Separation of spin–orbit coupled metastable states of Kr$^+$ and Xe$^+$ by ion mobility

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The spin–orbit coupled ground states of Kr$^+$ and Xe$^+$ (RG $^2P_{1/2}$ and RG $^2P_{3/2}$, RG=rare gas) are separated on the basis of ion mobility. Ion mobility separation of Kr$^+$ and Xe$^+$ is based on different interaction potentials of the $^2P_{1/2}$ and $^2P_{3/2}$ ionic states with helium. The ion mobility instrument used for these studies is a novel instrument based on a Fourier-transform ion cyclotron resonance mass spectrometer. The assignment of the spin–orbit coupled states of Xe$^+$ is consistent with results from charge exchange ion–molecule reactions of Xe$^+$ with N$_2$O.

I. INTRODUCTION

Rare gas ion–molecule interactions are significant in many chemical and physical processes including metastable ion spectroscopy and studies of interstellar atmospheres. One of the most important areas for rare gas interactions is that of lasers, where the use of rare gases is prevalent. Argon and krypton ion lasers are the most common lasing systems involving rare gas ion interactions, however both the He/Ne and excimer lasers depend on excited states of the neutral species and it is inevitable that some ions are produced during the excitation process. Therefore, knowledge of ion–neutral interactions and how ions interact with both ground and excited state neutrals are required for complete understanding of these lasers.

Rare gas ions, with the exception of helium, have ground state electron configurations of ns$^2$np$^5$ and are subject to spin–orbit coupling. According to Hund’s rules the multiplets are inverted due to the more than half filled p orbital; therefore, $^2P_{1/2}$ is the higher energy term and $^2P_{3/2}$ is the lower energy term. The spin–orbit interaction energy ranges from 0.090 eV in neon to 1.1 eV in xenon and when coupled with electron–electron interactions gives rise to long-lived metastable states of the same parity. Spontaneous decay from excited levels of ground state configurations via electric dipole (E1) transitions are forbidden by the parity selection rule; consequently, decay must proceed by magnetic dipole (M1) and electric quadrupole (E2) transitions, for which radiative transition probabilities are 4–8 orders of magnitude lower than allowed E1 transitions.

Metastable atomic ion studies typically involve trapping ions with an ion trap (e.g., Paul, Kingdon, or Penning), then monitoring photons emitted as the metastable states relax to their ground state. One can then correlate the wavelength of the emitted photon with the specific electronic transition and simultaneously gain information on the lifetime for a specific state. Experimental results obtained in this way are also readily compared with calculated transition probabilities of forbidden transitions, making this an important method for determining the accuracy of theoretical methods.

Methods based on ion–molecule reactions and ion mobility measurements have also been employed to identify and characterize metastable atomic ions. These techniques require prior knowledge of energetics and lifetimes for the ion under study, which often is provided by either the optical methods previously mentioned or by theoretical methods. Ion–molecule reactions involving metastable atomic ions can yield information on lifetime as well as reactivity and ion energetics (i.e., bracketing method). These traits make it an attractive alternative to optical methods that require low pressures (<10$^{-7}$ Torr) and do not permit studies that involve reactions. Separation of metastable and ground state ions by ion mobility was first demonstrated by Albritton and co-workers for O$^+$($^4S^0$) and (O$^+$)($^4D^0$), but this feature was not exploited for characterizing metastable ion populations until Bowers and co-workers used ion mobility to separate excited and ground states of first row transition metal ions. Separation of different atomic ion electronic states by ion mobility requires significantly different interaction potentials for each state. Ion–molecule reactions and ion mobility measurements of metastable ions can, therefore, provide fundamental information ranging from state specific reactivity to interaction potentials for different states.

We have recently developed an instrument that combines Fourier-transform ion cyclotron resonance (FTICR) mass spectrometry with a drift cell used for ion mobility measurements. This instrument makes it possible to trap ions for long time periods (1–100 s) to allow radiative or collisional cooling and/or ion–molecule reactions prior to mobility analysis and the near thermal energies of ions trapped in the ICR cell prevent energetic collisions that can induce isomerization. An additional benefit provided is the different time scale relative to previous selected ion mobility instruments (seconds versus micro- or milliseconds), which

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permits measurements to be extended into longer time regimes. Initial proof-of-concept studies with this instrument on rare gas ions revealed a bimodal arrival time distribution (ATD) for both Kr$^{+}$ and Xe$^{+}$. We assigned the two ATDs as the spin–orbit coupled ground state ions (RG $^{3}P_{1/2}$ and RG $^{3}P_{3/2}$, RG=rare gas). The RG $^{3}P_{1/2}$ ions are metastable and possess long lifetimes (>30 ms) for both Kr$^{+}$ and Xe$^{+}$, making them easily accessible on the time scale of our instrument. In the following paper we present comparison and justification of our findings with prior results obtained by ion mobility measurements and other methods are presented.

II. EXPERIMENT

The details of the FTICR ion mobility (FTICRIM) instrument are provided in a separate paper. Briefly the instrument consists of a two-section ICR cell, an ion mobility drift cell (7 cm), and a time-of-flight drift tube (1.5 m) all mounted collinearly in the bore of a 7 T superconducting magnet (Fig. 1). Differential pumping is accomplished by a concentric tube vacuum design, which allows a high buffer gas pressure (∼0.25 Torr) in the drift cell while maintaining adequate vacuum (∼1×10$^{-6}$ Torr) in the ICR region for mass spectroscopy. FTICR voltages, wave forms, data acquisition, and data processing are performed with a Finnigan Odyssey data system (ThermoQuest, Bremen GB). Performing mobility measurements in a 7 T magnetic field reduces transverse diffusion and thereby increases ion transmittance through the drift cell by one to two orders of magnitude shortening the number of scans needed to generate an ATD.

A. Ion mobility sequence

Ions are generated in the source cell by electron-impact ionization of gas leaked into the system through a variable leak valve (Varian model 951-5106). For the experiments described herein the ionizing electron energy was kept below the ionization potential for helium (24.587 eV) to prevent trapping of ions in the drift cell. The presence of He$^{+}$ in the drift cell permits charge transfer reactions with residual neutrals which appear as noise on the ATD signal. Ions formed in the source cell are trapped and unwanted ions are ejected through a series of chirp and/or SWIFT excitation events, thereby isolating the mass-to-charge ion(s) of interest. Once isolated the ion packet is partitioned through a 1 mm aperture into the analyzer cell where they are trapped for variable amounts of time (5 μs–1 s) prior to being pulsed into the drift cell. An ion gate is used to exclude all but a small packet of ions (5–10 μs) from entering the drift cell. Gating of ions into the drift cell and the start signal to the time-to-digital-converter are synchronized for acquisition of the ATD. Ions traverse the drift cell under the influence of a linear voltage gradient impeded by collisions with the buffer gas (usually helium). As ions elute from the drift cell they are extracted into the time-of-flight region where they are collected by a wire ion guide and transported down the flight tube to a microchannel plate detector assembly.

B. Ion–molecule reaction sequence

Xenon and dinitrogen oxide (N$_{2}$O) were leaked into the source region of the spectrometer to a total pressure of 1 ×10$^{-6}$ Torr (Xe:5×10$^{-8}$ Torr, N$_{2}$O:9.5×10$^{-7}$ Torr) while the analyzer region remained in the low 10$^{-9}$ Torr range. Both Xe$^{+}$ and N$_{2}$O$^{+}$ ions were produced during the ionization event, but N$_{2}$O$^{+}$ ions were ejected by several chirp and SWIFT excitation events to ensure full ejection of unwanted ions. Following ejection of N$_{2}$O$^{+}$, Xe$^{+}$ was partitioned into the analyzer cell (maintained at ∼3×10$^{-9}$ Torr) where the trapping time was varied (500 μs–1 s) allowing Xe$^{+}$ ($^{3}P_{1/2}$) to undergo radiative decay. During the relaxation event the source cell was quenched, permitting any ions not ejected by the excitation events to exit the cell, ensuring that measured ion signal is due only to charge transfer from Xe$^{+}$. Following the relaxation event Xe$^{+}$ was par-
tiated back into the source cell and allowed to react with N$_2$O. The reactions between Xe$^{+}$ and N$_2$O were studied for variable amounts of reaction and relaxation time (500 $\mu$s–750 ms).

C. Ion mobility

Ion mobility is a measure of the time required for an ion to traverse a specific distance in the presence of buffer gas under the influence of an external electric field [Eq. (1)], where $v_d$ is ion drift velocity (cm/s), $E$ is the electric field strength (V/cm)

$$K = \frac{v_d}{E},$$

and $K$ is ion mobility (cm$^2$/V s).$^{15}$ Inclusion of pressure, buffer gas temperature, and collisions yields

$$K = \frac{3q}{16N} \left( \frac{1}{m} + \frac{1}{M} \right)^{1/2} \left( \frac{2\pi}{kT} \right)^{1/2} \frac{1}{\Omega_D},$$

where $q$ is the number of charges on the ion, $N$ is the number density of the buffer gas, $m$ is the mass of the ion, $M$ is the mass of the buffer gas, $k$ is Boltzmann’s constant, $T$ is temperature, and $\Omega_D$ is the angle-averaged collision cross section. Ion–neutral forces such as attractive/repulsive interactions and ion–induced dipole interactions are included in the angle averaged cross section ($\Omega_D$) term.$^{15}$ Ion mobility is inversely proportional to collision cross section, therefore ions with larger cross sections traverse the drift cell slower than ions with smaller cross sections. Comparison of data obtained by different investigators is facilitated by converting ion mobility ($K$) to “reduced ion mobility” ($K_0$) by way of

$$K_0 = K \frac{p}{760(Torr)} \frac{273(K)}{T},$$

where $p$ and $T$ are the pressure and temperature of the buffer gas, respectively.

To measure ion mobility information the voltage across the drift cell is lowered systematically, thus lowering the electric field strength, and ATDs are obtained at each voltage. Voltages used in the current experiments are scanned from 3 to 35 V, placing the $E/N$ ratio outside of the “low field limit.” Higher $E/N$ ratios were necessary to separate the spin–orbit coupled states of Kr$^{+}$ and Xe$^{+}$, as the peaks coalesce at $E/N$ ratios below 15 Td. Each ATD is then analyzed and peak centroids are extracted by fitting peaks with a Gaussian function. A plot of $t$ (peak-centroid) vs $1/V$, yields a slope that is proportional to $1/K$ and $l$ is the length of the drift cell.$^{11}$ In all cases reported here triplicate runs were averaged to generate the $t$ vs $1/V$ plots, thus giving ion mobility ($K$) and the standard deviation associated with errors in time measurement.

III. RESULTS

ATDs for Kr$^{+}$ ions in He reveal two peaks (Fig. 2) in the ratio of ~1:2, in which the first peak is assigned as Kr$^{+}$ $^2P_{1/2}$ population, and the second peak is assigned to Kr$^{+}$ $^2P_{3/2}$ population. Justification for peak assignments will be addressed in Sec. IV. A plot of $t$ vs $1/V$ [according to Eq. (4)] for Kr$^{+}$ in He data is shown in Fig. 3. At drift fields lower than 1.4 V/cm the two ion populations are not resolved and is not included in the plot. The reduced mobility ($K_0$) values for $^2P_{3/2}$ and $^2P_{1/2}$ Kr$^{+}$ ions are compared with literature values for Kr$^{+}$ ions (no separation of spin–orbit states) in Table I.

The ion mobility spectrum for Xe$^{+}$ ions in helium is similar to that for Kr$^{+}$. Two signals with a 1:2 ratio (Fig. 4) are observed. The first peak is assigned as Xe$^{+}$ $^2P_{1/2}$ and the second is assigned as Xe$^{+}$ $^2P_{3/2}$. Correlation coefficients near one ($R^2=0.999$) are observed in $t$ vs $1/V$ plots (Fig. 5) for Xe$^{+}$. Unlike Kr$^{+}$, no deviation from linearity is

![Figure 2](image-url)  
**FIG. 2.** ATDs of Kr$^{+}$ in helium at 25, 20, 15, and 10 V across the drift cell. The peak assigned as the $^2P_{1/2}$ state is collisionally quenched due to interactions with the buffer gas.
observed due to unresolved peaks. Table I contains reduced mobility ($K_0$) values for Xe$^+$–$^2P_{1/2}$ and Xe$^+$–$^2P_{3/2}$ obtained from current experimental data, however, no other experimental data are available for comparison at 298 K.

Ar$^+$ ions drifted through helium exhibits a single peak (Fig. 6) in the arrival time distribution, in agreement with results obtained by other laboratories. The spin–orbit coupled states of Ar$^+$ are not resolved in any ATD, even though Ar$^+$($^2P_{1/2}$) has a lifetime on the order of 20 s. The peak width is wider than expected, based on results for Kr$^+$ and Xe$^+$, suggesting that the two states are not resolved. A $t$ vs $1/V$ plot for Ar$^+$ in He produces a linear plot (Fig. 7) as indicated by the correlation coefficient ($R^2=0.999$). The reduced mobility ($K_0$) obtained for Ar$^+$ in He, 20.5 (cm$^2$/V s) is in excellent agreement with literature values (Table I).

To further verify that the Xe$^+$–$^2P_{1/2}$ state was present, ion–molecule reaction chemistry specific to the $^2P_{1/2}$ state was used to confirm the state assignments. For example, charge transfer between Xe$^+$–($^2P_{1/2}$) and N$_2$O is exothermic by 0.55 eV, whereas reaction of Xe$^+$–($^2P_{3/2}$) is endothermic by 0.76 eV. Therefore, monitoring N$_2$O$^+$ ion abundance generated by reaction 1 [Fig. 8(a)] provides a direct measure of the $^2P_{1/2}$ metastable species.

### Table I. Comparison of measured and published literature mobilities for rare gas ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$K_0$ (this work)$^a$</th>
<th>$K_0$ (literature)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar$^+$</td>
<td>20.5</td>
<td>20.5$^b$ 20.9$^c$</td>
</tr>
<tr>
<td>Kr$^+$($^2P_{1/2}$)</td>
<td>19.9</td>
<td></td>
</tr>
<tr>
<td>Kr$^+$($^2P_{3/2}$)</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>Kr$^+$ (average)</td>
<td>18.9$^d$ 19.3$^e$</td>
<td></td>
</tr>
<tr>
<td>Xe$^+$($^2P_{1/2}$)</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>Xe$^+$($^2P_{3/2}$)</td>
<td>16.5</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Values reported in (cm$^2$/V s).

$^b$From Ref. 13.

$^c$From Ref. 7.

$^d$From Ref. 22.

$^e$From Ref. 26.

![FIG. 3. Time vs 1/V plot for $^2P_{1/2}$ and $^2P_{3/2}$ states of Kr$^+$. The inset gives the slope and the correlation coefficient for a linear regression fit to the data.](image)

![FIG. 4. ATDs of Xe$^+$ in helium at 25, 20, 15 and 10 V across the drift cell. The peak assigned as the $^2P_{1/2}$ state is collisionally quenched due to interactions with the buffer gas.](image)
Xe$^+$ ($^2P_{1/2}$ and $^2P_{3/2}$) in He

<table>
<thead>
<tr>
<th>Ion Symbol</th>
<th>Slope ($\mu$sec/volt)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe$^+$ ($^2P_{1/2}$)</td>
<td>737.1</td>
<td>0.999</td>
</tr>
<tr>
<td>Xe$^+$ ($^2P_{3/2}$)</td>
<td>893.8</td>
<td>0.993</td>
</tr>
</tbody>
</table>

Radiative decay of Xe$^+$ ($^2P_{1/2}$) is examined by varying the trapping (relaxation) time in the analyzer cell. This allows radiative transitions ($^2P_{1/2}$ → $^2P_{3/2}$) to occur, the extent (rate) of decay is monitored by N$_2$O$^+$ ion abundance data [Fig. 8(b)], which can only be formed through charge exchange from the $^2P_{1/2}$. Radiative decay rates ($19 \text{ s}^{-1}$) and lifetimes ($\sim 50 \text{ ms}$) obtained using this method are in agreement with those previously reported by Edlen, Beauchamp, and Marx. In this work we assigned two peaks observed in our ATDs for Kr$^+$ and Xe$^+$ as ground state species that differ only in terms of the total angular momentum ($J$) value (i.e., 1/2 vs 3/2).

Both spin–orbit-coupled states ($^2P_{1/2}$ and $^2P_{3/2}$) are formed during electron impact ionization in the ratio of $\sim 1:2$ ($^2P_{1/2}$ : $^2P_{3/2}$). The $^2P_{1/2}$ state is metastable and decays to the $^2P_{3/2}$ state via M1 and E2 transitions, which have lower transition probabilities than E1 transitions. Singly charged xenon and krypton ions have lifetimes on the order of $\sim 50$ and $\sim 350$ ms, respectively, making them readily accessible by ICR experiments. Excited states or other metastable states of Kr$^+$ and Xe$^+$ should not interfere because those assessable with the low ionizing electron energy used ($<20 \text{ eV}$) decay on a much faster time scale ($10^{-9} \text{ s}$) than can be probed by this instrument.

Helm and Elford previously studied ion mobilities and charge transfer of krypton and xenon in their parent gases. Both investigators observed a bimodal distribution in electron configurations. For example, an attractive potential exists between helium and transition metal ions that possess 4s$^0$3d$^n$ vs 4s$^1$3d$^{n+1}$ strongly affects the interaction potential between transition metal ions and helium. For example, an attractive potential exists between helium and transition metal ions that possess 4s$^0$3d$^n$ vs 4s$^1$3d$^{n+1}$ strongly affects the interaction potential between transition metal ions and helium. For example, an attractive potential exists between helium and transition metal ions that possess 4s$^0$3d$^n$ vs 4s$^1$3d$^{n+1}$ strongly affects the interaction potential between transition metal ions and helium. For example, an attractive potential exists between helium and transition metal ions that possess 4s$^0$3d$^n$ vs 4s$^1$3d$^{n+1}$ strongly affects the interaction potential between transition metal ions and helium. For example, an attractive potential exists between helium and transition metal ions that possess 4s$^0$3d$^n$ vs 4s$^1$3d$^{n+1}$ strongly affects the interaction potential between transition metal ions and helium. For example, an attractive potential exists between helium and transition metal ions that possess 4s$^0$3d$^n$ vs 4s$^1$3d$^{n+1}$ strongly affects the interaction potential between transition metal ions and helium. For example, an attractive potential exists between helium and transition metal ions that possess 4s$^0$3d$^n$ vs 4s$^1$3d$^{n+1}$ strongly affects the interaction potential between transition metal ions and helium.
cies by Cohen and Schneider indicate that the ion–molecular reaction rates, however they were unable to resolve the two states by ion mobility measurements. The difference in mobility for the two ions (2\textsuperscript{1/2} and 2\textsuperscript{3/2}) proposed to be less than their experimental error, thus explaining their observation of a single peak. They also employed various charge-transfer reactions as a means to vary the spin–orbit coupled states, utilizing ion–molecular reaction rates as a means to vary the spin–orbit coupled states (2\textsuperscript{1/2} and 2\textsuperscript{3/2}) of Kr\textsuperscript{+} utilizing ion–molecular reaction rates, however they were unable to resolve the two states by ion mobility measurements in helium. The difference in mobility for the two J values is proposed to be less than their experimental error, thus explaining their observation of a single peak. They also employed various charge-transfer reactions as a means to vary the two \textsuperscript{2}P\textsubscript{1/2} and \textsuperscript{2}P\textsubscript{3/2} populations, and monitored them by the ion–molecule reaction method.

In the present case of Kr\textsuperscript{+} and Xe\textsuperscript{+}, no difference in occupied orbitals can contribute to the difference in mobility, therefore factors other than volume differences must contribute. Ab initio calculations on homonuclear neon–neon species by Cohen and Schneider indicate that the \textsuperscript{2}P\textsubscript{1/2} ion state interaction with a \textsuperscript{1}S\textsubscript{0} neutral occurs on a repulsive surface ((1/2)\Sigma\textsubscript{u}) (Fig. 9). The \textsuperscript{2}P\textsubscript{3/2} ion can interact with neutrals on either an attractive curve ((1/2)\Pi\textsubscript{u}) or a repulsive curve ((3/2)\Pi\textsubscript{u}) as indicated in Fig. 9. The presence of spin–orbit coupling shifts the \textsuperscript{2}P\textsubscript{1/2} curve up in energy by an amount equal to the spin–orbit splitting (0.09 eV for neon), but does not affect the curve shape in any way. Scattering cross sections and excitation transfer were determined based on the ab initio wave functions. From these values a total cross section (Q\textsubscript{T}) and the reduced mobility (K\textsubscript{0}) for Ne\textsuperscript{+} ions in neon were calculated. Reduced mobility values in this region are very similar and cross at 600 K where they are identical. Consequently, it is not surprising that resolving these two spin–orbit coupled states is difficult. Kr\textsuperscript{+} and Xe\textsuperscript{+} (2\textsuperscript{P}\textsubscript{1}) interacting with helium (\textsuperscript{1}S\textsubscript{0}) should follow similar potential energy curves Consequently one would expect the \textsuperscript{2}P\textsubscript{1/2} population to traverse the drift cell faster due to repulsive interactions with neutral helium. Data obtained in this laboratory indicate that metastable \textsuperscript{2}P\textsubscript{1/2} ions migrate faster through the drift cell, which is consistent with results obtained by Helm and Elford for Kr\textsuperscript{+} and Xe\textsuperscript{+} in their parent gases. This behavior is characteristic of an isomass atomic ion experiencing a repulsive interaction potential with the buffer gas. Previous ion mobility investigations of Kr\textsuperscript{+} in helium report no observation of a bimodal distribution, most likely due to low instrumental resolution or lack of mass selection prior to the drift cell. The average reduced mobility (K\textsubscript{0}) for Kr\textsuperscript{+} in helium obtained in our lab agrees well with values obtained previously (Table I), further indicating that prior experiments did not resolve the metastable and ground state ions. Ground state \textsuperscript{2}P\textsubscript{3/2} ions interact with helium via either the ((1/2)\Pi\textsubscript{u}) or ((3/2)\Sigma\textsubscript{u}) potential energy curves, suggesting that a portion of faster migrating peak may be comprised of \textsuperscript{2}P\textsubscript{3/2} ions. Comparison of \textsuperscript{2}P\textsubscript{1/2} and \textsuperscript{2}P\textsubscript{3/2} peak areas suggest that this is not occurring, as a ratio of 1:2 (\textsuperscript{2}P\textsubscript{1/2} : \textsuperscript{2}P\textsubscript{3/2}) is observed as expected based on previous observations and

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**FIG. 8.** (a) Temporal plot of N\textsubscript{2}O\textsuperscript{+} increase (open circles) from Xe\textsuperscript{+} (2\textsuperscript{P}\textsubscript{1/2}) charge exchange. (b) Plot of Xe\textsuperscript{+} (2\textsuperscript{P}\textsubscript{1/2}) radiative decay (closed triangles) monitored by the relative abundance of N\textsubscript{2}O\textsuperscript{+} formed by the charge-exchange reaction.

**FIG. 9.** Potential curves for the interaction of np\textsuperscript{1} ions (2\textsuperscript{P}) with a neutral closed shell system (\textsuperscript{1}S\textsubscript{0}). Molecular terms identify each curve.
statistical arguments. If a portion of the $^2P_{3/2}$ ions co-migrated with $^2P_{1/2}$ ions, a ratio approaching or exceeding 1:1 would be observed, clearly this is not the case. Although there appears to a decrease associated with the earlier time component that we assign to the $^2P_{1/2}$ spin–orbit state in the ATDs for both Kr$^+$ and Xe$^+$, we do not consider this evidence for collisional quenching during the drift time. Quenching rates obtained by analysis of this decrease were inconsistent with the observation of $^2P_{1/2}$ states at low drift voltages. We currently ascribe these intensity fluctuations to experimental artifacts, rather than electronic quenching by helium, and attempts to characterize are currently in progress.

To further characterize the nature of the ion population, charge-transfer reactions with N$_2$O were employed. Electron impact ionization parameters are nearly identical from experiment to experiment, therefore characterizing the Xe$^+$ ion population will give information applicable to other rare gases. Figure 2 shows Xe$^+$ ($^2P_{1/2}$) radiative decay at 150 ms reaction time and N$_2$O$^+$ abundance as a function of reaction time. The radiative decay rate obtained is 52 ms, which agrees well with rates of ~49 and ~56 ms of Marx$^{13}$ and Beauchamp$^{18}$, respectively. In order to determine if N$_2$O$^+$ was formed by background ions that were not ejected, Xe$^+$ was kept in the analyzer cell and not partitioned back into the source cell. No ion signal was observed when this sequence was employed, thus all N$_2$O$^+$ ions are generated by charge transfer presumably from Xe$^+$ ($^2P_{3/2}$). A plateau at ~5% is observed in the decay of Xe$^+$ ($^2P_{1/2}$) agreeing with data from Marx$^{13}$ indicating that there is part of the population that doesn’t decay or another reaction mechanism other than charge transfer from Xe$^+$ ($^2P_{1/2}$) is present. This information provides additional assurance that the ion population contains only Xe$^+$ ($^2P_{1/2}$ and $^2P_{3/2}$), otherwise fragmentation of N$_2$O would be observed due to a higher energy state.

V. CONCLUSIONS

The ability to characterize ion populations without the need for rigorous spectroscopic analysis opens many avenues of study. In this paper we have demonstrated the ability to separate spin–orbit coupled states of rare gas ions (Kr$^{2+}$ and Xe$^{2+}$) based on different interaction potentials with helium. Extending this ability to transition metals and other atomic species will provide state-specific information on ion reactivity covering a time-scale not assessable with current instruments. Further studies (e.g., variable temperature, increased pressure) on krypton and xenon by ion mobility will provide insight into their respective reactivities and our ability to separate these states while others could not.

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