e^2$ of its initial value. The linear fit

$$\ln P(t) = -k_{eff}t + b \tag{33}$$

over this time interval then identifies an approximate, effective decay rate k_{eff} that at least sets the scale of the observed decay.

Defined in this way, the effective decay rates are plotted versus x in Fig. 3 for the three different numbers of open channels $N_o = 100$, 10, 1. Also reproduced for reference is the transition state theory rate k_{TST}, presented as a solid line. It is immediately clear that for a large number of open channels $N_o = 100$, the rate derived from the optical model nearly reproduces that from transition state theory, thus validating the use of this theory in cases such as KRb+KRb scattering, where the number of open channels is indeed large.

The decay rate may be expected to decrease linearly in the number of open channels, as implied by the RRKM formula in Eq. (3). Recall that in Fig. 3 this dependence is already accounted for, as k_{eff} is normalized to k_{RRKM}. Thus, the figure illustrates an extremely rapid *additional* reduction in k_{eff} as N_o decreases. Strikingly, this suppression below

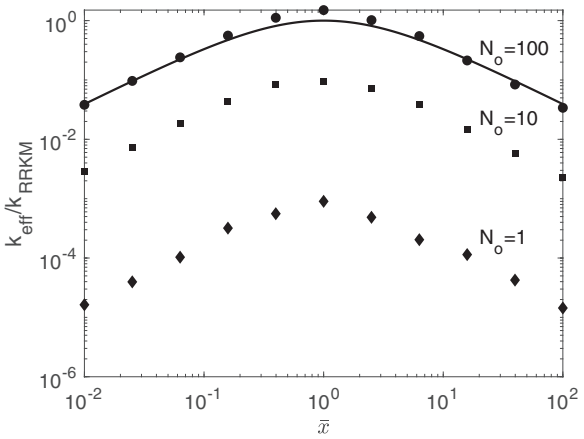

FIG. 3. Effective decay rates $k_{\rm eff}$ as defined by Eq. (33), normalized by the RRKM rate, vs mean sticking coefficient $\bar{x}$, for various numbers of open channels $N_{\rm o} = 100$ (circles), 10 (squares), and 1 (diamonds). Solid line: Transition state theory rate $k_{\rm TST}$.

$k_{\rm TST}$ appears to be a similar factor for all values of x. For x in a range something like $0.1 < x < 10$, and for a single open channel, a suppression of decay rates by three to four orders of magnitude is not unreasonable. This is intriguing news for observations of collision complexes in NaK+NaK, NaRb+NaRb, or Rb+KRb collisions, where such orders of magnitude increases in apparent lifetimes have been observed.

VI. CONCLUSIONS

It will be remembered that our overall goal here is to explore what the statistical theory might have to say about complexes forming and subsequently decaying in ultracold alkali dimer collisions. This we do in spite of doubts about the very applicability of such a theory, given the paucity of states within the $\sim k_B T$ energy range available. Nevertheless, the existence of the complexes, their essential randomness, and their utility in thinking about the problem appear no longer in doubt, as we have outlined in Sec. II.

In this article we have added to the qualitative interpretive power of statistical models, namely, to account for the apparently anomalously long lifetimes of the complex, as compared to the simple standard reference afforded by the RRKM decay rate. The RRKM rate sets a characteristic scale for the decay rate, which is an upper bound on the true decay rate. More properly, actual mean decay rates are subject to fluctuations inherent in the statistical nature of the complexes, which notes that for small numbers of open channels $N_{\rm o}$, the rate is not simply proportional to $N_{\rm o}$, as in the RRKM theory, but becomes far slower than this scaling, dramatically so for $N_{\rm o} = 1$. This slowing down is intimately tied to a preponderance of unusually long-lived resonant states in the optical model, as codified in the chi-squared distribution, and that is characteristic of a chaotic system.

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