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Threshold-field-ionization photoelectron spectroscopy and delayed forced autoionization of HCl

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A time-of-flight photoelectron spectrometer is oriented coaxially with a pulsed molecular beam to detect high Rydberg states of HCl with lifetimes as long as 7 μ s. Two classes of such states are found. Delayed extraction following double-resonant excitation field-ionizes Rydberg states of very high principal quantum number ($n \geq 100$) that converge to successive rotational limits for producing HCl^+ , effectively yielding a rotationally resolved threshold photoelectron spectrum. Surprisingly, excitation under more rigorously field-free conditions (< 100 mV/cm) produces additional resonances which can be assigned to series of long-lived Rydberg states extending to principal quantum numbers as low as 10. The lower-principal-quantum-number resonances isolated by their long field-free lifetimes appear to constitute a high-angular-momentum nonpenetrating subset of the autoionizing Rydberg series that converge both to accessible rotational levels of the upper $^2\Pi_{1/2}$ threshold and excited rotational limits of the $^2\Pi_{3/2}$ ground state of HCl^+ .

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Molecular Rydberg states very near series convergence limits are usually characterized by long natural lifetimes. On the other hand, autoionizing and/or predissociating molecular Rydberg states of low to moderate principal quantum number generally decay on timescales of nanoseconds or less [1]. This distinction is a cornerstone of a new technique termed threshold field ionization or zero-kinetic-energy (TFI-ZEKE) photoelectron spectroscopy, which has emerged recently as a powerful method for recording the rovibrational structure of ions [2–4], and establishing cross sections for their production via state-detailed photoionization [5–7]. ZEKE methods rely on the existence and accessibility of those long-lived Rydberg states of very high principal quantum number that lie just below the ionization limit of each ion internal state [8]. The delayed field ionization of such high Rydberg states provides a slightly redshifted mark of the corresponding bound-continuum threshold. However, to find ZEKE

structure in spectral isolation, other discrete resonances, associated with Rydberg orbitals of lower principal quantum number, must decay on short time scales, either by fragmentation or autoionization.

At variance with this picture, we have now found, in double-resonance experiments at zero field in a uniquely configured TFI-ZEKE spectrometer, conditions under which the delayed-field-ionization spectrum of a molecule, HCl, evidences spin-orbit and rotationally autoionizing states with natural lifetimes of many microseconds or longer, extending to surprisingly low principal quantum numbers.

This work continues an effort in which we have characterized the spectrum of spin-orbit autoionizing Rydberg states of HCl reached via intermediate resonance with the $J=2$ level of the $4p\pi^1\Delta$ Rydberg state [9]. The application of TFI-ZEKE photoelectron spectroscopy was essential to progress in the assignment that dense system of

transitions, which fills the 620-cm^{-1} interval between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ ionization thresholds of HCl.

We find that long-lived autoionizing resonances appear in the ZEKE spectrum of HCl under electron collection conditions that differ from those used for conventional TFI-ZEKE measurements only by the magnitude of the dc electric field present upon photoexcitation. As with transitions to high Rydberg states at photoionization thresholds, we isolate resonant absorption to these lower-lying long-lived Rydberg states by the delayed application of a larger pulsed field. The spectrum of the resulting long-lived resonant structure found far from threshold represents a fraction of the autoionizing Rydberg series that can be predicted to converge to accessible rotational levels of the upper $^2\Pi_{1/2}$ threshold and excited rotational limits of the $^2\Pi_{3/2}$ ground state of HCl^+ . Its interpretation opens an important window on the dynamical scope of low-energy spin-orbit and rotational autoionization dynamics. The present Rapid Communication offers an assignment that differentiates long-lived autoionizing structure from the spectrum of prompt autoionizing states, and details experimental conditions that most effectively isolate long-lived resonances.

The experimental key to isolating and observing long-lived Rydberg states is an alignment of the axis of the time-of-flight photoelectron spectrometer along that of the molecular beam. In our apparatus, a skimmed molecular beam enters the magnetically shielded spectrometer through a grid in the first plate (repeller) of a three-plate ion-optics assembly. The second (extractor) and third (entrance) plates also hold grids. The entrance grid caps a grounded 20-cm field-free flight tube that ends with a final grid isolating a two-plate multichannel electron detector.

Ultraviolet-visible two-plus-one-photon double-resonant excitation prepares high Rydberg states in the region between the repeller and extractor. We float this pair of plates with respect to the grounded entrance plate, and additionally supply a very low differential dc bias. We

find that we can easily adjust this differential bias to obtain an observable delayed signal from slow electrons produced by prompt autoionization. This signal generally appears within a very narrow range of bias at externally applied potentials of around 100 mV/cm , and we regard its presence, a few hundred nanoseconds after the laser pulse, to signify a true local zero field between the repeller and extractor. Under these conditions, with no other fields present, we also find a wavelength-varying electron signal, which appears at the detector some microseconds after the laser pulse. We interpret this signal to mark the passage of molecules excited to long-lived Rydberg states from the region between the repeller and the extractor to that between the extractor and the entrance grid. The 2-V potential maintained between the latter two plates field-ionizes those molecules as they enter this region, producing a resonant signal identical to that we obtain by pulsed-field threshold ionization or ZEKE photoelectron spectroscopy performed between the repeller and extractor [10].

In addition, we find that Rydberg states which we can identify as converging to the upper spin-orbit threshold, but which lie much further below that threshold than the range of $6\sqrt{E}\text{ cm}^{-1}$ which can be reached by field ionization, also appear as resonant structure on this long-delayed electron signal. We attribute the appearance of this lower-energy delayed structure to autoionization forced by Stark mixing [11]. We find that equivalent spectra can be obtained at varying earlier delays by forcing autoionization in the first region with the application of a 5–10 V pulsed field between the repeller and extractor.

At low pulse energies of the photoionizing laser ($< 1\text{ mJ}$) [12], the spectrum of this long-time signal contains no contributions from fast-autoionizing states, and is much simpler than the spectrum of all electrons collected promptly either by a small static field or by a pulsed field at little or no delay [13]. Figure 1 shows a center segment of this long-lived spectrum, which, in its entirety, spans

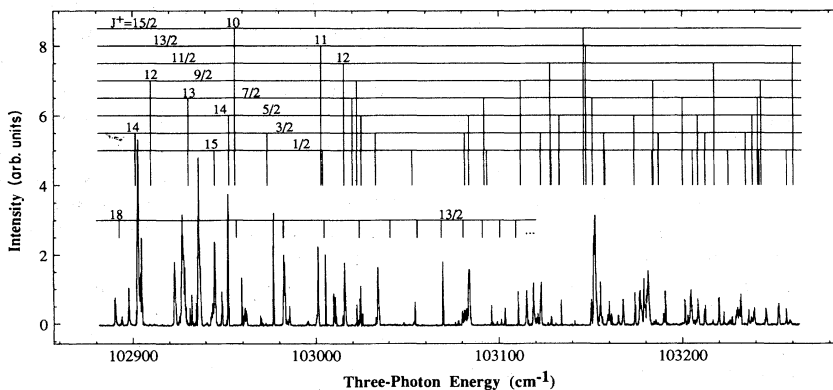


FIG. 1. A center segment of the spectrum of long-lived spin-orbit autoionizing states in HCl, reached in double-resonance via the $J=2$ level of the $4p\pi F^1\Delta$ Rydberg state. The sharp resonances shown have lifetimes in excess of $7\text{ }\mu\text{s}$. They are isolated by monitoring electrons produced following 2 V cm^{-1} pulsed-field forced autoionization at a delay of $5\text{ }\mu\text{s}$ after laser photoexcitation. The ladders shown correspondence between the spectrum and calculated series of Rydberg states, all with zero quantum defect converging to the rotational states of $^2\Pi_{1/2}\text{ HCl}^+$ accessible for orbital angular momentum quantum number $l=4$. The small ladder shows a Rydberg series of rotationally autoionizing states converging to $^2\Pi_{3/2}\text{ }J^+=\frac{13}{2}$, again assuming a constant quantum defect of zero.

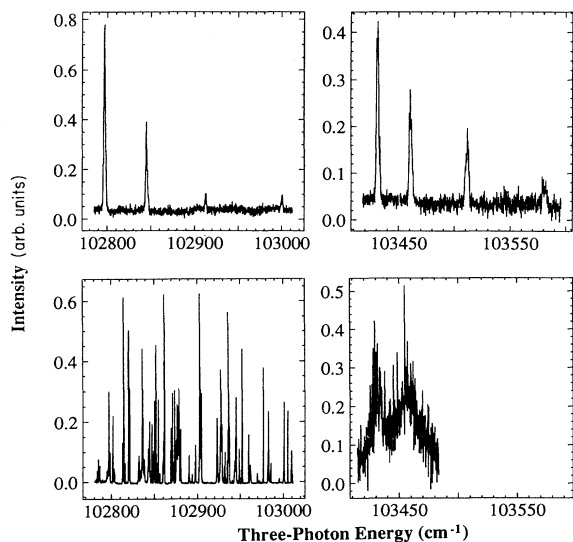


FIG. 2. TFI-ZEKE photoelectron spectra of the rotational levels associated with the ${}^2\Pi_{3/2}$ (left-hand-side) and ${}^2\Pi_{1/2}$ (right-hand side) electronic ionization limits of HCl. The top frames show the cleanly resolved rotational structure obtained under conditions of ca. 500 mV/cm static reverse bias, which is sufficient to force prompt autoionization of long-lived zero-field states that lie in the neighborhood of the lower threshold, and sweep away near-zero kinetic-energy electrons formed above the upper threshold. The lower frames show spectra taken at zero static bias, in which the threshold photoelectron structure is obscured by these additional sources of signal. The top spectra have been corrected for laser-pulse energy to accurately reflect the relative intensities of transitions from $J=2$ of the $4p\pi F {}^1\Delta$ state to the states on the left-hand side $J^+ = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$, and $\frac{9}{2}$ of the lower $\Omega^+ = \frac{3}{2}$, and on the right-hand side $J^+ = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$, and $\frac{7}{2}$ of the upper $\Omega^+ = \frac{1}{2}$ spin-orbit manifolds of HCl^+ .

the interval between the ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$ ionization limits of HCl. Also shown for comparison is a simple ladder of Hund's case-(e) spin-orbit autoionizing series [14] of constant (zero) quantum defect converging to successive accessible rotational levels of the ${}^2\Pi_{1/2}$ cation. Precise convergence limits for these ladders are established by rotationally resolved threshold photoionization (ZEKE) spectra (cf. Fig. 2), in concert with precise information on positions of ion rotational levels [15], and Rydberg extrapolations based on our earlier assignment of the conventional cation-detected double-resonant spin-orbit autoionization spectrum [9].

Our earlier work shows that principal features of the conventional spin-orbit autoionization spectrum are reasonably well described in terms of series of differing quantum defect converging primarily to levels of low J^+ in the spin-orbit excited core [9]. We assign the most intense resonances in the spectrum of fast-autoionizing states to p and d series exhibiting moderately penetrating quantum defects of from 0.2 to 0.6.

In contrast, a nearly complete account of the long-lived structure in Fig. 1 is given by the ladders shown of series with zero quantum defect. Successful interpretation in terms of such uniformly low quantum defects suggests ac-

tivity in this spectrum by Rydberg orbitals exclusively of high l . Supporting this hypothesis is the presence of strong transitions that fall into series converging to values of J^+ which can be reached in double resonance via $4p\pi F {}^1\Delta J=2$ only for final states of $l=4$.

We note that a small fraction of the resonances pictured in Fig. 1 do not fit with this simple zeroth-order picture of high- l long-lived spin-orbit autoionizing series. However, we find that these latter peaks correspond well with the calculated positions of similarly nonpenetrating series of rotationally autoionizing levels converging to excited rotational limits of the lower ${}^2\Pi_{3/2}$ core. Note, for example, the resonances in Fig. 1 marked by the abbreviated ladder corresponding to a single series of rotationally autoionizing states of zero quantum defect converging to the $J^+ = \frac{13}{2}$ rotational level of ${}^2\Pi_{3/2} \text{HCl}^+$. Here again, the high values of J^+ involved appear to confirm high Rydberg orbital angular momentum. Further analysis of evident perturbations and an examination of the precise correspondence between experimental positions and calculated ones are subjects of a more detailed exploration of these autoionization dynamics employing the methods of multichannel quantum defect theory [16].

Nearer the ${}^2\Pi_{3/2}$ threshold, the spectrum of long-lived autoionizing states overlaps the ZEKE spectrum of transitions to the lower rotational states of the lower spin-orbit limit. Here we find that features associated both with long-lived autoionizing states and near-zero kinetic-energy electrons appear together in the zero-field TFI-ZEKE spectrum. Figure 2 shows an example. In the absence of reverse bias, the threshold photoelectron spectrum over the rotational states of the ${}^2\Pi_{1/2}$ limit are contaminated by slow, above-threshold photoelectrons. The structure associated with the ${}^2\Pi_{3/2}$ threshold is obscured by long-lived spin-orbit autoionizing states. The upper frames of Fig. 2, which show the TFI-ZEKE spectra obtained upon application of a 500-mV/cm reverse bias, indicate that only a very weak external field is necessary to completely suppress this long-lived structure. This suggests that Stark mixing of nonpenetrating (e.g., f and g) series with penetrating (e.g., p and d) series is quite facile [17], and thus reverse bias sufficient to sweep away slow electrons also forces prompt autoionization.

In summary, we find the coaxial orientation of a threshold-field-ionization photoelectron spectrometer enables the detection of very-long-lived Rydberg states in HCl. These states span the spin-orbit autoionization interval in this molecule, forming an extensive spectrum of transitions which are isolated by rotational selection via double-resonant photoexcitation together with their long lifetimes under field-free conditions. We find that this spectrum can be described almost totally in terms of series of near-zero quantum defect converging to successive rotational levels up to $J^+ = \frac{9}{2}$, the highest accessible for $l=4$. Additional long-lived resonances, which do not fit with low-quantum-defect spin-orbit autoionizing series, correspond well with zero-quantum-defect Rydberg ladders converging to excited rotational levels of the ground-state ${}^2\Pi_{3/2}$ ion. Again, rotational levels as high as those that can be reached for $l=4$ are implicated, indicating that, under field-free conditions, rotational autoioniza-

tion is also slow for high- l nonpenetrating Rydberg orbitals. Non-ZEKE long-lived structure of all kinds disappears in the presence of even a weak electrostatic field (< 500 mV/cm) suggesting facile Stark mixing with prompt autoionizing states. HCl is not unusual in its pathways for unimolecular decay; underlying the resonances assigned are open channels for electronic and rotational autoionization as well as neutral fragmentation. Thus, we suspect the behavior evidence by this system, in which, under zero bias, long-lived Rydberg states appear,

may be an observable feature in many other molecules under conditions of low-bias delayed field ionization.

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