Crossover from the Ultracold to the Quasiclassical Regime in State-Selected Photodissociation

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Processes that break molecular bonds are typically observed with molecules occupying a mixture of quantum states and successfully described with quasiclassical models, while a few studies have explored the distinctly quantum mechanical low-energy regime. Here we use photodissociation of diatomic strontium molecules to demonstrate the crossover from the ultracold, quantum regime where photofragment angular distributions strongly depend on the kinetic energy to the quasiclassical regime. Using time-of-flight imaging for photodissociation channels with millikelvin reaction barriers, we explore photofragment energies in the 0.1–300 mK range experimentally and up to 3 K theoretically, and discuss the energy scale at which the crossover occurs. We find that the effects of quantum statistics can unexpectedly persist to high photodissociation energies.

Recent progress in atomic and molecular physics has resulted in the development of an unprecedented degree of control over molecular degrees of freedom. This includes targeted preparation of molecular samples in specific internal and motional states. The ability to create molecular samples at a range of low temperatures has enabled detailed studies of few-body chemistry in the regime where quantum mechanical effects, such as resonant scattering and barrier tunneling, define the reaction cross sections.

Approaches to exploring the formation and breaking of molecular bonds across the low-energy regime include photoassociation [1], ultracold atomic collisions [2, 3], ultracold molecular collisions [4], state-selected molecular beams with relative velocity control [5–10], and molecule collisions with trapped ions [11]. Each method has benefits such as tunability of collision energies, access to ultralow energies, or adaptability to diverse molecular species. We study molecular photodissociation [12] in the ultracold regime as a path to detailed quantitative understanding of ultracold chemistry phenomena [13]. If the molecules are trapped at sub-millikelvin temperatures, optical control of the bond breaking process allows to reach the near-threshold regime with extremely high energy resolution and tunability. The resolution is limited only by the natural lifetime of the photofragments and the initial trap temperature (both typically < 5 mK, and in this work ~ 1 μK), and the tunability only by the laser intensity and field of view. This reverse-collision technique permits studies of any collisional thresholds that can be reached with one or a few photons, even those with short natural lifetimes that would prevent a successful measurement in a scattering configuration.

Previously we reported photodissociation of ultracold Sr₂ molecules in the near-threshold quantum regime [13] including interference of photofragment matter waves, sensitivity to reaction barriers, shape resonances, and control of reactions by magnetic fields [14]. The measured photofragment angular distributions disagreed with quasiclassical intuition to varying degrees [13]. It remained an open question whether a crossover into quasiclassical behavior could be observed and explained from first principles. Here, we observe the crossover from the ultracold, quantum mechanical to the quasiclassical regime of photodissociation. We show that the photofragment angular distributions exhibit strong variations with the continuum energy, but stabilize to energy-independent quasiclassical patterns at energies that exceed reaction barrier height. We find that photodissociation of very weakly bound molecules can exhibit quantum mechanical behavior to still higher energies. Our study includes an electronically excited multichannel continuum in addition to the ground-state continuum. We describe and clarify different levels of approximation for predicting the photofragment angular distributions [15–20]. Finally, we show that quantum statistics of the photofragments can prevent the photodissociation outcome from reaching the quasiclassical limit even at high energies.

In the experiment, ⁸⁸Sr atoms are laser cooled and photoassociated in a one-dimensional optical lattice, yielding ~ 7,000 Sr₂ molecules trapped at a few microkelvin [21]. The lattice at the wavelength of ~ 910 nm has ~ 30 μm radius and ~ 730 μm length. The molecules predominantly occupy the most weakly bound vibrational level, v = −1, in the electronic ground state that correlates to the atomic ¹S + ¹S threshold. They are distributed between two angular momenta J_i = {0, 2}, either of which can be selected as the starting state for photodissociation, with selectivity of the projection quantum number M_i. Alternatively, weakly bound levels that correlate to the singly excited ¹S + ³P₁ continuum can be populated prior to photodissociation by 689 nm light that co-propagates with the lattice. The photodissociation light pulses are 10–20 μs, the photofragment time of flight varies from ~ 800 μs near threshold to ~ 20 μs at higher energies, and the imaging pulse is 10–20 μs long. The absorption


imaging beam is resonant with the strong 461 nm Sr transition, nearly co-aligned with the lattice, and expanded to \( \sim 300 \) \( \mu \)m in order to intercept the outgoing photofragments [13]. The (vertical) quantization axis is set by the lattice polarization, or by a \( \sim 3 \) G magnetic field when required for state selection, while the photodissociation light has polarization that is parallel \( (P = 0) \) or perpendicular \( (P = 1) \) to this axis. The continuum energy is determined by the frequency of the photodissociation light. Reaching high energies can be challenging because of diminishing bound-continuum transition strengths and rapid expansion of the photofragments.

Figure 1(a,b) shows two photodissociation processes used in this work. In case (a), a single molecular quantum state \( (v, J_i, M_i) \) of the \( \{0_u^+, 1_u\} \) electronic manifold is resonantly populated and immediately photodissociated to the ground continuum \( X0_g^+ \), while process (b) samples the electronically excited continuum from a single ground molecular quantum state. The upper continuum has contributions from the barrierless \( 0_u^+ \) potential and the \( 1_u \) potential with a \( \sim 1 \) mK electronic barrier, where the potentials are labeled by \( \Omega_i \), the atomic angular momentum projection onto the internuclear axis. Rotational barriers present for all continuum states with angular momentum \( J \neq 0 \) are not shown. An image of a photofragment angular distribution and the data analysis procedure are illustrated in Fig. 1(c). Panels (i-iv) show an azimuthally symmetric time-of-flight image, a three-dimensional distribution that results in this image via line-of-sight integration, the cross section of the distribution obtained with the inverse Abel transform, and the radial average of the cross section showing the measured angular photofragment density.

We explore experimentally and theoretically the crossover from ultracold to quasiclassical chemistry, and the applicability of a range of approximations. The quantum mechanical treatment involving bound and continuum wave functions with Fermi’s golden rule to calculate the photodissociation cross sections is in agreement with data across all sampled energies and for molecules in all initial quantum states, with further improvement possible only by introducing small corrections to the ab initio molecular potentials. It is necessary to use the quantum mechanical treatment to model our observations near threshold. At high energy, the axial recoil limit is reached, where photodissociation is much faster than molecular rotation and the photofragments emerge along the molecular axis. The main questions we address are (1) at what energy scale do the angular distributions approach the axial recoil limit; (2) how does this scale depend on the quantum numbers and binding energy of the molecule; and (3) how can quantum state selection prevent the high-energy axial recoil limit from agreeing with quasiclassical intuition?

We address the applicability of the WKB approximation and of a semiclassical model (that considers classical rotation of the molecule during photodissociation) [22]. We find that (i) near threshold, the quantum mechanical treatment correctly captures the observed photofragment angular distributions and their dependence on the continuum energy; (ii) the axial recoil limit is reached at energies that exceed any potential barriers in the continuum; (iii) for very weakly bound molecules, quantum effects can dominate to higher energies than specified in (ii); and (iv) while the axial recoil approximation is usually equivalent to the ubiquitous quasiclassical model, this is not the case if additional selection rules are imposed by bosonic or fermionic nature of the photofragments.

Figure 2 illustrates the evolution of an angular distribution as a function of the continuum energy \( \varepsilon \) for \( 0_u^+ \) \((v = -4, J_i = 1, M_i = 0)\) molecules and \( P = 0 \), which is a feature of near-threshold photodissociation. The molecules are photodissociated over \( \sim 2 \) orders of magnitude of energies, with Fig. 2(a) displaying the angular photofragment densities as a function of \( \varepsilon/k_B \) where \( k_B \) is the Boltzmann constant. Quantum chemistry calculations of the expected density curves, based on ab initio \( \text{Sr}_2 \) potentials [23, 24], are overlayed with the data. The measured images for \( \varepsilon/k_B = 1.6 \) and 14 mK are shown in the leftmost panels of Fig. 2(b,c), followed by the theoretical images. Figure 2(c) also shows an image calculated for the axial recoil limit, which is already approached at 14 mK. Here the angular distribution in
Approaching the quasiclassical limit. With increasing energy, the photofragment distribution approaches the quantum mechanical and quasiclassical predictions on the right. This convergence as well as the initial-state-dependent reaction outcome. For example, in photodissociation of state-selected $^{88}\text{Sr}_2$ molecules to the ground-state continuum some reaction channels (odd $J$) are excluded. This inherently quantum effect influences the photofragment distributions even at high energies. We investigate this phenomenon by measuring and calculating the angular distributions for the photodissociation pathway in Fig. 1(a) with $\Omega = 1$. We find that if $\{M_i = 0, P = 0\}$ are not both true [22], the quantum mechanical angular distributions do not match the quasiclassical predictions in the high-energy limit.

Quantum statistics of photofragments can affect the reaction outcome. For example, in photodissociation of state-selected $^{88}\text{Sr}_2$ molecules to the ground-state continuum some reaction channels (odd $J$) are excluded. This inherently quantum effect influences the photofragment distributions even at high energies. We investigate this phenomenon by measuring and calculating the angular distributions for the photodissociation pathway in Fig. 1(a) with $\Omega = 1$. We find that if $\{M_i = 0, P = 0\}$ are not both true [22], the quantum mechanical angular distributions do not match the quasiclassical predictions in the high-energy limit.

Quantum statistics of identical particles prevents agreement with quasiclassical predictions at large photofragment energies. Here, $P = 1$. (a) Photofragment angular distributions for $1_u(-1,1,0)$ molecules at $\varepsilon/k_B = \{0.63, 2.5\}$ mK ($\varepsilon/h = \{13, 53\}$ MHz) on the left along with quantum mechanical and quasiclassical predictions on the right. This case is energy-independent. The quasiclassical picture fails to describe the process due to quantum statistics, or the missing $J = 1$ partial waves in the ground-state continuum. (b) Energy-dependent angular distributions for the $1_u(-1,3,0)$ molecules at $\varepsilon/k_B = \{3.4, 6.3\}$ mK ($\varepsilon/h = \{70, 130\}$ MHz) are shown on the left, where the insets show the corresponding calculations. High-energy quantum mechanical and quasiclassical predictions are shown on the right. While the highest energy regime could not be reached experimentally, at lower energies the experiment fully agrees with quantum mechanical calculations (shown in the insets).
Figure 3 shows two examples of photodissociation for selected initial states such that the resulting angular distributions do not converge to the quasiclassical expectation. In Fig. 3(a), the $I_u(-1, 1, 0)$ molecules are dissociated at 0.63 and 2.5 mK (13 and 53 MHz) above threshold. Due to the $\Delta J = \pm 1$ and $\Delta M = \pm 1$ selection rules, only $J = 2$ is allowed in the continuum, and therefore no energy dependence is expected or observed [22]. The data confirms an unchanged angular distribution that matches the quantum mechanical prediction and clearly fails to match the quasiclassical model. Figure 3(b) illustrates energy-dependent photodissociation of $I_u(-1, 3, 0)$ molecules. Here, the near-threshold energy dependence arises from interference of the $J = 2$ and $J = 4$ continuum states. The right-hand panels show the calculated quantum mechanical angular distribution in the axial recoil limit that disagrees with the quasiclassical result. To demonstrate experimental agreement with the quantum mechanical model, the left-hand side shows angular distributions at 3.4 and 6.3 mK (70 and 130 MHz) above threshold that match the calculated distributions in the insets. While the axial recoil regime ($> 50$ mK) was not reached in this case due to weak bound-continuum transition strengths and insufficient photodissociation laser power, this limitation is not fundamental. Note that if optical selection rules (rather than spin-statistics restrictions) allow only a single partial wave $J$ in the continuum, then quantum mechanical and quasiclassical angular distributions strictly agree [13].

A key feature of photodissociation is the ability to select one of many possible continua. In Fig. 4 we photodissociate ground-state $X^2\sigma_g(-1, 0, 0)$ molecules to the $\{0_u^+, 1_u\}$ continuum, and sample energies in the range of 0.07-260 mK (1.5-5,500 MHz). Here the electronic potential barrier height is only $\sim 1$ mK, being proportional to the very small $C_3$ dispersion coefficient that is determined by the inverse of the metastable $3P_1$ atomic lifetime. The photofragments have only angular momentum $J = 1$ but two possible $\Omega = \{0, 1\}$ that are mixed via nonadiabatic Coriolis coupling, especially at the lower energies [26]. This mixing has a strong and nontrivial effect on photofragment angular distributions. For the spherically symmetrical initial molecular state, the angular distributions can be described as $I_{QC}(\theta)$ for all continuum energies, but with a varying $\beta_2(\varepsilon)$ that becomes constant at the axial recoil limit. Figure 4 shows the plot of $\beta_2(\varepsilon)$ across a wide energy range that is limited only by the photodissociation laser power, where the smaller error bars arise from the image quality and the larger ones conservatively estimate possible contamination by molecules initially in $J_i = 2$. In the case of mixed $\Omega$ in the continuum, the quasiclassical picture does not predict which $\Omega$ dominates at high energy and whether the observed pattern tend to a perpendicular ($\Omega = 1$) or a parallel ($\Omega = 0$) dipole. For the experiment in Fig. 4, the $ab\ initio$ pattern tends to a parallel dipole ($\beta_2 = 2$) in the axial recoil limit, but for the very weakly bound molecules this regime is expected to be reached only at $> 0.5$ K above threshold. In the energy regime that is currently accessible, photofragment angular distributions vary steeply with energy in the region of the $\sim 1$ mK electronic barrier, then stabilize at $\beta_2 \approx -1$. The energy interval where $\beta_2 \approx -1$ is sensitive to long-range molecular potentials, as we have confirmed by adjusting the $C_6$ coefficients. The measurements in this energy regime allow us to distinguish between the $ab\ initio$ [23], long-range [24], and fitted $ab\ initio$ [25] potentials to which the angular distributions are sensitive, as shown in Fig. 4.

In conclusion, we have explored how ultracold, quantum mechanical state-selected photodissociation crosses over into the classical regime at increasing photofragment energies. The question of applicability of quasiclassical descriptions to photodissociation reactions has lingered in the literature for several decades [13, 15, 18, 19, 27], and this work presents a conclusive resolution of this debate. We find that the high-energy axial recoil limit is reached when the continuum energies exceed any elec-
tronic and rotational barriers, although quantum effects can dominate to larger energies for very weakly bound molecules. We study a hierarchy of approximations (WKB, semiclassical, and axial recoil) [22], and experimentally confirm that the commonly used quasi-classical formula for photofragment angular distributions [16–18] correctly describes the axial recoil limit for a variety of initial molecular states with different sets of quantum numbers, while in the ultracold regime there is a strong nonclassical variation of the angular distributions with energy. We demonstrate that the effects of spin statistics for identical photofragments can persist to indefinitely large photodissociation energies and prevent the angular distributions from approaching the quasi-classical picture. We probe a molecular continuum with a mixture of Ω quantum numbers in an energy range of over three orders of magnitude and with fine resolution, resolving between the \textit{ab initio} potentials and those that have been adjusted using molecular spectroscopy. Photodissociation of ultracold molecules with isolated quantum states uniquely enables studies of molecular continua, and for relatively simple molecules such as \textit{Sr}_2 the state-of-the-art quantum chemistry theory yields excellent agreement with measurements. These features enable us to directly observe and accurately model the crossover from ultracold to quasi-classical chemistry.

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