Very strong Rydberg atom scattering in K(12p)–CH₃NO₂ collisions: Role of transient ion pair formation

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Collisions between K(12p) Rydberg atoms and CH₃NO₂ target molecules are studied. Whereas CH₃NO₂ can form long-lived valence-bound CH₃NO₂[−] ions, the data provide no evidence for production of long-lived K⁺⋯CH₃NO₂[−] ion pair states. Rather, the data show that collisions result in unusually strong Rydberg atom scattering. This behavior is attributed to ion-ion scattering resulting from formation of transient ion pair states through transitions between the covalent K(12p) + CH₃NO₂ and ionic K⁺ + (dipole bound) CH₃NO₂[−] terms in the quasimolecule formed during collisions. The ion-pair states are destroyed through rapid dissociation of the CH₃NO₂[−] ions induced by the field of the K⁺ core ion, the detached electron remaining bound to the K⁺ ion in a Rydberg state. Analysis of the experimental data shows that ion pair lifetimes ≥ 10 ps are sufficient to account for the present observations. The present results are consistent with recent theoretical predictions that Rydberg collisions with CH₃NO₂ will result in strong collisional quenching. The work highlights a new mechanism for Rydberg atom scattering that could be important for collisions with other polar targets. For purposes of comparison, results obtained following K(12p)–SF₆ collisions are also included. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4982935>]

I. INTRODUCTION

Collisions between atoms in Rydberg states with values of n in the range $10 \lesssim n \lesssim 20$, and neutral attaching targets can lead to formation of weakly bound ion-pair states through electron transfer reactions of the type

where AB^{−*} denotes a short-lived excited state populated by initial electron capture, AB[−] a long-lived metastable negative ion typically formed by intramolecular vibrational relaxation, and X⁺⋯AB[−] a weakly bound ion-pair state.^{1–8} Since many properties of such states parallel those of Rydberg atoms, they are also frequently referred to as heavy-Rydberg states.^{9–13} Ion-pair states represent a novel class of weakly bound, long-range molecules which, as shown by recent measurements, possess unusual physical and chemical properties.

Many questions remain, however, relating to the dynamics of ion pair formation in Rydberg atom collisions and, once created, the factors that govern their lifetimes and decay channels. Earlier studies of ion-pair formation through non-dissociative electron transfer (reaction (1)) have focused on targets that form valence-bound anions. However, electron transfer in low- n Rydberg collisions with polar targets can also lead to the formation of free dipole-bound negative ions in which the extra electron is weakly bound by the dipole moment of the neutral molecule in a diffuse orbital localized at the positive end of the dipole.^{14–27} The question then arises as to whether dipole binding can play a significant role in the formation of bound ion-pair states. Here we examine this question using as a target CH₃NO₂ which has a dipole moment, 3.46 D, that is more than sufficient to support dipole bound states yet is also known to form long-lived valence-bound anions. Theory indicates that the dipole- and valence-bound states are

strongly coupled leading to the suggestion that, in Rydberg atom collisions, dipole binding might provide a “doorway” for creation of valence-bound anions^{28–34} and hence ion-pair states. In the present work, we examine ion pair formation in K(12p)–CH₃NO₂ collisions. The data, however, provide no evidence for the production of long-lived K⁺⋯CH₃NO₂[−] ion-pair states. Rather, the data show that collisions result in strong Rydberg atom scattering with a collision cross section that is comparable to the geometrical size of the K(12p) atom itself. This behavior is attributed to ion-ion scattering initiated by the formation of transient ion pair states through transitions between the covalent K(12p) + CH₃NO₂ and ionic K⁺ + (dipole bound) CH₃NO₂[−] terms in the quasimolecule formed during collisions. The ion-pair states are destroyed through dissociation of the CH₃NO₂[−] ion induced by the field of the K⁺ ion, the detached electron remaining bound to the K⁺ ion in a Rydberg state. The results are consistent with recent theory which predicts that K(12p)–CH₃NO₂ collisions lead to strong resonant quenching, i.e., strong n, ℓ changing.^{35,36}

The data are interpreted using a semiclassical collision code that models the detailed dynamics of electron transfer reactions. For purposes of comparison, measurements were also undertaken of ion-pair production through the reaction

SF₆ is a well-known electron scavenger that can form stable (valence-bound) negative ions.

II. APPARATUS

The present apparatus, shown in Fig. 1, has been described in detail elsewhere.⁸ Briefly, potassium atoms contained in a collimated beam are photoexcited to the 12p²P_{3/2} state near the center of a small gas cell where they interact with the

FIG. 1. Schematic diagram of the apparatus. (a) View in the xy plane defined by the laser and atom beams. (b) View in a vertical plane through the center of the gas cell and analysis region.

target gas. A fraction of the neutral reactant products exit the gas cell via a narrow slit and enter the analysis region where they are detected through dissociation/ionization induced by application of a ramped electric field. The resulting positive or negative charged particles are detected by a position sensitive detector (PSD) that records their arrival times and positions.

The $K(12p)$ atoms are created using 294 nm UV radiation provided by an extra-cavity doubled CW Rh6G laser whose output is chopped into a series of 10- μ s duration pulses with a pulse repetition frequency of ~ 1 kHz using an acousto-optic modulator. ($n = 12$ Rydberg states were selected for study because they offer relatively high photo-excitation rates and because earlier studies have shown that Rydberg atoms with values of $n \sim 12$ interact particularly strongly with CH_3NO_2 .) To help tune the laser to the desired state, a small transverse electric field, ~ 45 V cm^{-1} , is maintained across the interaction region to direct electrons produced by collisions or blackbody-radiation-induced photoionization to a microchannel plate (MCP) detector. Neutral reaction products formed traveling within $\pm 4^\circ$ of the xy plane defined by the laser, and atom beams exit the gas cell through a narrow slit that subtends “scattering angles” θ , defined as the angle between the initial direction of travel of the Rydberg atom and the product neutral, of $\sim 22.5^\circ$ to 67.5° , and enter the analysis region which is bounded by two parallel fine mesh grids. Here the surviving ion pair states are dissociated by application of a pulsed electric field with a maximum value of ~ 7.5 kV cm^{-1} . The various grids and the PSD can be biased so as to detect either the positive or negative products. However, the PSD electronics limit the voltages that can be applied to the PSD anode to $\leq \pm 3$ kV. Furthermore, tests showed that a potential difference of 2.4 kV was required across the pair of MCPs used in the PSD to

saturate the count rate. In consequence, the bias that could be applied to the front of the first MCP when detecting negative ions (or electrons) was limited to $\lesssim 500$ V which leads to a low overall negative ion detection efficiency. (Electrons produced by field ionization of scattered Rydberg atoms present in the analysis region, however, can be efficiently detected even for impact energies of ~ 200 – 300 eV.³⁷) No similar limitation exists when detecting K^+ ions, where kiloelectronvolt impact energies can be realized with the application of a large negative bias to the front of the MCP, while the anode operates near ground potential.

For ion pair states with a given binding energy, E_B , field induced dissociation can occur over a sizable range of fields governed by the values of their angular momentum, L , and its projection, L_z , along the z (field) axis. While it is therefore not possible to assign a unique value of E_B to states that dissociate in a particular field, earlier work suggests that a “typical” value for the binding energy of states that dissociate in some field F is given by³⁸

$$E_B(\text{meV}) = 14[F(\text{kV cm}^{-1})]^{1/2}. \quad (3)$$

The present applied field is thus sufficient to dissociate states with typical binding energies approaching 40 meV. Since only a small fraction of the reaction products enter the analysis region, data must be accumulated following many laser pulses to build up arrival position distributions, i.e., the initial spatial distributions of the parent particles themselves. Furthermore, use of a ramped electric field coupled with measurement of the time during the ramp at which dissociation (or ionization) occurs allows selection of ion pair states (or Rydberg atoms) with selected ranges of binding energy.

The measured arrival time position distributions are analyzed using a semiclassical Monte Carlo collision code that models the detailed reaction dynamics and that is based on the essentially free electron model. Electron transfer is viewed as resulting from a binary interaction between the Rydberg electron and target molecule. The initial velocities of the Rydberg atom and target molecule are chosen at random from their velocity distributions. The probability of electron capture at some point is taken to be proportional to the local electron probability density.³⁹ (To account for the quantum defect of $K(np)$ states, $\delta \sim 1.71$, the experimental data for the 12p state are compared to model predictions obtained using 10p hydrogenic wavefunctions.) Following attachment, the kinetic energy of relative motion of the ion pair is computed to determine its final total (kinetic plus potential) energy and determine whether or not it is bound. If bound, the trajectory of the ion pair is computed. Ion pairs that travel into the analysis region are identified and their positions at the time of application of the dissociation field were computed taking into account the fact that, if the ion pairs have finite lifetimes, some will decay en route to the analysis region. The field at which dissociation will occur is computed from the calculated binding energy (Eq. (3)) and used to determine the point (time) during the field ramp at which detachment occurs. The trajectory of the resulting (positive or negative) ion as it travels to the PSD is calculated using SIMION⁴⁰ to obtain its expected arrival time and position. Ion arrival position distributions are built up by considering many collision events. Simulations are run using

different assumed input parameters to evaluate how sensitive the arrival position distributions are to these parameters and for comparison to experimental data.

III. RESULTS AND DISCUSSION

A. SF_6

SF_6 has a sizable electron affinity, ~ 1 eV, and a large rate constant for thermal electron attachment, $\sim 3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$.⁴¹ Once capture occurs, the excess energy can be rapidly redistributed to internal vibrational motions within the anion. Autodetachment is therefore suppressed because, once it is redistributed, the energy must be reconcentrated in a mode(s) from which autodetachment can occur, which is statistically unlikely resulting in long SF_6^- lifetimes. Capture of suprathermal electrons typically results in measured ion lifetimes of a few to a few tens of microseconds, whereas capture of electrons with subthermal energies typically results in millisecond lifetimes. Indeed, Rydberg studies at higher n (where post-attachment electrostatic interactions are unimportant) show that electron transfer can lead to formation of SF_6^- ions with lifetimes of several milliseconds,⁴² more than sufficient to allow creation of long-lived ion-pair states.

Earlier studies of Rydberg electron transfer in collisions with SF_6 at low n have revealed the formation of $\text{K}^+ \cdots \text{SF}_6^-$ ion pair states with lifetimes in the range of ~ 1 – $20 \mu\text{s}$ whose decay is attributed to two mechanisms: transfer of internal energy in the anion into relative translational kinetic energy of the ion pair, which then allows them to separate, and near-resonant charge transfer between the ion pair in a close encounter during their orbital motion whereupon they separate as neutrals.⁴ These earlier lifetime measurements, however, were undertaken over a relatively narrow time window, ~ 0 – $10 \mu\text{s}$, and are therefore particularly sensitive to the decay of short-lived ion pairs. The present measurements, undertaken after sizable time delays, show that electron transfer can also lead to the production of ion pair states with lifetimes $\geq 100 \mu\text{s}$.

Figure 2 presents measured position distributions for $\text{K}^+ \cdots \text{SF}_6^-$ ion pairs with “typical” binding energies (Eq. (3)) in the range ~ 3 to 40 meV for a variety of different delay times t_D (measured from the end of the laser pulse) before application of the field ramp. (The distributions shown were recorded by measuring the K^+ ions rather than the SF_6^- ions as their detection efficiencies are significantly higher.) To emphasize how the shapes of the arrival position distributions change with increasing delay time, the results in each of the distributions shown on the left hand side of the figure are normalized to the peak signal seen in each distribution. To better show the time dependence of the total observed ion signals, the results for each time series shown on the right hand side of the figure are normalized to the peak value observed within that series. Inspection of Fig. 2 shows that as the delay time increases, the ion pairs move steadily away from their point of formation with velocities of $\sim 2 \times 10^4 \text{ cm s}^{-1}$ and an angular distribution that is strongly peaked in the forward direction. The ion pair velocities are significantly smaller than the most probable velocity of the parent $\text{K}(12\text{p})$ atoms, $\sim 5 \times 10^4 \text{ cm s}^{-1}$, and are comparable to those of the target molecules, $\sim 1.8 \times 10^4 \text{ cm s}^{-1}$.

FIG. 2. Position distributions for K^+ ions formed by detachment from $\text{K}^+ \cdots \text{SF}_6^-$ ion pairs created in $\text{K}(12\text{p})$ – SF_6 collisions. The ion pairs have “typical” binding energies of ~ 3 – 40 meV , and the data were recorded following the time delays, t_D , indicated. The white lines denote the area viewed by the PSD and the lower left corner in each panel corresponds to the center of the gas cell. Each panel corresponds to an area of $3 \times 3 \text{ cm}^2$. The distributions shown in the left hand two columns are normalized to the peak signal seen in each distribution, and those in the right hand two columns are normalized to the peak signal observed within each series. The results in columns (a) and (c) are experimental data. The results of model calculations that assume the $\text{K}^+ \cdots \text{SF}_6^-$ lifetimes shown in the inset in Fig. 3 are presented in (b) and (d).

Two factors govern this behavior. First, if capture into a bound state occurs, the momentum of the core ion can only induce a relatively small change in the velocity of the more massive SF_6 target molecule. Second, efficient ion pair formation requires the kinetic energy of relative motion of the K^+ and SF_6^- ions be small, which is best achieved when the Rydberg atom and target molecule are initially traveling in the same general direction, i.e., in the forward direction.

As is evident from Fig. 2, sizable ion pair populations are observed even after flight times of $\sim 100 \mu\text{s}$, demonstrating that Rydberg electron transfer can lead to the production of ion pair states with lifetimes extending up to at least this value. (At later times, the ion pairs move out of the analysis region and can no longer be detected.) The time evolution of the total number of ion pairs observed in selected binding energy windows is shown in Fig. 3. Also shown in Fig. 3 are the results of model calculations. These calculations assume constant Rydberg atom production/destruction rates during the $10\text{-}\mu\text{s}$ -long laser pulse. This is reasonable because, for the present target gas densities of $\sim 2 \times 10^{11} \text{ cm}^{-3}$, the effective lifetime of a Rydberg atom, once created, is only $\sim 3 \mu\text{s}$, limited by the radiative decay and collisional destruction. Calculations were undertaken using a variety of assumed ion pair lifetimes, and the results presented in Fig. 3 show the best fits to the data which were obtained using the lifetimes indicated. These lifetimes are plotted in the inset in Fig. 3 and decrease steadily with increasing binding energy. This trend is similar to that observed in earlier measurements⁴ undertaken using a different experimental approach and much smaller delay times, the measured lifetimes decreasing from ~ 18 to $5 \mu\text{s}$ over the corresponding range of binding energies. Taken together, the available data show that Rydberg electron transfer can lead to formation of ion pair states with a very broad range of lifetimes, the

FIG. 3. K^+ ion signal resulting from dissociation of $K^+ \cdots SF_6^-$ ion pairs formed in $K(12p)-SF_6$ collisions as a function of delay time t_d for the “typical” binding energy ranges indicated. The data sets are normalized to 1.0 at a delay of 40 μs . The solid symbols show experimental data. The lines show the best fits to the experimental data obtained using the present model and which correspond to the lifetimes indicated. The inset shows these lifetimes expressed as a function of average binding energy together with the straight line fit which is used in computing the model predictions presented in Figs. 2 and 4.

observed lifetimes being dependent on the delay times over which observations are made, i.e., measurements at late times necessarily only observe ion pairs with long lifetimes.

The process responsible for the finite ion pair lifetimes was investigated by applying a small dc field ($\sim 45 \text{ V cm}^{-1}$) across the analysis region and looking for a K^+ ion signal. Such a signal might result from ion pair decay in this region due to transfer of internal energy from the SF_6^- ion into translational motion of the ion pair leading to their dissociation. No significant ion signal, however, was detected indicating that ion pair loss must result primarily from charge transfer and mutual ion neutralization. This is consistent with the shorter lifetimes observed for the more tightly bound ion pairs. As the binding energy increases, the ion pair states become more compact and the probability for close encounters between the K^+ and SF_6^- ions increases which will facilitate charge exchange.

Figure 2 includes the results of model calculations undertaken using the lifetimes given by the straight line fit to the measured values shown in the inset in Fig. 3. The calculated distributions are in good agreement with the experimental observations. The good agreement between model predictions and experiment is further highlighted in Fig. 4 which shows the time dependence of the measured K^+ ion signal during application of the field ramp in the analysis region together with the calculated signal.

B. CH_3NO_2

Collisions between low- n Rydberg atoms and CH_3NO_2 are known to result in the formation of (free) $CH_3NO_2^-$ ions with a rate that depends markedly on n , peaking at $n \sim 15$.^{28,31} Earlier work using a variety of polar targets has shown that such a behavior is typical of that expected for formation of dipole-bound negative ions. However, measurements on $CH_3NO_2^-$ ions formed in low- n Rydberg collisions have shown that,

FIG. 4. (a) Time dependence of the electric field ramp applied in the analysis region. (b) —, time dependence of the measured K^+ ion signal at the PSD during application of the field ramp following $K(12p)-SF_6$ collisions; ---, results of model predictions using the lifetimes shown in Fig. 3. (c) —, time dependence of the measured K^+ ion signal during the field ramp following $K(12p)-CH_3NO_2$ collisions; ---, results of model predictions. The inset shows the equilibrium structure for both CH_3NO_2 molecules and $CH_3NO_2^-$ anions.

whereas such ions can undergo field-induced detachment in strong electric fields, their field detachment behavior does not mirror that seen with other dipole-bound anions such as CH_3CN^- . In addition, the product $CH_3NO_2^-$ ions have a range of lifetimes that extends up to several milliseconds, whereas the lifetimes of dipole-bound anions typically lie in the range $\sim 50\text{--}100 \mu s$ and are governed by blackbody-radiation-induced photodetachment. To explain the differences seen for $CH_3NO_2^-$ ions, a model was proposed in which it was argued that Rydberg electron transfer leads to formation of a dipole-bound state that, through strong coupling to the valence-bound state, serves as a “doorway” for the creation of a valence-bound state.^{28,33} Density of states arguments were advanced to suggest that such coupling should lead to states with predominantly valence-bound character. This picture in which the dipole-bound state rapidly evolves into a valence-bound state is consistent with theoretical predictions of strong coupling between such states in $CH_3NO_2^-$.³²

Figure 5 shows K^+ ion arrival position distributions following $K(12p)-CH_3NO_2$ collisions. These distributions are similar in many respects to those seen following $K(12p)-SF_6$

FIG. 5. (a) K^+ arrival position distributions recorded following $K(12p)-CH_3NO_2$ collisions and the delay times t_d indicated. (b) Electron arrival position distributions. ((c)-(e)) Model predictions obtained by assuming that transient $K^+ \cdots CH_3NO_2^-$ ion pairs are formed at a radius of 200 a.u. and that they have the lifetimes indicated. The data in each panel are normalized to the peak signal seen in each distribution.

collisions, except that they correspond to larger product velocities. Model calculations undertaken assuming that $K(12p)-CH_3NO_2$ collisions result in the formation of long-lived ion pair states, however, predicted ion pair velocities that were significantly smaller than suggested by the time dependence of K^+ arrival position distributions. Furthermore, as shown in Fig. 4, which includes the time dependence of the K^+ ion signal observed during the field ramp applied in the analysis region, the distribution of ion arrival times is very different from that predicted by the model (and seen with SF_6). Taken together these observations indicate that electron transfer does not lead to creation of long-lived $K^+ \cdots CH_3NO_2^-$ ion-pair states.

Earlier studies of free $CH_3NO_2^-$ ions produced in low- n Rydberg collisions show that a large fraction of the product ions undergo detachment in fields $\lesssim 30 \text{ kV cm}^{-1}$.^{28,31} This behavior is explained by calculations which show that the vertical electron affinity of CH_3NO_2 is negative indicating that it will not retain an electron and form a valence-bound anion in its ground-state equilibrium geometry.²⁹ The electron binding energy depends critically on the tilting angle between the ONO plane and the line through the C–N bond (see inset in Fig. 4). The sizable adiabatic electron affinity of CH_3NO_2 , $\sim 0.26 \text{ eV}$, requires the product anions be formed with strong vibrational excitation whereupon field-induced detachment might be possible at the extremes of the vibrational motion where the tilting angle is small and the electron binding weak. The observation that detachment occurs over a wide range of fields is then attributed to creation of states with different amounts of vibrational excitation. However, Coulomb fields $\gtrsim 30 \text{ kV cm}^{-1}$ are present at distances $\lesssim 400 \text{ a.u.}$ from a K^+ core ion, whereas the radius of a $K(12p)$ atom, given by $\sim 2n^2 = 2(n - \delta)^2$, is only $\sim 200 \text{ a.u.}$ The presence of the strong Coulomb field therefore suggests that the formation of stable $K^+ \cdots CH_3NO_2^-$ ion pair states bound at radii characteristic of the parent Rydberg state is problematic since, if an electron were to be captured at such radii, the resulting negative ion would undergo rapid field-induced detachment, the product electron remaining bound to

the core ion, but in a different Rydberg $n\ell$ state. However, the possibility also exists that the electron might then, during a single collision between the reactants, subsequently reattach to the target molecule leading to successive formation of transient ion pair states. (No similar behavior is expected for SF_6 as SF_6^- ions show no evidence of field induced detachment at high fields.)

To better understand the reaction dynamics, measurements of the arrival position distributions for the negative particles resulting from application of the ramped field in the analysis region were instituted. As is evident from Fig. 5, these measurements yielded arrival position distributions that mirrored those seen for the K^+ ions. However, as illustrated in Fig. 6, the time delay between application of the field and detection of the resulting negative particles was very short indicating that the negatively charged particles were electrons, not $CH_3NO_2^-$ ions. Indeed, the arrival time distribution contains no evidence of a peak at the arrival time expected for $CH_3NO_2^-$ ions. Since only neutral species can exit the interaction region and pass into the analysis region, the electrons are attributed to field ionization of scattered Rydberg atoms. (Measurements with SF_6 , while demonstrating the production of SF_6^- ions, revealed no prompt electron signal such as is evident in Fig. 6 indicating that the observed K^+ signals shown in Figs. 2–4 result solely from detachment of $K^+ \cdots SF_6^-$ ion pairs.) Given that the size of the ion signals observed when detecting K^+ product ions was similar to the size of those seen using SF_6 at a similar target gas density, the data suggest that the rate constant for Rydberg atom scattering is sizable and much larger than what might be expected for simple ion-neutral scattering in a binary $K^+-CH_3NO_2$ collision, $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

FIG. 6. (a) Time dependence of the electric field ramp applied in the analysis region. (b) Time dependence of the measured (electron) signal during application of the field ramp following $K(12p)-CH_3NO_2$ collisions. The arrows indicate the times (fields) at which diatomic ionization of Rydberg states with the values of n indicated is expected (see text). The heavy solid arrow shows the time at which $CH_3NO_2^-$ ions are expected to begin arriving.

A large reaction rate, however, is consistent with recent theoretical studies by Lebedev and co-workers^{35,36,43} of resonant quenching in Rydberg collisions with highly polar molecules through reactions of the type

In their discussion of resonant quenching, Lebedev and co-workers consider the transition amplitudes between the covalent $\text{K}(12p)\text{-CH}_3\text{NO}_2$ and ionic $\text{K}^+\text{-(dipole bound)}\text{CH}_3\text{NO}_2^-$ terms in the quasi-molecule formed during collisions. (Since the binding energy of a dipole-bound CH_3NO_2^- ion is expected to be ~ 13 meV,⁴³ the crossing between the covalent $\text{K}(12p)\text{-CH}_3\text{NO}_2$ and $\text{K}^+\text{-(dipole bound)}\text{CH}_3\text{NO}_2^-$ potential curves occurs at a separation $R_c \sim 200$ a.u. which is similar in size to the radius of a $\text{K}(12p)$ atom and in the region where the Rydberg electron probability density is maximum.) The theory assumes that the transitions between the covalent and ionic channels occur at separations in the vicinity of the crossing radius R_c . The population of the covalent product channels results from the decay of the negative ion in the Coulomb field of the K^+ core ion. The interactions within the quasimolecule are treated dynamically. Theoretical calculations using this approach yield, for CH_3NO_2 , resonant quenching cross sections that are strongly peaked in the n^* range from ~ 8 to 14 and that, for $n^* \sim 10$ and a collision velocity of 10^{-3} a.u. (2.2×10^5 cm s⁻¹), are large, $\sim 3 \times 10^{-12}$ cm², comparable to the geometric size of the atom. Although the assumed collision velocity is somewhat higher than that in the present work, the calculations predict sizable reaction rate constants $k \sim 6 \times 10^{-7}$ cm³ s⁻¹, consistent with the experimental observations. Detailed analysis of the experimental data, however, is challenging because, given the large predicted reaction rates, n, ℓ -changed Rydberg atoms might, provided they have values of n^* in the range $\sim 8\text{--}14$, undergo further resonant quenching collisions as they enter and traverse the analysis region, thereby enhancing their scattering. Nonetheless, the sizable off-axis signals seen in the present work do require that resonant quenching be associated with significant scattering. Such scattering implies that the lifetime of a transient $\text{K}^+\text{-CH}_3\text{NO}_2^-$ ion pair is sufficient to allow significant joint orbital motion of the ion pair prior to dissociation of the CH_3NO_2^- ion. Figure 5 includes the results of model simulations which assume, as a first approximation, that the observed scattered Rydberg atoms result from a single scattering event in the gas cell, that ion pair formation occurs at a radius of 200 a.u., and that the transient pairs have the lifetimes indicated prior to separating as a Rydberg atom (with velocity equal to the instantaneous velocity of the K^+ ion at the time of neutralization) and a neutral molecule. Results obtained using this simple model suggest that anion lifetimes ≥ 10 ps are sufficient to explain the present measurements.

The scattered Rydberg atom signal was observed to decrease rapidly with increasing flight time at a rate that corresponded to an effective Rydberg lifetime of ~ 20 μs , suggesting that collisional quenching tends to predominantly populate low- n states, i.e., states close to the parent n level. This is confirmed by the field ionization signal shown in Fig. 6. Assuming that collisional quenching populates primarily higher- ℓ states, these will ionize diabatically at fields that, depending as to the

initial value of ℓ and m , span a broad range. However, states of a given n typically ionize at fields near $\sim 1/9n^4$ a.u.,⁴⁴ and these are indicated in Fig. 6 for different values of n . (The fields that can be applied in the analysis region are insufficient to ionize states with $n \leq 16$.) Inspection of Fig. 6 shows that much of the ionization signal is associated with ionization of states with $n \lesssim 25$, a result that is consistent with population of short-lived Rydberg states.

IV. CONCLUSIONS

The present work demonstrates that, whereas $\text{K}(12p)$ collisions with SF_6 can lead to creation of long-lived ($\tau \geq 100$ μs) $\text{K}^+ \cdots \text{SF}_6^-$ ion-pair states, collisions with CH_3NO_2 (which can also form long-lived valence bound negative ions) do not. Rather, the data show that collisions with CH_3NO_2 lead to strong Rydberg atom scattering that is attributed to the formation of transient ion-pair states, the lifetimes of which are governed by the decay of the CH_3NO_2^- ions in the Coulomb field of the core ion resulting in the formation of a (state-changed) Rydberg atom and a neutral molecule. The lifetime of the transient ion pair state, however, is sufficient (≥ 10 ps) to allow significant mutual scattering of the constituent ions prior to decay. Transient ion pair formation is associated with transitions between ionic and Rydberg covalent terms of the quasimolecule formed during collisions, reaction being facilitated by the sizable dipole moment of CH_3NO_2 and the strong coupling between dipole- and valence-bound CH_3NO_2^- states. The observed Rydberg scattering rates are much larger than those that might be expected for simple scattering of the K^+ core ion in a binary $\text{K}^+\text{-CH}_3\text{NO}_2$ interaction but are consistent with recent calculations of resonant quenching of Rydberg states by highly polar molecules. Future experiments using higher-velocity, and velocity-selected, Rydberg atoms promise additional insights into this new mechanism for Rydberg atom scattering.

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