Suppression of Penning ionization by orbital angular momentum conservation

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The efficient suppression of Penning-ionizing collisions is a stringent requirement to achieve quantum degeneracy in metastable rare gases. Thus far, such loss processes have been avoided by electron-spin polarizing the collision partners. Here, we report on the efficient suppression of Penning ionization in collisions between metastable He and laser-excited Li atoms. The results illustrate that not only the electron spin, but also Λ – the projection of the total molecular orbital angular momentum along the internuclear axis – is conserved during the ionization process. Our findings suggest that Λ conservation can be used as a more general means of reaction control, for example, to improve schemes for the simultaneous laser cooling and trapping of metastable He and alkali atoms.

INTRODUCTION

The study of autoionization dynamics in metastable rare gas collisions has a long research tradition, since atoms in electronically excited, long-lived (“metastable”) states have various applications in cold chemistry, atomic optics, statistical physics and in surface science [1–4].

A reactive collision between a metastable atom A* and a collision partner B, whose ionization potential is lower than the energy of A*, can lead to the ionization of B (Penning ionization, PI) or to the formation of a molecular ion AB+ (associative ionization, AI):

\[
\text{A}^* + \text{B} \rightarrow [\text{AB}]^* \rightarrow \begin{cases} 
\text{A} + \text{B}^+ + e^- \\
\text{AB}^+ + e^- 
\end{cases}
\] (1)

Recently, it has been shown that the relative rates of Penning and associative ionization can be influenced by changing the relative orientation of the interacting atomic orbitals [5–7]. Autoionization reactions can also be controlled by other means, e.g., by preparing the colliding species in a specific internal quantum state, by lowering the collision energy, as well as by implementing coherent control schemes [8–9]. For instance, in sub-Kelvin collisions of metastable rare gas species, where only few partial waves are involved, the low collision energy has enabled the observation of orbiting resonances [10–11]. Such experiments provide opportunities to understand the nature of the intermediate collision complex, which is not possible in conventional scattering experiments.

Reaction control is particularly important to achieve quantum degeneracy in a dilute, ultracold gas of metastable atoms. To prevent rapid trap losses, reactive collisions must be greatly suppressed in these experiments. In the past, this has been achieved by preparing the atoms in spin-stretched magnetic substates [2]. This preparation scheme exploits the fact that, according to Wigner’s spin-conservation rule, electron-spin flips are strongly forbidden during a reactive encounter. For example, in He(2S1/2)-He(2S1/2) collisions, the Penning ionization rate of spin-polarized atoms is about five orders of magnitude lower compared to the unpolarized case [12].

For He(2S1/2)-Rb(5S1/2) collisions, electron-spin statistics were also found to dominate the reactivity [13].

It is known that, for single-species collisions in the ultracold temperature regime, the electronic excitation of one of the collision partners can either lead to an enhancement or to a suppression of the ionization rate depending on the detuning of the excitation light with respect to the atomic resonance [15]. The rate enhancement for red-detuned light can be rationalized by a more attractive long-range potential V(R), which changes from \( \alpha 1/R^6 \) to \( \alpha 1/R^3 \) upon electronic excitation [16, 17]. For excitation with blue-detuned light, the atoms are brought to a repulsive state, which prevents the atoms from approaching one another at close distance, where reactions can occur [18–19]. For two-species collisions, the reaction rates are not expected to change upon electronic excitation, since the shape of the attractive long-range potential remains V(R) \( \propto 1/R^6 \) even when one of the colliding atoms is in an excited state.

In this article, we present two-species Penning collision studies between metastable He atoms and electronically excited Li atoms. We show direct experimental evidence for a Penning suppression mechanism based on the conservation of the projection of the orbital angular momentum along the internuclear axis, Λ. This suppression mechanism is fundamentally different from the physical concepts underlying the previous studies on single- and two-species autoionizing collisions mentioned above. We show experimentally determined reaction rate constant ratios for He(2S1/2)-Li(2S1/2,2P3/2) scattering and we illustrate that our findings can be brought into remarkable agreement with theoretical concepts which are based solely on electron-spin and Λ conservation.

EXPERIMENTAL SETUP

All individual parts of the setup have already been described elsewhere [20, 21]. Therefore, only the most relevant details are given here. The setup consists of a pulsed supersonic beam for \(^4\)He and a magneto-optical trap (MOT) for ultracold \(^7\)Li. Metastable He (He*), a
mixture of He(2S0) and He(2S1), is produced in an electron-seeded discharge at the front of a pulsed valve (7.14 Hz repetition rate). The He∗ beam intensity and its mean velocity \((v_{\text{He∗}} = 1850 \pm 20 \text{ m/s})\) are measured on two gold-coated Faraday cup detectors located downstream from the Li-MOT. In order to determine the role of He(2S0) and He(2S1) on the reaction rate, we optically deplete the population in the 2S0 state using 46 mW of diode laser radiation resonant with the 2S0-4P1 transition at 397 nm [21]. To minimize influences by the Doppler effect, the laser beam is incident perpendicular to the supersonic beam. The interaction time with the sample is increased by retro-reflecting the laser beam on a mirror at the opposite side of the vacuum chamber. Under these conditions, the quenching efficiency of the He(2S0) state is ≥ 99 %. The He∗ singlet-to-triplet ratio is measured on a Faraday cup detector taking into account the secondary electron ejection efficiencies of He(2S0) (\(\gamma = 0.45 \pm 0.02\)) and He(2S1) (\(\gamma = 0.55 \pm 0.02\)) on gold-plated surfaces [22].

Li atoms are continuously laser-cooled in a setup which consists of a Li oven for the production of an effusive Li beam, a Zeeman slower for Li deceleration and a 3D-MOT. Laser intensities of 67 mW/cm² and 49 mW/cm² are used for the pump and the repump laser beams, respectively. To distinguish between Li-ground-state and Li-excited-state collisions with He∗, we use fast mechanical shutters to block the laser light for the MOT and for the Zeeman slower. The shutters are closed just before and after the He∗ atoms have collided with the Li atoms (see Fig. 1), respectively. The expansion of the Li cloud during the absence of laser irradiation (≤ 150 µs) is small and does not lead to a decrease in ion signal (cf. Ref. [20]). The population in the Li(2P3/2) state is varied by simultaneously changing the detuning \(\delta\) of the MOT pump and repump lasers in between different measurement series (−12 MHz ≥ \(\delta\) ≥ −50 MHz).

Reactive collisions are studied in the center of the MOT by continuously extracting all ions, which are produced during the He∗-Li interaction time, onto a channel electron multiplier. The detector is operated in ion counting mode (time bins of 2 µs intervals). After each reaction rate measurement, a background ion trace without Li is taken to filter out all ions not produced by He∗-Li collisions. The AI/PI ratio (obtained using pulsed ion extraction) is typically ≤ 2 %, so that our measurements are mostly sensitive to PI. Relative rate measurements are carried out by alternating the quench laser on and off on a shot-by-shot basis and by increasing the shutter time delay by \(\Delta t = 150 \text{ µs}\) for each third and fourth shot of the pulsed valve.

**RESULTS AND DISCUSSION**

Fig. 1 shows measured time traces of the total ion yield for state-selected He∗-Li collisions at a detuning of \(\delta = -12 \text{ MHz}\). The ion signal intensities are proportional to the He∗ flux, as confirmed by comparison of the ion traces with the signals on the Faraday cup detectors. By comparing the relative ion signal intensities in Fig. 1 it can be seen that the reactivity of He(2S0) is higher than the reactivity of He(2S1). Likewise, the reactivity of Li(2P3/2) is found to be higher than that of Li(2P3/2). To extract relative reaction rates for different He∗-Li state combinations, the measured ion signals are integrated over time and normalized to the He(2S0) and He(2S1) flux obtained from the Faraday cup traces. Relative steady-state populations of Li(2P3/2) with respect to Li(2S1/2) are obtained from a rate model of the optical pumping process in Li, taking into account all electric-dipole-allowed transitions between the hyperfine states, the natural linewidth (\(\gamma = 2\pi \cdot 5.872 \text{ MHz} \text{[23]}\)) and the experimentally determined laser intensities.

![Fig. 1. Measured ion yields for state-selected He∗-Li collisions at δ = -12 MHz as a function of time delay with respect to the valve trigger (solid lines). In the legend, He∗ and He0 are abbreviations for the He(2S0) and He(2S1) states, respectively. Li(S) and Li(S, P) denote Li(2S1/2) and a mixture of Li(2S1/2) and Li(2P3/2), respectively. The blue dash-dotted and green dashed curves have been scaled with respect to the singlet-to-triplet ratio in the He∗ beam to aid the comparison between relative signal intensities. The integration time window used for the calculation of rate coefficients is indicated by the gray shading. Traces of MOT laser stray light (thin gray lines), recorded using a fast photodiode, illustrate the shutter closing characteristics for the two time delays at which the traces were taken.](image-url)
(see Tab. I for notation) may be attributed to an underestimation of the actual laser intensities and to the low signal-to-noise ratio associated with this specific rate determination.

FIG. 2. Experimentally measured rate constant ratios $P_{i}^{\text{exp}}/P_{1}^{\text{exp}}$ (where $i = 3, 4, 6$; see Tab. I for notation) as a function of Li(2$^{2}P_{3/2}$) population relative to Li(2$^{2}S_{1/2}$) (markers). Ratios for Li(2$^{2}P_{3/2}$) collisions are not displayed for Li(2$^{2}P_{3/2}$) populations below 0.1, since low ion signal contrast resulted in large measurement uncertainties under these conditions. The solid lines and the shaded areas weighted means of the rate constant ratios and the resultant standard deviations, respectively. The uncertainties are statistical only (2σ). The ratios $P_{i,S,A}$, which are calculated from the ratio of reactive to total number of states assuming electron-spin and $\Lambda$ conservation, are shown as dashed lines for comparison.

All values for the experimentally determined He$^{*}$-Li reaction rate ratios are summarized in Tab. I. The given overall uncertainties include both statistical errors and systematic effects, i.e., uncertainties in the determination of the laser intensity and the singlet-to-triplet ratio.

To understand the experimental results, we have considered different rate-influencing effects. In general, the reaction rate coefficients for autoionization depend on spin-statistical effects, on atomic orbital overlap and – since autoionization can be considered as a Franck-Condon-type process – on the shape of the potential curves for the incoming and the outgoing channel. Based on Wigner’s spin conservation rule, we expect that all He$^{*}$-Li molecular states with $^{2}\Sigma$ or $^{2}\Pi$ symmetry are reactive. This means that all (only $1/3$) of the He atoms in the $^{2}\Sigma_{0}^{+}$ state ($^{2}\Pi_{1/2}$ state) are reactive. Our measured value of 0.38$^{+0.06}_{-0.02}$ for He$^{*}$-Li($^{2}\Sigma_{1/2}$) collisions is consistent with this spin-statistical argument, and it is also in rough agreement with the previous experimental result of 0.26$\pm$0.08 by Ruf et. al. [24]. However, our rate constant ratios for He$^{*}$-Li($^{2}\Pi_{3/2}$) collisions are about a factor of 2 lower than what would be expected from Wigner’s rule. Therefore, it is evident that, besides spin conservation, an additional process must also cause Penning suppression. Since autoionization predominantly occurs via an electron-exchange mechanism [1], the reaction rate is high when there is constructive overlap between the $1s$ core orbital of the He$^{+}$ atom and the Li valence shell atomic orbital. Orbital shape is also related to molecular symmetry. For He$^{*}$-Li(S,P) collisions, only HeLi$^{+}$ in the $^{3}\Sigma^{+}$ state, which correlates to the He($^{1}\Sigma_{0}^{+}$)+Li($^{1}\Sigma_{1}^{+}$) asymptote, is energetically accessible. Since the next higher-lying states (correlating with the $^{1}\Sigma^{+}$ and $^{3}\Sigma^{+}$ states) are $\approx 19$ eV higher in energy ($^{25}$), the admixture of other electronic states is negligible.

Therefore, for He($^{2}\Sigma_{0}^{+}$,$^{2}\Pi_{1/2}$)-Li($^{2}\Sigma_{1/2}$,$^{2}\Pi_{3/2}$) collisions, only quasimolecular states of $\Sigma$ symmetry can autoionize. If we assume that the $\Pi$ states are not reactive, our results can be brought into excellent agreement with predictions which are solely based on spin-statistical and symmetry arguments (cf. $P_{i,S,A}$ in Tab. I). Our observations are in line with previous work by Morgner and co-workers, who have – based on the results of previous Penning ionization experiments using other metastable-rare-gas collision systems – suggested that the projection of the orbital angular momentum onto the internuclear axis, $\Lambda$, must be conserved in an autoionization reaction $^{[1,26,27]}$.

Owing to the small spin-orbit coupling in the He$^{*}$-Li system, the free electron cannot carry away angular momentum. On the one hand, He$^{*}$ does not feature spin-orbit interactions at all. In Li, on the other hand, the energy splitting between the two spin-orbit states is $\Delta E(2^{2}P_{1/2}-2^{2}P_{3/2}) = 0.34 \text{ cm}^{-1}$ [28], which corresponds to a spin-orbit-interaction time which is more than two orders of magnitude higher than the classical collision time of $\approx 250 \text{ fs}$ for this autoionization process at thermal energies. Therefore, the electron leaves the collision complex long before a significant coupling to the internal degrees of freedom can occur.

The influence of potential shape on the relative autoionization rates is expected to be small for He$^{*}$-Li(S,P) collisions, since the positions of the He$^{*}$-Li potential minima are similar [29]. We have estimated the reaction rates at thermal energies using a classical capture model, in which only long-range interactions are assumed to contribute to chemical reactivity [30]. In this simple theoretical approach, the reaction probability is unity (zero) if the energy of the collision pair is above (below) the centrifugal barrier of the effective long-range potential

$$V(R) = \sum_{n}^{\infty} \frac{C_n}{R^n} \left(\frac{\mu v_{\text{rel}} b}{2\mu R^2}\right)^2.$$  

Here, $R$ is the internuclear distance, $C_n$ (with $n = 6, 8, 10$) are the dispersion coefficients, $\mu$ is the reduced mass, $v_{\text{rel}} \approx v_{\text{He}^{*}}$ is the relative velocity and $b$ is the impact parameter.

Capture rate coefficients for the different interaction channels $k^c = \pi b^{2}_{\text{max}} v_{\text{rel}}$, where $b_{\text{max}}$ is the impact parameter at the centrifugal barrier, are numerically calculated.
using the dispersion coefficients $C_{6,8,10}$ given by Zhang et al. [31]. At a collision temperature of 530 K [32], the relative He*-Li rates obtained from the capture model are not significantly different from each other (Tab. I). The shape of the potential curves alone can thus not account for the observed rate ratios. The results from these calculations can only be brought into agreement with the experimental results if both electron-spin and Λ conservation are included (cf. $P_{i,S,Λ}$ in Tab. I).

| $i$ State assignment | $P_{i,S}$ | $P_{i,S,Λ}$ | $P_{i,S,Λ}^c$ | $P_{i,S,Λ}^{exp}$ |
|----------------------|-----------|-------------|--------------|---------------|
| 1 He($2^3S_0$)+Li($2^3S_1/2$): $^2\Sigma^+$ | 1 | 1 | 1 | 1 |
| 2 He($2^3S_0$)+Li($2^3P_{1/2}$): $^3\Pi_{1/2}$ | 1 | 0 | 1.02 | 0 |
| 3 He($2^3S_0$)+Li($2^3P_{3/2}$): $^2\Sigma^+$, $^2\Pi_{3/2}$ | 1 | 1/2 | 1.20 | 0.68 | 0.46 $^{+0.13}_{-0.08}$ |
| 4 He($2^3S_0$)+Li($2^3S_1/2$): $^2\Sigma^+$, $^4\Sigma^+$ | 1/3 | 1/3 | 0.84 | 0.28 | 0.38 $^{+0.06}_{-0.02}$ |
| 5 He($2^3S_1$)+Li($2^3P_{1/2}$): $^2\Pi_{1/2}$, $^4\Pi_{1/2,3/2}$ | 1/3 | 0 | 0.74 | 0 |
| 6 He($2^3S_1$)+Li($2^3P_{3/2}$): $^2\Pi_{3/2}$, $^4\Pi_{1/2,3/2}$, $^2\Sigma^+$, $^4\Pi^+$ | 1/3 | 1/6 | 0.87 | 0.17 | 0.19 $^{+0.06}_{-0.04}$ |

CONCLUSION

While Λ conservation has already been considered to play a role in Penning collisions, our experiments unambiguously show – for the first time – that both the electron spin and Λ are strictly conserved. We are confident that the reported findings can also be extended to heavier He*-alkali atom collision systems, for which spin-orbit interactions are still reasonably small (He*-Na, He*-K). However, in He*-K collisions, the autoionization rates are also influenced by resonances with core-excited states in K [33]. In metastable rare gases other than He, Λ-changing collisions are possible, since the spin-orbit electron is so strong that the associated time constants are comparable to the collision time.

Therefore, He*-Li represents an especially favorable system for applications in which autoionizing collisions must be suppressed, such as the laser cooling of He* and Li in a two-species He*-Li magneto-optical trap. As can be inferred from Tab. I, Penning ionization should not occur in collisions between He* and Li($2^3P_{1/2}$). To avoid trap loss by Penning ionization, Li could thus be laser cooled via the D$_1$ line using a gray molasses scheme [34]. Experiments aimed at probing Penning suppression by excitation of Li to the $2^3P_{1/2}$ state are underway in our laboratory. The spin-orbit interaction in the laser-excited $2^3P$ state of He, which is used for He($2^3S_1$) laser cooling, is also very small, so that Λ conservation will also hold for He($2^3P$)-Li collisions.

In certain collision systems, the presence of non-reactive $^2\Pi$ potentials may also be interesting for the generation of interspecies Feshbach resonances [35, 36] which can be used for the study of universal few-body physics. However, for this purpose, Λ conservation still remains to be confirmed at ultracold temperatures.

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