I. INTRODUCTION

The ability to create ultracold atomic gases has engendered extraordinary progress in a diverse range of physical areas. In few-body physics the first experimental observation of Efimov states was made in a gas of ultracold caesium [1]; in many-body physics experimental observation of zero-temperature quantum phase transitions has been made in a gas of ultracold rubidium atoms trapped in an optical lattice [2]; in precision measurement the development of new atomic-clock technologies has used ultracold strontium trapped in an optical lattice [3]. What all these diverse applications have in common is that they take advantage of the exquisite precision and control uniquely attainable in the ultracold regime.

Ultracold molecules share the precision and control of ultracold atomic gases, while their richer internal structure and long-range anisotropic interactions open up an even more diverse range of applications. Cold and ultracold molecules have been used to study chemical reactions at their most fundamental level [4], measure the shape of the electron [5,6], and perform precision spectroscopy of complex molecules [7]. There is a wide array of theory proposals for ultracold molecular samples, which take advantage of the complexity of molecules relative to atoms, from studying novel quantum phases [8-11] to quantum information processing [12-15]. Such proposals rely on the ability to produce a stable ultracold molecular gas without significant loss.

The rich structure of molecules is however both a blessing and a curse. Trap loss has been found to be a limiting factor in ultracold molecule experiments with alkali dimers [16-19]. This loss persists even when the molecules are in their absolute ground-state and only elastic collisions are possible. One possible mechanism for this loss is the formation of long-lived complexes. Based on statistical arguments, Mayle et al have proposed that due to the high density-of-states (DOS) in such systems 4-body complexes can have lifetimes of order 1-10 ms [20, 21]. If these lifetimes are reasonable then this could explain the experimentally observed trap loss, which limits trap lifetime to the order of seconds. Lifetime estimates for 3-body alkali complexes formed in atom-dimer collisions using this DOS approach have been shown to be reasonable when compared to estimates from classical trajectory calculations [22]. So far, however, there has been no explicit experimental measurement or theory predication based on quantum calculations for such lifetimes.

Such complexes can however also be considered a feature not a bug. They are expected to exhibit the Wigner-Dyson energy level statistics associated with quantum chaos. There has been recent interest in understanding the role of chaos in cold collisions [20-32]. Ultracold molecular collisions are complex and understanding them in chaotic terms could allow for the considerable insight gained in nuclear physics to be applied to ultracold atomic and molecular physics [33]. For example Mayle et al have developed a statistical scattering formalism which assumes the formation of chaotic complexes at short range [20, 21].

In this work we report explicit delay times for elastic K$_2$+Rb collisions, obtained from numerically-exact quantum-scattering calculations. We compare these delay times with lifetimes for the collision complex predicted by a simple DOS approach finding them to be reasonable and validating their use for other similar systems. We also examine the statistics of resonance positions and widths finding that they follow the Wigner-Dyson and Porter-Thomas distributions respectively. Both distributions are characteristic of quantum chaos.

II. METHODS

We use the atom-diatom scattering formalism as developed by Pack and Parker [34, 35]. In the short range we use adiabatically-adjusting principle-axis hyperspherical (APH) coordinates, an approach which ensures that all arrangements are treated fully equivalently, while in the long range we use Delves hyperspherical coordinates. The wavefunction in the short-range APH region is expanded in an orthonormal basis capable of accurately representing the hyperspherical harmonics [36]. This basis is therefore capable of fully representing the complex collision dynamics of 3 atoms at short range which is
the source of the long lifetimes predicted by Mayle et al [20, 21]. We emphasize that while in this work we are primarily interested in elastic scattering this reactive formalism is in fact required as many of the channels open at short hyper-radius correspond asymptotically to configurations with a bound KRb dimer. The lowest 2500 adiabatic potential curves are shown in figure 1 where the high DOS which leads to the complex short-range dynamics can easily be seen. All calculations are for total angular momentum \( J = 0 \) even parity and even identical-particle exchange symmetry. Coupling of the orbital angular momenta with both the electron and nuclear spins is omitted. For non-zero \( J \), the computational cost is prohibitive scaling as \( \mathcal{O}((J + 1)^3) \), even when we take advantage of parity and exchange symmetries. Fortunately, we are primarily interested in the ultracold regime where only \( s \)-wave collisions contribute (that is, only \( J = 0 \) is required for \( K_2 \) in the ground rotational state \( j = 0 \)). The log-derivative matrix was propagated using the method of Johnson [30]. The details of the calculation are the same as used for the \( K+KRb \) reaction, for details see [20]. An \( ab initio \) ground-state potential energy surface was used which accurately accounts for the long-range dispersion behavior, for more details see [20].

III. RESULTS

A. Long-lived complexes

The long lifetimes predicted for complexes in ultracold alkali-dimer collisions are due to two main factors. Firstly deep potentials and heavy atoms lead to a high DOS, classically this corresponds to many ro-vibrational degrees-of-freedom for the energy to distribute into. Secondly few exit channels mean the complex spends a long time exploring these degrees-of-freedom before finding a way out. These concepts are codified by Rice-Ramsperger-Kassel-Marcus (RRKM) theory [37–39]. RRKM theory predicts a lifetime given by,

\[
\tau = \frac{2\pi \hbar \rho}{N_0}.
\]  

(1)

Where \( \rho \) is the DOS and \( N_0 \) is the number of energetically allowed exit channels. The RRKM lifetime originated in transition state theory however it has been used by Mayle et al as a way to estimate lifetimes in ultracold molecular collisions [20, 21]. The beauty of equation (1) is its simplicity, only an estimate of the DOS and the number of open channels is needed to calculate a complex lifetime at a given energy.

We proceed to calculate the lifetime of a KRbK complex, formed in elastic \( K_2+Rb \) collisions, by following the method detailed by Mayle et al for estimating \( \rho \) [20]. For the \( K_2 \) dimer potential we use a Lennard-Jones potential with \( C_6 \) and \( D_\sigma \) taken from [31]. To obtain the \( C_6 \) and \( D_\sigma \) required for the Lennard-Jones \( K_2+Rb \) potential we use the \( C_6 \) and \( D_\sigma \) for KRb taken from [31] and assume the three-body potential is pairwise additive, with \( C_6 \) and \( D_\sigma \) chosen to be double the atom + atom value for the atom + dimer potential. In this way the choice of \( C_6 \) used to estimate the DOS is the same as the \( C_6 \) used in the scattering calculations. The 1d-Schrödinger equation was solved using the Fourier-grid-Hamiltonian method [42, 43]. Only even rotational levels are included for \( K_2 \) to account for the identical particle symmetry. Using this approach the estimate for \( \rho \) is 3.5 mK\(^{-1}\) which gives a complex lifetime of 167 ns.

The long lifetimes based on the DOS approach manifest themselves quantum mechanically as scattering resonances. This can be understood intuitively from the energy-time uncertainty principle,

\[
\Delta E \Delta t \geq \frac{\hbar}{2}
\]  

(2)

This can be interpreted as saying that a narrow resonance implies a long lifetime,

\[
\tau \approx \frac{\hbar}{2\Gamma}
\]  

(3)

where \( \Gamma \) is the width of the resonance and \( \tau \) is the lifetime, which quantify the uncertainty in energy and time respectively. One has to be careful interpreting these equations as time is not an observable in quantum mechanics, however they do make clear that long-lived complexes correspond to narrow resonances in quantum scattering. Figure 2 shows the elastic cross-section for collisions of \( K_2(v = 0, j = 0) \) with Rb as a function of energy, for total angular momentum \( J = 0 \). It is seen that there is a forest of narrow resonances starting at about 10 mK, each of which corresponds to a long-lived KRbK complex. The zero-energy cross-section gives a scattering length of 90 Å which compares well to the average scattering length of 47 Å obtained from the \( C_6 \) coefficient [44].

![Figure 1](image1.jpg)  

**FIG. 1.** The adiabatic potential curves for the KRbK complex at short hyper-radius for even exchange symmetry. Only every 100th curve is shown due to the high DOS for this system. The horizontal red line corresponds to the \( v = 0 \) \( j = 0 \) threshold of \( K_2 \).
While equations 2 and 3 give an intuitive understanding of why narrow resonances correspond to long lifetimes, we can be more rigorous by computing Smith’s Q matrix,\[ Q = i\hbar S \frac{\partial S^\dagger}{\partial E}. \] (4)

The eigenvalues of Q are the time delays between a collision with and without a potential \[ E \] and \[ E - \Delta E \] respectively. This allows for the direct calculation of Q from the energy derivatives of K, and S. This approach has been extensively used to compute Smith delay times in a variety of systems and contexts \[ 15, 50 \].

Figure 3 plots \[ \text{Tr}(Q) \] as a function of energy along with the cross-section on the same energy grid. The lifetimes are computed on a energy grid with over 1600 points. The small gaps seen in the energy grid are regions where the delay time is negative. Smith time delays are the difference between the time for a collision and the time for a collision without a potential, we refer to the latter as the background collision time. This definition leads to negative delay times away from resonances as the background collision time is large due to the lack of an attractive potential, compared to the collision time with a potential, especially at low collision energies. It is easily seen that there are many resonances which exceed the DOS estimate for the lifetimes of 167 ns.

Following 49 we fit each of the resonances to a Breit-Wigner form,\[ Q(E) = \frac{\Gamma_r/2}{\left[E_r - E \right]^2 + (\Gamma_r/2)^2}. \] (5)

Where \( E_r \) and \( \Gamma_r \) are the resonance energy and width respectively. This allows us to unambiguously assign a delay time,\[ Q_r = \frac{4\hbar}{\Gamma_r}. \] (6)

to each resonance seen in figure 3. The parameters \( E_r \) and \( Q_r \) are shown on figure 3 as solid red vertical lines and red dots respectively. The delay times for the 10 narrowest resonances are given in Table I. Having assigned to each resonance an explicit delay time we can compare them to the DOS estimate of 167 ns. We find that many resonances have lifetimes longer than the DOS estimate. In fact the lifetimes of the narrowest resonances are around an order of magnitude longer than that predicted by the DOS approach. It is noticeable however that we find far fewer such resonances than we would expect based on the DOS used to estimate the lifetime.

The delay time is a well defined quantity however it does not correspond to the lifetime as experimentally understood. As discussed earlier the Smith delay time includes a significant negative contribution from the collision partners traversing the long range which does not correspond to what would generally be considered the lifetime of a collision complex (the time collision partners spend strongly interacting at “short range” before eventually escaping to infinity). Due to this difference the delay time should therefore be considered a lower bound on the complex lifetime of experimental relevance.

The results shown here suggest that the DOS lifetime estimates for complexes formed during ultracold collisions between molecules similar to those studied here are also reasonable. This in turn suggests that long-lived 4-body complexes formed in ultracold dimer-dimer collisions are the cause of trap loss seen experimentally.

\section*{B. Quantum chaos}

Quantum-scattering calculations for collisions of ultracold molecules are extremely computationally expensive. Even though here we have presented results for only total angular momentum \( J = 0 \), even exchange symmetry and parity, included no spin or field effects the calculations still required over 300,000 hours of CPU time. It is possible that numerically exact quantum scattering calculations including all the effects omitted in these calculations will never be computationally tractable. As such statistical approaches offer an alternative way to attack such problems 20, 21, 24, 51.

Atom-dimer ultracold collisions have been shown to be classically chaotic 22, and the analysis of short range adiabats of KRbK have been shown to exhibit the characteristics of quantum chaos 26. While quantum systems cannot exhibit the non-linearity characteristic of classical chaos (in quantum mechanics operators are linear 52) quantum analogs of classically chaotic systems do exhibit certain statistical signatures 53, 54, Such as Wigner-Dyson energy-level statistics 55, 56, Ericson fluctua-
We now proceed to examine the statistical distribution of resonance positions for evidence of quantum chaos. The distribution of scaled nearest-neighbor spacings for non-chaotic systems is given by the Poisson distribution,
\[ P_p(s) = \exp(-s), \]
where small spacings predominate. However in quantum systems chaos manifests itself in the repulsion between energy levels \[54\], the distribution of scaled nearest-neighbor spacings is then given by a Wigner-Dyson distribution \[55\]. For Hamiltonians with time-reversal symmetry, such as we have here, the nearest-neighbor spacings are given by,
\[ P_{wd}(s) = \frac{\pi}{2} s \exp\left(-\frac{\pi}{4} s^2\right). \]
Figure 4 shows the distribution of scaled nearest-neighbor spacings between the 44 resonances shown in figure 3. While we have not found enough resonances to make a definitive statement as to whether this system exhibits quantum chaos we do clearly see the repulsion between neighbouring resonances characteristic of quantum chaos.

The degree to which the observed distribution matches the Wigner-Dyson distribution can be quantified by the Brody parameter \[59, 60\]. The Brody parameter is itself not physically meaningful, rather is defined to smoothly

| Energy (K) | Lifetime (µs) | Width (µK) |
|------------|---------------|------------|
| 0.24       | 1.47          | 20.80      |
| 0.29       | 1.33          | 22.90      |
| 0.41       | 0.44          | 68.75      |
| 1.23       | 0.44          | 68.83      |
| 0.11       | 0.33          | 91.63      |
| 0.39       | 0.32          | 95.72      |
| 0.03       | 0.27          | 111.65     |
| 0.01       | 0.23          | 132.01     |
| 0.31       | 0.15          | 207.77     |
| 0.70       | 0.12          | 256.15     |

TABLE I. Position, lifetime and width of the 10 narrowest resonances.
interpolate between the Poisson distribution and the Wigner-Dyson distribution,

\[ P_b(s) = As^\eta \exp(-\alpha s^{\eta+1}), \]

\[ A = (\eta + 1)\alpha, \]

\[ \alpha = \Gamma\left(\frac{\eta + 2}{\eta + 1}\right)^{\eta+1}, \]

where \( \eta \) is the Brody parameter. For \( \eta = 0 \) the distribution reduces to \( P_p \) and for \( \eta = 1 \) it reduces to \( P_{wd} \). Performing a least-squares fit of equation (9) to the data shown in figure 4 we obtain a Brody parameter of \( \eta = 0.78 \pm 0.4 \).

Despite the relatively small number of resonances found this value is clearly suggestive of a chaotic system.

We now move on to examine another statistical characteristic of chaos in quantum systems, the Porter-Thomas distribution of resonance widths [58]. Porter-Thomas statistics describe the distribution of velocity-independent reduced widths,

\[ \Gamma_0^n = \Gamma_n/E_0^{\frac{1}{2}}. \]

The reduced widths for chaotic systems follow the \( x_k^2 \) of degree \( k = 1 \),

\[ P_{pt}(s) = s^{-\frac{1}{2}}e^{-s}, \]

where the scaled reduced width is given by \( s = \Gamma_0^n/\langle \Gamma_0^n \rangle \).

Figure 5 shows the distribution of reduced widths for the resonances shown in figure 3. Despite the relatively small statistical sample we clearly see broad agreement with the overall trend of the Porter-Thomas distribution towards resonances with smaller widths.

**IV. CONCLUSIONS**

We have examined ultracold elastic K\(_2\)-Rb collisions and reported explicit lifetimes for long-lived collision complexes formed during the collision process, finding that such lifetimes can be of the order of microseconds. These lifetimes were compared with those predicted using a simple DOS approach based on RRKM theory which are shown to be reasonable. The accuracy of such methods is of current interest as long-lived complexes formed in ultracold dimer-dimer collisions have been proposed as the cause of observed experimental trap loss.

Long-lived complexes correspond to narrow resonances in quantum scattering. We have analyzed the distribution of nearest-neighbor spacings and widths of these resonances and have found that they both exhibit the statistical signature of quantum chaos. Quantum scattering calculations for collisions of ultracold molecules are extremely computationally expensive. It is possible that numerically-exact quantum-scattering calculations including all the effects of interest will never be computationally tractable. As such the chaotic nature of system such as this suggests a statistical approach to tackling such problems could be fruitful.

In future work we intend to examine the effect of including the excited doublet state on the lifetimes. Including the excited state in the calculations will allow for the full treatment of the conical intersection and the possibility of long-lived quasi-bound states on the upper surface.

**V. ACKNOWLEDGMENTS**

We acknowledge C. Makrides, M. Li, and S. Kotchoigova for helpful discussions. We acknowledge support from the US Army Research Office, MURI grant No. W911NF-12-1-0476 (N.B.), the US National Science Foundation, grant No. PHY-1505557 (N.B.). BKK acknowledges that part of this work was done under the auspices of the US Department of Energy, Project No. 20170221ER of the Laboratory Directed Research and
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