Time-Delay Distributions in Ultracold Collisions

JLB

1 Blah Blah

A landmark result by Croft *et al.* demonstrated that statistical estimates of resonances, and their lifetimes, in sticky complexes are perhaps reasonable. It did this by comparing them to actual spacings and time delays for a real calculation [1]. This result follows from consideration of many resonances spanning a collision energy range of order Kelvin. On the other side of this question, for the handful of complexes whose lifetimes have been estimated in laboratory experiments, their lifetimes are sometimes in accord with the simplest, RRKM, estimate of the lifetime; but sometimes, far longer.

Further complicating the issue is the fact that, even for most of the molecule-molecule cases considered, the mean spacing of the resonant energies is $\gg k_B T$, so that, at most, one resonance is accessible. This makes statistical ideas, such as averaging over many resonances, suspect. (Note, however, that at least one fast-talking snake oil salesman tried to wave away these concerns in Ref. [2].) Thus, mean values of the possible lifetimes, associated to the RRKM result, may be less useful to understanding the variety of experimental reality than the *distributions* of possible lifetimes.

One would therefore like to establish, in a controlled way, an ensemble of scattering calculations, each producing its own characteristic lifetime, on which statistics may be performed. These simulations would cover cases where the resonances are dense or sparse, wide or narrow, close or far from the scattering threshold. Here we intend to accumulate statistics, not by means of many large-scale close-coupling calculations, but by – what else? – a statistical model of the complex.

2 Model

To this end we incorporate the original model of Mayle *et al* [3, 4], which has, astonishingly, not yet been used for this purpose. Or if it has been, I've forgotten. The gist of the current calculation is as follows. We assume a single open channel $N_o = 1$, with threshold at energy $E_{\text{thresh}} = 0$, in which elastic, s-wave scattering occurs. This channel is coupled to a vast reservoir of resonant states defined by a short-range reactance-matrix,

$$Y(E) = -\pi \sum_\mu \frac{W_\mu^2}{E - E_\mu}. \tag{1}$$

The resonance positions E_μ and couplings W_μ are randomly selected in the usual way, whereby each realization of the spectrum can lead to a distinct time delay. Within this model we calculate a unitary, one-channel S-matrix, $S(E)$, which includes the resonances and the influence of threshold. We then compute the time delay

$$Q(E) = -i\hbar S^* \frac{dS}{dE}, \tag{2}$$

which can be thermally averaged if necessary.

We will handle the threshold behavior following Ruzic [5]. To this end, it is useful to deploy natural units for scattering. We have collision partners with reduced mass μ and van der Waals coefficient C_6, whereby natural units of length, energy, and time, are

$$\beta = \left(\frac{2\mu C_6}{\hbar^2}\right)^{1/4}, \qquad E_\beta = \frac{\hbar^2}{2\mu\beta^2}, \qquad \tau_\beta = \frac{2\pi\hbar}{E_\beta}. \tag{3}$$

to remain in the threshold regime, we require $k_B T \leq E_\beta$.

The remaining parameters that define the model are then dimensionless ratios. One is the mean spacing of resonances, d, in units of the natural van der Waals energy,

$$\bar{d} = \frac{d}{E_\beta}. \tag{4}$$

So the spectrum is dense or sparse on the scale of collision energies, for $\bar{d} < 1$ or $\bar{d} > 1$, respectively. The other is the standard parameter relating the resonant coupling strength to the mean level spacing,

$$x = \pi^2 \frac{\bar{\nu}^2}{\bar{d}}, \tag{5}$$

which defines the variance of W's in reduced units as

$$\langle \bar{W}_\mu^2 \rangle = \bar{\nu}^2 = \frac{\bar{d}}{\pi^2} x. \tag{6}$$

Thus we can contemplate the statistics of time delays for given values of $\bar{d}$ and x.

Given the short-range matrix Y, one constructs the full K-matrix as [5]

$$K = \frac{AY}{1 + \mathcal{G}Y}, \tag{7}$$

where the s-wave MQDT parameters in our units are given by

$$A = \bar{a}k, \qquad \mathcal{G} = \left(\frac{1}{3} - \bar{a}^2\right) k^2, \tag{8}$$

in terms of the Gribakin-Flambaum scattering length $\bar{a} = (\pi 2^{-3/2}/\Gamma(5/4)\Gamma(1/2))^2$. The full, unitary S-matrix is given by

$$S = e^{2i\eta} \frac{(1 + iK)}{(1 - iK)}, \tag{9}$$

in terms of the background scattering length

$$\eta = -\bar{a}k. \tag{10}$$

Using this model, the time delay is given by

$$Q = -i\hbar S^* \frac{dS}{dE} = 2\hbar \left(\eta' + \frac{K'}{1 + K^2}\right), \tag{11}$$

where primes denote derivatives with respect to energy. The derivative of K is in turn given by

$$K' = \frac{A'Y + AY'}{(1 + \mathcal{G}Y)} - AY \frac{\mathcal{G}'Y + \mathcal{G}Y'}{(1 + \mathcal{G}Y)^2}. \tag{12}$$

The derivative of Y itself is

$$Y' = \pi \sum_\mu \frac{W_\mu^2}{[E - E_\mu]^2}. \tag{13}$$

Finally, it is convenient to normalize the time delay with respect to the RRKM lifetime for a single open channel, $\tau_{\mathrm{RRKM}} = 2\pi\hbar/d$, whereby we determine the reduced time delay

$$Q_{\mathrm{red}} = \frac{Q}{\tau_{\mathrm{RRKM}}} = \frac{d}{\pi}\left(\eta' + \frac{K'}{1 + K^2}\right). \tag{14}$$

This makes a convenient reference, since you are naively expecting τ_{RRKM}.

An important issue is that the time delay can in many cases, be negative. For example, away from resonances, if the scattering is dominated by the background phase shift, the time delay is given by

$$Q_{\mathrm{non-resonant}} = 2\hbar\eta' = -2\hbar\bar{a}/\sqrt{k}. \tag{15}$$

Negative time delay corresponds to positive background scattering length, that is, an effective repulsion that makes the collision last less time that if the molecules hadn't interacted at all. In the results below, we will accordingly count the fraction of sample spectra whose time delay is positive, and only track the statistics of only those time delays that are positive.

3   Preliminary Results

In all the results so far, we take the temperature to be $k_B T = 0.5E_\beta$, to stay basically in the threshold regime. Each spectrum consists of roughly 200 resonances, the randomly chosen values of E_μ come from a GOE distribution with mean spacing $\bar{d}$ and the couplings W_μ are chosen from a Gaussian distribution with variance $\bar{\nu}^2$, as in [2]. The thermally averaged time delay $\langle Q_{red} \rangle$ is given in units of the RRKM lifetime $\tau_{RRKM} = 2\pi\hbar/d$.
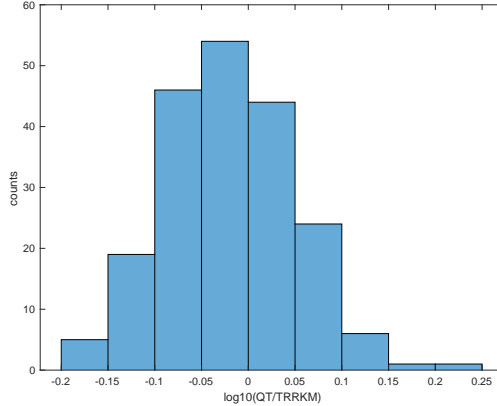
Figure 1: Histogram of time delay for 200 dense spectra, all with $\bar{d} = 0.1$ and mean coupling $x = 0.1$. Lifetimes are normalized by the RRKM lifetime.

We start with a relatively dense spectrum, $\bar{d} = 0.1$, that is, 10 resonances per van der Waals energy, and choose a channel coupling $\bar{x} = 0.1$. We run 200 random spectra and display the resulting time delays in Figure 1. These time delays are normalized to the RRKM lifetime. Moreover, they span many orders of magnitude, whereby it is useful to make a histogram of $\log_{10}(\langle Q_{red} \rangle)$. This distribution is, if not normal, at least normal-ish.

In this example with lots of available resonances, we find that the fraction of spectra leading to positive time delays is 1.0, that is, in the dense spectrum, there are always resonances close enough to captivate the molecules, at least temporarily. The mean of the quantity plotted is -0.0195, meaning that the ratio of time delay to the RRKM time delay in this sample is $10^{(-0.0195)} = 0.96$. That is, RRKM is indeed a pretty good guess. But the distribution is pretty broad, the largest value giving $\langle Q_{red} \rangle = 10^{(.25)} = 2$, twice as big!
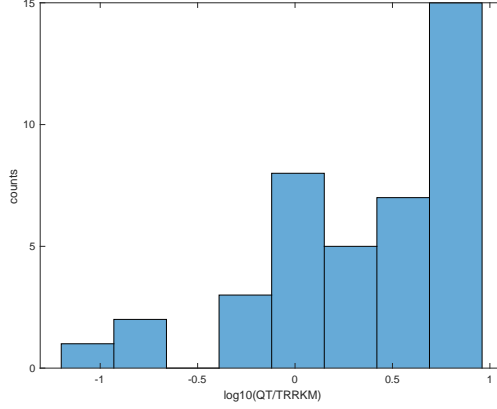
Figure 2: Histogram of time delay for 200 sparse spectra, all with $\bar{d} = 10$ and coupling $\bar{x} = 0.1$. Lifetimes are normalized by the RRKM lifetime.

For comparison, we do the exact same thing, except for a sparse spectrum, with $\bar{d} = 10$, that is, mean spacing ten times larger than the van der Waals energy. Retaining the coupling $\bar{x} = 0.1$, and again running 200 spectra, we get the statistics in Figure 2. It does not look as good, and this is because there is not as much data: only 20 percent of the spectra return a positive time delay. That is, in spectra with wide energy spacing, the most likely thing is not to stick at all. However, when it does stick, it sticks pretty well. The mean of this histogram is 0.33, implying a mean lifetime relative to the RRKM lifetime of $10^{(.33)} = 2.1$. The greatest lifetime reported here is about eight times the RRKM lifetime.
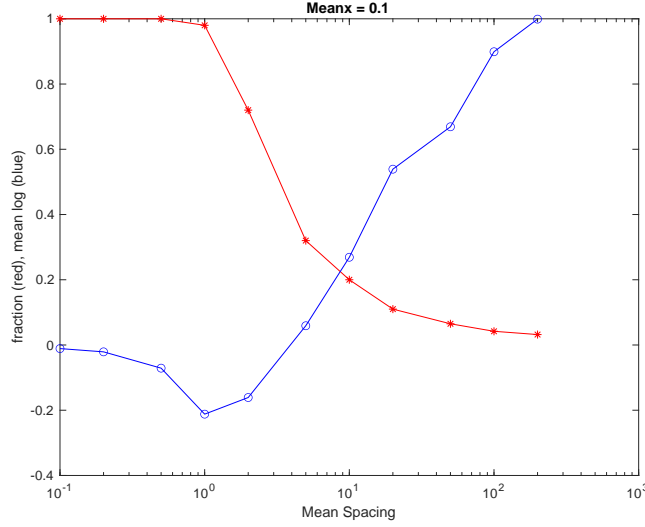
Figure 3: For spectra with mean coupling $\bar{x} = 0.1$: Fraction of spectra leading to positive time delay (red); and mean value of $\log_{10}(\langle Q \rangle / \tau_{RRKM})$ (blue). Both quantities conveniently fit on the same scale.

There is therefore a clear tradeoff here: you can achieve longer lifetimes for molecules that stick, but at the expense of fewer systems where they stick at all. So let's look at that systematically. So, in Figure 3 we set the mean coupling to $\bar{x} = 0.1$, and vary the mean spacing $\bar{d}$ on the horizontal axis.

The red curve is the fraction of spectra for which the time delay is positive. For small spacing, it is all of them, as suggested above. After the mean spacing exceeds $\bar{d} = d/E_\beta \approx 1$, this fraction starts to drop toward zero.

But: at the same time, the mean lifetime (blue) increases. Here we plot $\log_{10}(\langle Q_{red} \rangle)$, so at small mean spacing we recover the RRKM result. But then after the spacing exceeds $\bar{d} \approx 1$, this mean continues to rise. When the spacing is 200 times E_β, the mean lifetime is 10^1, ten times the RRKM lifetime - and growing! Well, every once in a while you do happen to have a resonance handy, and its time delay is large. (I won't bother to plot it, but very nearly the same figure results for strong coupling, $\bar{x} = 10$. Well, this is what we expected, $\bar{x}$ and $1/\bar{x}$ are about the same.)
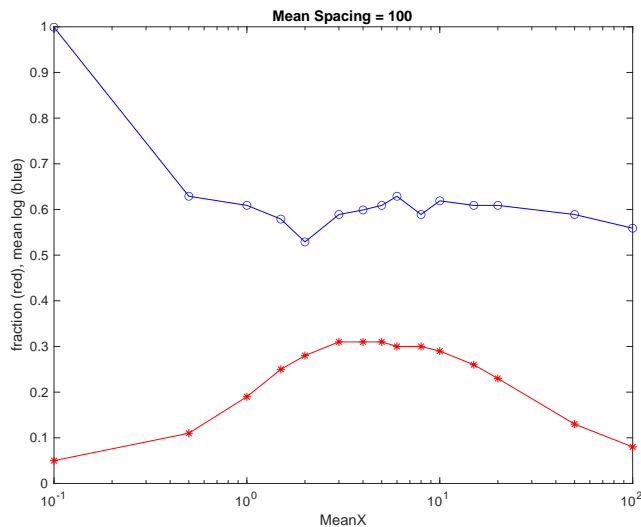
Figure 4: For spectra with mean resonance spacing $\bar{d} = 100$: Fraction of spectra leading to positive time delay (red); and mean value of $\log_{10}(\langle Q \rangle / \tau_{RRKM})$ (blue). Both quantities conveniently fit on the same scale.

Well, maybe it's worthwhile to see how to maximize the fraction of spectra with positive time delay. To this end, I vary the coupling in in Figure 4. Here I choose a very large mean spacing $\bar{d} = 100$, and vary the coupling $\bar{x}$ on the horizontal axis. The mean time delay (blue) is pretty much indifferent to the coupling. But the fraction of spectra that support positive time delays can, strikingly, get as high as 30 percent, for couplings $\bar{x}$ near unity.

Tentative conclusion: It may not be completely crazy to expect lifetimes a lot bigger than the RRKM lifetime. But it might be 70 percent crazy?

4 Optimal Coupling

Since we are, frankly, looking for long lifetimes, let's go ahead and set the coupling to its optimal value, for example, $\bar{x} = 4.0$, reading off the red curve in Figure 4. Doing so, we can look at the scaling of mean lifetime with mean spacing. This is shown in Figure 5. Note that in all these cases, the fraction of molecules sticking is about one third (not shown). Meanwhile, the lifetime grows linearly with the mean spacing. So very roughly, at optimal

coupling, we would have

$$\left(\frac{\langle Q_{red}\rangle}{\tau_{RRKM}}\right) = 0.04\left(\frac{d}{E_\beta}\right). \tag{16}$$
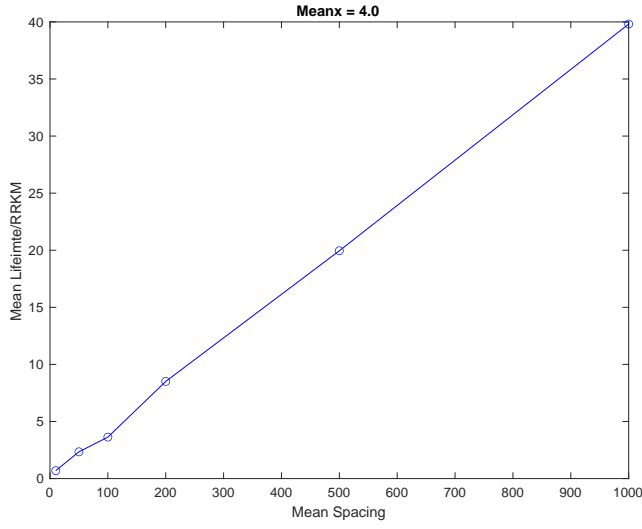

Figure 5: For spectra with mean coupling $\bar{x} = 4.0$: Fraction of spectra leading to positive time delay (red); and mean value of $\log_{10}(\langle Q\rangle/\tau_{RRKM})$ (blue).

This is interesting, but not altogether helpful. For example, for NaK we have $d = 8\ \mu$K, $E_\beta = 10\ \mu$K. This is too small a value of $\bar{d}$ for the scaling to apply to. In fact, for $\bar{d}$ this small, the mean time delay goes back to the RRKM lifetime again, whereas the observed lifetime is > 100 times larger.

References

[1] J. F. E. Croft, N. Balakrishnan, and B. K. Kendeick, Phys. Rev. A **96**, 062707 (2017).

[2] J. F. E. Croft, J. L. Bohn, and G. Quéméner, Phys. Rev. A **107**, 023304 (2023).

[3] M. Mayle, B. P. Ruzic, and J. L. Bohn, Phys. Rev. A **85**, 062712 (2012).

[4] M. Mayle, G. Quéméner, B. P. Ruzic, and J. L. Bohn, Phys. Rev. A **87**, 012709 (2013).

[5] B, P. Ruzic, C. H. Greene, and J. L. Bohn, Phys. Rev. A **87**, 032706 (2013).