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# Resonance enhanced multiphoton ionization photoelectron spectroscopy and pulsed field ionization via the $F^1\Delta_2(v'=0)$ and $f^3\Delta_2(v'=0)$ Rydberg states of HCl

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In this paper, we report the first rotationally resolved one- and two-color resonance enhanced multiphoton ionization photoelectron spectroscopy (REMPI-PES) study of the HCl molecule. The agreement between our experimental branching ratios and theoretical investigations is excellent. We also report the first zero kinetic energy pulsed field ionization (ZEKE-PFI) experiments carried out in a "magnetic bottle" electron spectrometer. A direct comparison is made between ZEKE-PFI and REMPI-PES spectra for ionization via several rotational levels of the  $F^1\Delta_2(v'=0)$  and  $f^3\Delta_2(v'=0)$  Rydberg states of HCl. Large differences in both the spin-orbit and rotational branching ratios are found between the ZEKE-PFI and REMPI-PES spectra. These differences can be understood qualitatively on the basis of rotational and spin-orbit autoionization mechanisms.

## I. INTRODUCTION

Valuable information on the fundamental physics involved in molecular photoionization processes can be obtained from a detailed investigation of the ionic state branching ratios. In particular, rotational branching ratios are a direct measure of the angular momentum composition of the photoelectron, making them a sensitive probe of the ionization dynamics. Photoionization from the initial (ground) state may take place by absorption of a single vacuum ultraviolet (VUV) photon or via resonance enhanced multiphoton ionization (REMPI). When the latter technique is used, ionization of a selected rovibronic level of an excited state can be studied, thus significantly reducing the number of final ionic states accessed. With a resolution of several millielectron volts achievable in REMPI-PES, rotationally resolved spectra have only been obtained in a few cases, e.g., for the diatomic hydrides  $H_2$ ,<sup>1,2</sup>  $OH$ ,<sup>3</sup> and  $NH$ ,<sup>4,5</sup> and for the NO radical.<sup>6</sup>

Recently, Müller-Dethlefs *et al.*<sup>7</sup> developed a novel technique which allows the investigation of ionic states with sub-wave-number resolution, an improvement by two to three orders of magnitude over more conventional methods. In their original scheme, electrons with zero kinetic energy (ZEKE) are formed and probed after a delay time by accelerating them by means of a pulsed electric field. In an alternative scheme (ZEKE-PFI), which is now more widely used, long-lived high- $n$  Rydberg states are probed via delayed pulsed field ionization (PFI).<sup>8,9</sup>

Theoretical interpretation of ZEKE-PFI spectra has been carried out using *ab initio* calculations<sup>10-12</sup> and multichannel quantum defect theory (MQDT).<sup>13</sup> In the former calculations, direct ionization to the continuum is assumed, without invoking a transition to high- $n$  Rydberg states. In the latter calculations, interactions between Rydberg series are computed which lead to rotational autoionization. A similar autoionization mechanism has been proposed by Tonkyn *et al.*<sup>14</sup> to explain the strong  $\Delta N < 0$

signals that appear to be a common feature of many ZEKE-PFI spectra. Reasonably good agreement between both the *ab initio* and MQDT calculations and experiment is obtained in some cases, whereas in others, appreciable discrepancies remain. To help elucidate the origin of these discrepancies, we have studied ionization via the same intermediate states using both REMPI-PES and ZEKE-PFI detection.

Rotational branching ratios for ZEKE-PFI via the  $F^1\Delta_2(v'=0, J'=2)$  state of HCl have been determined experimentally by Haber *et al.*<sup>15</sup> and through the use of *ab initio* calculations by Wang and McKoy.<sup>10</sup> The experimental and theoretical spectra show both  $\Delta N = -1$  being the strongest transition, and give an overall good agreement. From this agreement, it might be concluded that ZEKE-PFI results are very similar to those expected for direct ionization. For this low- $J$  intermediate state, the resolution achievable using conventional photoelectron spectroscopy is insufficient to resolve the rotational branching, thus preventing a direct comparison between ZEKE-PFI and REMPI-PES rotational branching ratios. In this paper, a direct comparison is made between ZEKE-PFI and REMPI-PES spectra for ionization via higher rotational levels of the  $F^1\Delta_2$  and  $f^3\Delta_2$  intermediate states. Large differences in both the spin-orbit and rotational branching ratios are found between the REMPI-PES and ZEKE-PFI spectra, and possible explanations for these differences are discussed.

## II. EXPERIMENT

The experimental setup for the REMPI-PES experiments has been described previously.<sup>16</sup> Briefly, the laser system consists of an excimer laser (pulse duration  $\sim 10$  ns) pumping either one or two dye lasers at a repetition rate of 30 Hz. The output of (one of) the dye lasers is frequency doubled using a BBO crystal.

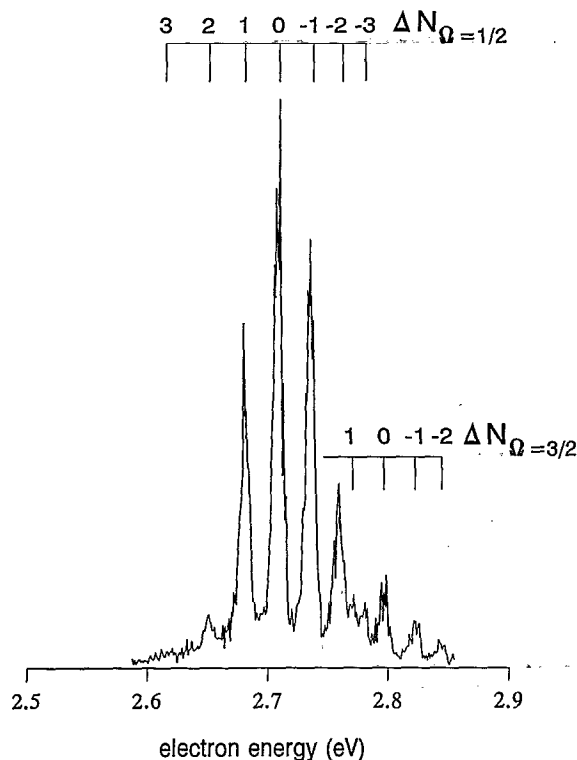


FIG. 1. The photoelectron spectrum resulting from one-color (2+1) REMPI via the  $S(8)$  rotational transition associated with the  $F^1\Delta_2(v'=0)$  state at a two-photon energy of  $83\,222\text{ cm}^{-1}$ .

The laser output is focused by a quartz lens with a focal length of 25 mm in the ionization region of a "magnetic bottle" electron spectrometer. A diverging magnetic field (diverging from  $\sim 1\text{ T}$  in the ionization region to  $\sim 10^{-3}\text{ T}$  in the flight tube) allows for the kinetic energy resolved detection of photoelectrons with 50% collection efficiency and an energy resolution of 6–8 meV. The original design<sup>17</sup> has been modified to allow the study of reactive and transient species.

The ZEKE-PFI experiments are based on pulsed field ionization of long-lived Rydberg states with very high principal quantum numbers, converging to a rovibronic state of the ion. The ZEKE-PFI experiments are carried out using the electron spectrometer described above. On the pole faces of the 1 T electromagnet, small copper plates coated with colloidal graphite are mounted. In the present experiments, a d.c. voltage of 5 V/cm was applied to these plates to sweep out electrons created by direct ionization processes. After a delay of  $\sim 0.2\ \mu\text{s}$ , an electric field pulse of 5–20 V/cm is used to ionize the long-lived Rydberg states.

### III. RESULTS

Figure 1 shows the rotationally resolved PE spectrum resulting from one-color (2+1) REMPI via the  $S(8)$  transition of the  $F^1\Delta_2(2^2\Pi_{1/2}\ 4p\pi)(v'=0)$  Rydberg state of HCl. Ionization takes place only to the vibrational ground state of the ion and the transition to the  $2^2\Pi_{1/2}$  spin-orbit component dominates. This strong core preservation is ex-

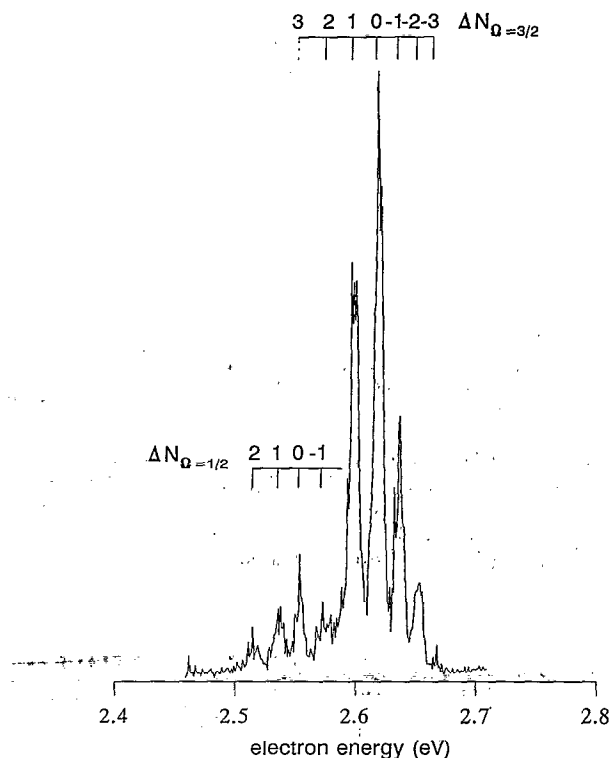


FIG. 2. The photoelectron spectrum resulting from one-color (2+1) REMPI via the  $P(8)$  rotational transition associated with the  $f^3\Delta_2(v'=0)$  state at a two-photon energy of  $81\,865\text{ cm}^{-1}$ .

pected for direct ionization of an unperturbed Rydberg state and has indeed been observed previously for ionization via a low  $J'$  component of the  $F^1\Delta_2$  state.<sup>18</sup> For ionization via low rotational levels, the accessed rotational levels of the ion are too close together to resolve the rotational branching. From approximately  $J'=5$  onwards, rotationally resolved PE spectra can be obtained.

For the  $S(8)$  transition, the splitting between the accessed rotational levels of the ion exceeds the instrumental linewidth and, hence, rotational resolution is achieved. For both the strong  $2^2\Pi_{1/2}$  and the weak  $2^2\Pi_{3/2}$  spin-orbit states, the  $\Delta N=0$  transition is strongest and  $\Delta N=\text{even}$  and  $\Delta N=\text{odd}$  transitions occur with comparable intensity.

In Fig. 2, the PE spectrum associated with ionization via the  $P(8)$  transition to the  $f^3\Delta_2(2^2\Pi_{3/2}\ 4p\pi)(v'=0)$  Rydberg state is depicted. As in the PE spectrum of the  $F^1\Delta_2(v'=0)$  Rydberg state, only  $v^+=0$  is observed. In ionization via the  $f^3\Delta_2$  state, the transition to the  $2^2\Pi_{3/2}$  spin-orbit component dominates, again indicating core preservation. The vibrational and spin-orbit branching ratios agree very well with those obtained previously for REMPI via the  $f^3\Delta_2(v'=0)$   $Q(2)$  transition.<sup>18</sup> The rotational ion distribution shows both  $\Delta N=\text{even}$  and  $\Delta N=\text{odd}$  transitions, with  $\Delta N=0$  being the strongest line. The  $\Delta N>0$  transitions are slightly more intense than the  $\Delta N<0$  transitions, opposite to what was observed for ionization via the  $F^1\Delta_2$  state. In Fig. 3, the ZEKE-PFI spectrum for ionization via the  $S(0)$  rotational transition to the  $F^1\Delta_2(v'=0)$  Rydberg state is shown. A striking difference

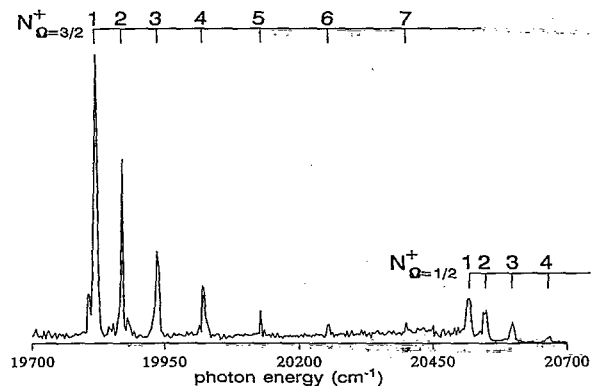


FIG. 3. The ZEKE-PFI spectrum resulting from ionization via the  $S(0)$  rotational transition associated with the  $F^1\Delta_2(v'=0)$  state. The pump laser frequency is fixed on the  $S(0)$  rotational transition to the  $F^1\Delta_2(v'=0)$  state at a two-photon energy of  $82\,909\text{ cm}^{-1}$ , while the probe laser frequency is scanned over the indicated energy range.

with the PE spectrum associated with (2+1) REMPI as shown in Fig. 1 is that in the ZEKE-PFI spectrum, transitions to the  $^2\Pi_{3/2}$  spin-orbit state dominate, whereas in Fig. 1, the transitions to the  $^2\Pi_{1/2}$  spin-orbit state are strongest. Due to the enhanced spectral resolution of the ZEKE-PFI technique, the rotational distribution of the ion is well resolved, even for this low  $J$  transition. The strongest feature in the spectrum corresponds to the transition to the lowest rotational component of the  $^2\Pi_{3/2}$  ionic state, implying a change of core rotation of  $\Delta N = -1$ . For the much weaker transitions to the  $^2\Pi_{1/2}$  state, the  $\Delta N = -1$  transition is also favored. A series of ZEKE-PFI spectra associated with  $P(3)$ – $P(8)$  rotational lines are shown in Fig. 4. In all spectra, the transitions to the  $^2\Pi_{3/2}$  spin-orbit state are favored over the transitions to the  $^2\Pi_{1/2}$  state. Transitions in which the core rotation decreases ( $\Delta N < 0$ ) are much more prominent than transitions in which the core rotation increases by an equal amount. These results differ dramatically from the rotational distributions observed for one-color (2+1) REMPI-PES, as shown in Fig. 1. A similar series, shown in Fig. 5, was obtained for ionization via the  $P(3)$ – $P(8)$  rotational transitions associated with the  $f^3\Delta_2(v'=0)$  Rydberg state. The extremely weak transitions to the higher lying  $^2\Pi_{1/2}$  spin-orbit state are not shown. In contrast to what was observed for the  $F^1\Delta_2(v'=0)$  Rydberg state, the spin-orbit branching ratios observed in the REMPI-PES (see Fig. 2) and ZEKE-PFI experiments differ only little. However, the  $\Delta N < 0$  transitions are anomalously intense compared to their  $\Delta N > 0$  counterparts.

In order to assess a possible energy dependence of the spin-orbit and rotational branching ratios, a two-color REMPI-PES experiment was performed. In this experiment, the first laser wavelength is fixed on a two-photon transition, selecting a specific rotational level of the  $F^1\Delta_2$  or  $f^3\Delta_2$  intermediate state. The second laser, fixed at 440 nm, is used for the ionization step. The wavelength of the ionizing laser is chosen such that ionization can energetically take place to both the  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  ionic states.

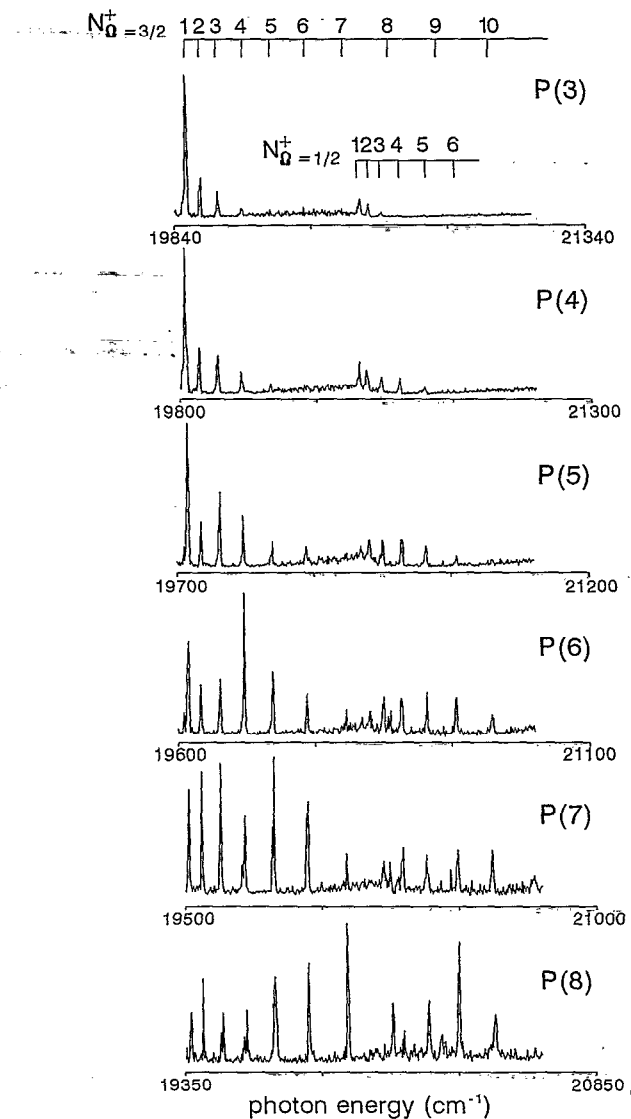


FIG. 4. ZEKE-PFI spectra resulting from ionization via the  $P(3)$ – $P(8)$  rotational transitions associated with the  $F^1\Delta_2(v'=0)$  state. The pump laser frequency is fixed on the indicated rotational transitions to the  $F^1\Delta_2(v'=0)$  state, while the probe laser frequency is scanned over the indicated energy range.

The PE spectrum for two-color (2+1') REMPI via the  $S(8)$  transition associated with the  $F^1\Delta_2(v'=0)$  intermediate state is shown in Fig. 6. The photoelectron energy associated with the transition to the  $^2\Pi_{1/2}$  spin-orbit state is approximately 0.3 eV, whereas in the one-color experiment, this transition corresponded to an energy of 2.7 eV. The branching ratios observed in the two-color experiment are nearly identical to those observed in the one-color process, both with respect to the distribution over spin-orbit states as well as the distribution over the rotational states. A similar two-color REMPI experiment was carried out via the  $f^3\Delta_2$  intermediate state. Also here the two-color (not shown) and the one-color PE spectra were found to be identical.

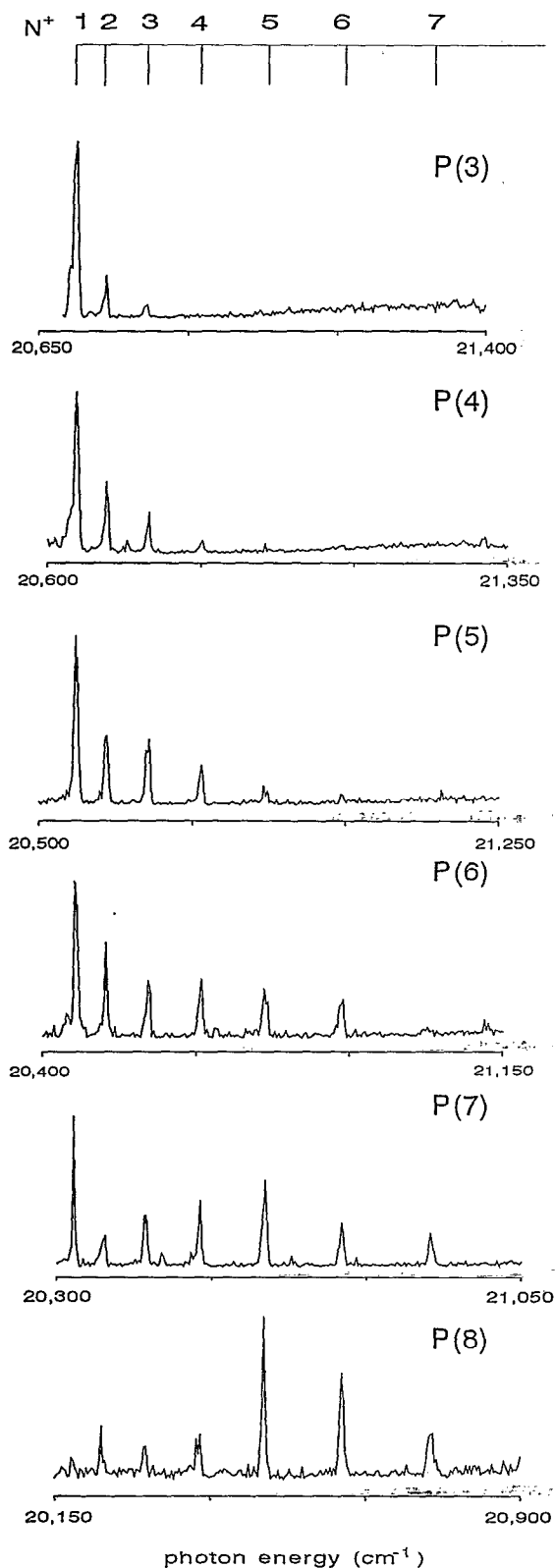


FIG. 5. ZEKE-PFI spectra resulting from ionization via the  $P(3)$ – $P(8)$  rotational transitions associated with the  $f^3\Delta_2(v'=0)$  state. The pump laser frequency is fixed on the indicated rotational transitions to the  $f^3\Delta_2(v'=0)$  state, while the probe laser frequency is scanned over the indicated energy range.

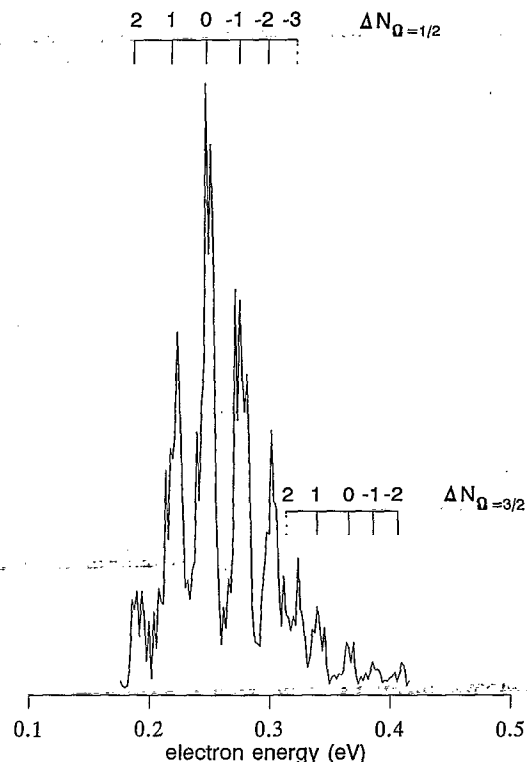


FIG. 6. The photoelectron spectrum resulting from two-color ( $2+1'$ ) REMPI via the  $S(8)$  rotational transition associated with the  $F^1\Delta_2(v'=0)$  state. The pump laser frequency is fixed at a two-photon energy of  $83\,222\text{ cm}^{-1}$ , while the ionizing laser frequency is fixed at  $22\,727\text{ cm}^{-1}$ .

#### IV. DISCUSSION

##### A. ZEKE-PFI in the magnetic bottle electron spectrometer

ZEKE experiments can be divided into two categories, based on different detection schemes. The acronym ZEKE derives its name from the original concept, in which electrons with zero kinetic energy are probed after a certain delay time with respect to the laser pulse. Due to this delay, the ZEKE electrons are temporally and spatially separated from promptly produced energetic electrons and the ZEKE electrons are subsequently extracted by means of a pulsed electric field. The ZEKE signal can be collected separately due to the difference in flight time of the ZEKE and energetic electrons. It is evident that the detection of these “true” ZEKE electrons will be greatly hampered by the presence of any stray electric fields that will accelerate the ZEKE electrons. In the alternative ZEKE scheme, Rydberg states with very high principal quantum numbers ( $n \sim 150$ – $200$ ) converging to a rovibronic state of the ion are populated. These very long-lived Rydberg states are field ionized after a time delay by application of an electric field pulse. As this technique relies on pulsed field ionization (PFI) of Rydberg states, it has been named ZEKE-PFI. It is this scheme that is most commonly used and is indeed employed in the present experiments. As in the true ZEKE experiments, in most ZEKE-PFI setups stray fields are carefully minimized to avoid any field-induced effects.

Before the present results can be discussed, there is, therefore, a major point of concern that should be dealt with. This is the possible effect on the ZEKE-PFI results of the stray electric fields and the permanent magnetic field, inherent in the design of the magnetic bottle electron spectrometer. In particular, the 1 T magnetic field present in our spectrometer contrasts dramatically with the minimal stray magnetic fields in most ZEKE setups and its possible effects should be considered carefully. The electromagnet can be switched off, reducing the magnetic field considerably, but when no special precautions are taken to demagnetize the spectrometer, a small magnetic field will still remain. In the Rb atom, it has been demonstrated that in a 1 T magnetic field,  $l$  mixing due to the quadratic Zeeman effect is strong for Rydberg states with principal quantum numbers as low as  $n=43$ .<sup>19</sup> For the high Rydberg states ( $n\sim 150$ – $200$ ) probed in ZEKE-PFI, a magnetic field of  $\sim 0.01$  T will consequently induce considerable  $l$  mixing. In the presence of magnetic fields, another aspect has to be considered. A particle moving with velocity  $v$  in a magnetic field  $B$  experiences an electric field of  $E=v\times B$ .<sup>20</sup> The mean velocity of HCl at room temperature is  $\sim 400$  m/s, leading to a maximum electric field strength of 4 V/cm for molecules moving perpendicular to the 1 T magnetic field. When the electromagnet is switched off, the maximum experienced electric field strength will drop to a value negligible compared to the value of the applied d.c. voltage.

The second factor that may influence the ZEKE-PFI results is the presence of electric fields. Above we have seen that the presence of the 1 T magnetic field already induces an electric field in moving molecules. This electric field can be minimized by switching off the electromagnet. However, we are still left with the permanent fields due to applied voltages. In the present experiments, a d.c. voltage of 5 V/cm is applied to sweep out all electrons formed via direct ionization or rapid autoionization. This permanent electric field may have several additional effects.<sup>8,21,22</sup> First, it will shift the ionization threshold (in  $\text{cm}^{-1}$ ) by approximately  $6\sqrt{E}$  (V/cm), directly field ionizing the highest Rydberg states. Second, in the presence of an electric field,  $l$ ,  $J$ , and  $n$  are no longer good quantum numbers. For Rydberg states with a principal quantum number  $n=150$ , the extremes of its Stark manifold overlap the manifolds of the neighboring states ( $n=149$  and  $151$ ) for an electric field strength of 27 mV/cm. This is known as the Inglis–Teller limit.<sup>22</sup> Above this limit, the appropriate description of Rydberg series is by parabolic quantum numbers, which are linear combinations of  $l$  and  $n$  quantum numbers. This implies that in the present experiments, where a d.c. voltage of 5 V/cm is used, the quantum numbers  $l$  and  $n$  have no physical meaning for the high- $n$  Rydberg states probed in the ZEKE-PFI experiment. Also, it is important to note that  $l$  mixing cannot be ruled out even in the more carefully designed ZEKE-PFI spectrometers where stray fields of  $\sim 50$  mV/cm are present. Another factor that is of general importance in all ZEKE-PFI experiments is the presence of any charged particles in the ionization region. As the formation of prompt electrons and ions is a probable process, it should be realized that, in view of the spatially

large orbits of high- $n$  Rydberg electrons, it is difficult to eliminate their effects altogether. Some of the possible effects are  $l$  and  $m_l$  mixing.<sup>21</sup> The implications of this will be discussed later on. From the above discussion, it is clear that one may have reservations about the use of the magnetic bottle spectrometer for ZEKE-PFI experiments. To check the validity of our ZEKE-PFI results, spectra were recorded under a range of experimental conditions and were, where possible, compared to previously published results. The main difference between our apparatus and conventional setups is the 1 T magnetic field, so an obvious test is to measure spectra with and without a current running through the electromagnet. The resolution of ZEKE-PFI spectra recorded without the 1 T magnetic field is slightly better than that recorded with this field. More importantly, however, no effect was found on either the spin-orbit or the rotational branching ratios. Effects of the delay time have also been considered. Since the aperture to the flight tube in the magnetic bottle spectrometer has a diameter of only 2 mm, this delay could not be changed as much as in regular ZEKE-PFI experiments as for long delay times, the molecules would have drifted out of the ionization region. Within the possible range of delay times ( $\sim 0.1$ – $1$   $\mu\text{s}$ ), we have, however, not observed significant variations in the branching ratios though, as expected, the signal intensity decreased towards longer delay times. Also, variation of the d.c. voltage from 1–10 V/cm did not influence the branching ratios. We tried to decrease the d.c. field further, but for lower fields, problems were encountered in separating the ZEKE-PFI electrons from the prompt electrons. Finally, the influence of the strength of the extraction field has been considered. Variation of the extraction field  $E$  from 2–25 V/cm was observed to leave spin-orbit and rotational branching ratios virtually unchanged.

As explained above, in the presence of an electric field  $E$ , the ionization limit (in  $\text{cm}^{-1}$ ) is lowered by  $\sim 6\sqrt{E}$  (V/cm). Thus, a field of 25 V/cm should ionize Rydberg states which are  $< 30$   $\text{cm}^{-1}$  below the ionization energy (I.E.). It should be noted, however, that these Rydberg states are observed only if their lifetime exceeds the delay period. The linewidths observed with a 25 V/cm extraction field are  $\sim 10$   $\text{cm}^{-1}$ , indicating that Rydberg states that are  $> 10$   $\text{cm}^{-1}$  below the I.E. have decayed before the extraction pulse is applied. The standard resolution of  $\sim 6$   $\text{cm}^{-1}$  achieved in the present experiments is rather poor compared to the “few tenths of a wave number” reported in other ZEKE-PFI experiments. Still, this is an improvement by a factor of 20 when compared to the typical 10–15 meV (80–120  $\text{cm}^{-1}$ ) resolution achieved in the present REMPI-PES experiments, allowing ionic rotational resolution in HCl even for low rotational quantum numbers.

From the variation of all possible parameters in the present experiments, we have seen that the spin-orbit and rotational branching ratios are not influenced. Thus, we would be inclined to conclude that ZEKE-PFI experiments can be carried out reliably in the magnetic bottle spectrometer. However, the ultimate test is the comparison with

results obtained in setups especially designed for ZEKE-PFI studies.

The ZEKE-PFI spectrum associated with the  $F^1\Delta_2(v'=0)S(0)$  transition, shown in Fig. 3, can be compared to the spectrum recorded by Haber *et al.*<sup>15</sup> The spectrum shown in Fig. 3 is not corrected for the dye laser output, which drops off slightly toward the blue end of the spectrum. As the transitions to the two spin-orbit components of the ion recorded by Haber *et al.*<sup>15</sup> are shown in two separate figures, the spin-orbit branching ratio in that experiment is not reported. When the signal-to-noise ratios of the transition to the two spin-orbit states are compared, it seems that Haber *et al.* observed the transition to the  $^2\Pi_{3/2}$  state as being the strongest, in line with the present results.

The rotational branching ratios observed by Haber *et al.* can be compared directly to the present results. Both for transitions to the  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  spin-orbit states, the rotational branching ratios observed in these two experiments are very similar. Very weak transitions to higher rotational levels of the  $^2\Pi_{3/2}$  state were not observed previously. For this low rotational level, the results obtained in the magnetic bottle spectrometer are very satisfactory. As no ZEKE-PFI results have been reported for higher rotational levels of HCl, we turned to the much-studied NO radical. Recently, Reiser and Müller-Dethlefs<sup>23</sup> have reported  $(1+1')$  ZEKE-PFI via  $N'=0-8$  rotational levels of the  $A^2\Sigma^+$  intermediate state of NO. In all spectra, the transition in which the core rotation does not change ( $\Delta N=0$ ) is the dominant feature, with  $\Delta N=\pm 3$  being the largest observable change in rotation. To further test the validity of the magnetic bottle for performing ZEKE-PFI studies, these experiments were repeated in the magnetic bottle spectrometer. The rotational branching ratios were readily reproduced, the only difference being the difference in linewidth.

In conclusion, we have reproduced spectra on both low and high rotational lines under various experimental conditions in the magnetic bottle spectrometer, indicating that our experimental conditions do not have a significant effect on the branching ratios.

## B. REMPI-PES

The electron configuration of the  $F^1\Delta_2$  Rydberg state in HCl [ $\cdots(3p\sigma)^2(3p\pi)^3(4p\pi)^1$ ] consists of a  $^2\Pi_{1/2}$  ionic core and a Rydberg electron with dominant  $p$  character.<sup>18,24</sup> The one-color REMPI photoelectron spectrum for ionization via the  $S(8)$  transition to the  $F^1\Delta_2(v'=0)$  intermediate state is shown in Fig. 1. The observed photoelectron energies are in agreement with the accurate I.E. of  $102\,802.8 \pm 2$   $\text{cm}^{-1}$  determined by Tonkyn *et al.*<sup>14</sup> for the  $X^1\Sigma^+(J''=0) \rightarrow X^2\Pi_{3/2}(J^+=3/2)$  transition. The dominant transition to the  $v^+=0$  vibrational level of the  $^2\Pi_{1/2}$  spin-orbit state indicates strong core preservation, as expected for direct ionization of an unperturbed Rydberg state. At approximately the three-photon energy level, transitions to the Rydberg series converging to the  $A^2\Sigma^+$  ionic state are energetically possible. However, the present experimental results show that these states do not influence

the ionization behavior. The changes in rotational quantum number on photoionization depend critically on the character of the Rydberg electron and the nature of the molecular potential. In an atomic-like picture, ionization of a pure  $p$  Rydberg electron will give rise to  $s$  and  $d$  partial waves for the photoelectron. The parity selection rules that govern the changes of rotational angular momentum upon photoionization are of the form<sup>25</sup>

$$\Delta J + \Delta S + \Delta p + l = \text{even}, \quad (1)$$

where  $p=0$  for  $e$  states and 1 for  $f$  states, and  $l$  is the partial wave component of the photoelectron. Ionization of a  $p$  Rydberg electron should give rise to  $l=\text{even}$  partial waves and thus lead to population of  $(-)$  parity states. As each of the rotational levels of the  $F$  intermediate and  $X$  ionic states consists of a  $(+)$  and  $(-)$  parity component, both  $\Delta N=\text{even}$  and  $\text{odd}$  transitions can be expected. In molecular photoionization, the anisotropy of the potential may lead to  $l$  mixing in the continuum, which may give rise to other angular momenta of the photoelectron than can be expected on the basis of the character of the Rydberg electron alone. Careful quantum chemical calculations are necessary to unravel these details of the molecular photoionization process. Wang and McKoy<sup>10</sup> have carried out calculations for both ZEKE ionization via the  $S(0)$  transition and one-color ionization via the  $S(10)$  transition of the  $F^1\Delta_2(v'=0)$  state of HCl. The angular momentum composition of the Rydberg electron at the  $R_2$  of 2.484 a.u. has been found to be 95.25%  $p$  and 4.70%  $d$ .<sup>10</sup> As expected on the basis of the above parity selection rule, most population is found in the  $(-)$  parity components of the ionic state. However, 18% population is found in the  $(+)$  component, which is due to nonatomic behavior. In the paper by Wang and McKoy,<sup>10</sup> the rotational ion distributions resulting from REMPI via the  $S(10)$  transition are presented, but the spin-orbit branching ratios were not included in the calculation. Experimentally, the  $S(10)$  transition was extremely weak. A comparison will, therefore, be made between the observed  $S(8)$  and the calculated  $S(10)$  transition. This comparison is justifiable as two rotational quanta should not have a strong effect on the changes in rotational angular momentum. In the experimental spectrum, shown in Fig. 1, the transitions to the  $^2\Pi_{1/2}$  spin-orbit state dominate and the associated rotational structure is well resolved. In both the experimental and calculated rotational distributions in the  $^2\Pi_{1/2}$  state, the  $\Delta N=0$  transition dominates. The calculated strong  $\Delta N=\pm 1$  and weaker  $\Delta N=\pm 2$  transitions are also in agreement with the present results. However, in the calculated spectra, the  $\Delta N>0$  transitions are slightly more intense than their  $\Delta N<0$  counterparts, opposite to what is observed experimentally. The calculations predict that the most significant difference between the rotational distributions in the  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  ionic states is in the intensity of the  $\Delta N=0$  and  $\Delta N=-1$  transitions. In the case of the  $^2\Pi_{3/2}$  state, these intensities are calculated to be equal; in the  $^2\Pi_{1/2}$  state,  $\Delta N=0$  dominates. In the experimental spectrum, this rotational structure is partially overlapped with the much stronger features associated

with the  ${}^2\Pi_{1/2}$  ionic state, complicating a comparison between theory and experiment in this respect. The overall agreement between the calculated and experimentally observed rotational branching ratios is, however, good.

Ionization via the  $F^1\Delta_2$  intermediate state was also investigated with two-color ( $2+1'$ ) REMPI. The ionization wavelength in this two-color REMPI process is such that ionization can energetically take place to rotational levels of both the  ${}^2\Pi_{1/2}$  and the  ${}^2\Pi_{3/2}$  ionic states, while giving rise to low photoelectron energies ( $\sim 0.3$  eV). If there is a strong energy dependence of the photoionization matrix element, the photoelectron spectra for one-color and two-color REMPI should show appreciable differences. The PE spectra for one-color (Fig. 1) and two-color (Fig. 6) ionization via the  $S(8)$  transition of the  $F^1\Delta_2$  states are very similar, indicating that the branching ratios are hardly energy dependent in the photoelectron energy regions of interest.

One-color and two-color ionization via a second unperturbed Rydberg state, the  $f^3\Delta_2(v'=0)$  state, was also carried out. This state is of particular interest since it has the same electron configuration as the  $F^1\Delta_2$  state. While the  $F^1\Delta_2$  state has a  ${}^2\Pi_{1/2}$  ionic core, the  $f^3\Delta_2$  state, in contrast, has a  ${}^2\Pi_{3/2}$  ionic core.<sup>18,24</sup> The rotationally resolved PE spectrum for ionization via the  $P(8)$  transition associated with the  $f^3\Delta_2(v'=0)$  state is shown in Fig. 2. As in the PE spectrum associated with the  $F$  intermediate state, only the  $\Delta v=0$  transition is observed. Also, just as was observed for the  $F$  state, the transition in which the ionic core spin-orbit state remains unaltered dominates. These spin-orbit branching ratios agree very well with those previously observed for ionization via a low rotational level of the  $f^3\Delta_2$  state. No quantum chemical calculations for ionization via  $f^3\Delta_2$  are available at this point. Still, some general considerations can be made. From the parity selection rule mentioned above, transitions with both  $\Delta N = \text{even}$  and  $\text{odd}$  changes in rotational angular momentum can be expected. The observed ionic rotational distribution is similar to that obtained for the  $F$  state, exhibiting both  $\Delta N = \text{even}$  and  $\text{odd}$  transitions, as expected. The  $\Delta N=0$  transition is strongest, with  $\Delta N = \pm 1$  also being prominent. The largest observed changes in rotational angular momentum are very weak  $\Delta N = \pm 3$  transitions. This is in line with the results for the  $F$  state, which also has a Rydberg electron with dominant  $p$  character.<sup>18,24</sup>

In the two-color ( $2+1'$ ) REMPI experiments via the  $f^3\Delta_2$  intermediate state, the wavelength of the ionizing laser was chosen such that the continua above both spin-orbit states of the ion are accessed just above the ionization threshold. The photoelectron spectrum associated with this two-color experiment (not shown) is very similar to the one-color photoelectron spectrum. This indicates that the branching ratios do not strongly depend on the photoelectron energy in the energy range of interest, analogous to what was observed for the  $F^1\Delta_2$  state.

### C. ZEKE-PFI

As already mentioned above, the ZEKE-PFI spectrum for ionization via the  $F^1\Delta_2(v'=0)$   $S(0)$  rotational transi-

tion (see Fig. 3) is very similar to the spectrum presented by Haber *et al.*<sup>15</sup> For both the transition to the  ${}^2\Pi_{3/2}$  and  ${}^2\Pi_{1/2}$  states, the transition in which the rotational angular momentum is reduced by one quantum ( $\Delta N = -1$ ) is the most intense. This is significantly different from the rotationally resolved ( $2+1$ ) and ( $2+1'$ ) REMPI-PES spectra obtained for the  $S(8)$  transition. In these photoelectron spectra, the  $\Delta N=0$  transition dominates.

A detailed theoretical analysis of the ZEKE-PFI spectrum at the  $S(0)$  line of the transition to the  $F^1\Delta_2(v'=0)$  state has been given by Wang and McKoy.<sup>10</sup> In their calculations, rotational branching ratios have been calculated for a direct ionization process, assuming a photoelectron energy of 50 meV. As there is a continuity of oscillator strength across the ionization threshold, calculations for direct ionization are directly related to ZEKE-PFI, i.e., the same branching ratios should be observed when excitation takes place to high- $n$  Rydberg states just below the ionization threshold or directly to the continuum just above the threshold. The calculated rotational branching ratios are in good agreement with those observed experimentally.

Transitions with  $\Delta N > 2$  have not been reported by Haber *et al.*,<sup>15</sup> nor have they been presented in the theoretical paper.<sup>10</sup> As discussed above, the ionization of the Rydberg electron of the  $F^1\Delta_2$  state gives rise mainly to  $s$  and  $d$  photoelectron partial waves. Our observation of very weak  $\Delta N > 2$  transitions is in line with the calculated 15%  $f$  and 0.6% higher angular momenta of the photoelectron wave function.<sup>10</sup>

Apart from the difference in the rotational branching ratios for the two modes of ionization, a dramatic difference is also observed in the spin-orbit branching ratio. Figures 1 and 6 show that in the one- and two-color REMPI-PES spectra, ionization to the  ${}^2\Pi_{1/2}$  state dominates and that ions in the  ${}^2\Pi_{3/2}$  state are only produced in minor quantities. Figure 3 demonstrates that the reverse is true for ZEKE-PFI—here transitions to the  ${}^2\Pi_{3/2}$  state dominate the spectrum. While the difference in rotational branching ratios is in agreement with theoretical calculations, the difference in the spin-orbit branching ratio seems to be at odds with theoretical expectations, though no theoretical calculations of the spin-orbit branching ratio are available for comparison.

In Fig. 4, a series of ZEKE-PFI spectra for ionization via the  $F^1\Delta_2(v'=0)$   $P(3)$ – $P(8)$  rotational transitions is shown. The  $P(3)$  spectrum, shown in the top frame, is very similar to the spectrum obtained at  $S(0)$ , indicating that the alignment, i.e., the population of the  $M_j$  levels in the intermediate state, does not have a strong effect on the rotational and spin-orbit branching ratios. In all spectra presented in Fig. 4, the transitions to the  ${}^2\Pi_{3/2}$  state are much more intense than those to the  ${}^2\Pi_{1/2}$  state. Two important observations can be made from Fig. 4. First, it is seen that the dominant change in rotational angular momentum upon ionization differs for each transition. For ionization via the  $P(3)$  transition, the transition to the lowest rotational level of the  ${}^2\Pi_{3/2}$  state ( $J^+ = 3/2$ ) is strongest, corresponding to a decrease in rotational angular momentum of  $\Delta N = -1$ . For ionization via  $P(4)$  and



$P(5)$ , the transition to  $J^+ = 3/2$  is still the most intense feature. However, this transition now corresponds to  $\Delta N = -2$  and  $\Delta N = -3$ , respectively. When ionization is performed via higher rotational levels of the  $F^1\Delta_2(v'=0)$  state, the intensity distribution gradually shifts to higher rotational levels, but even for ionization via  $P(8)$ , the transition to  $J^+ = 3/2$ , corresponding to  $\Delta N = -6$ , is still appreciable. Second, in all spectra presented in Fig. 4, the  $\Delta N < 0$  transitions are significantly more intense than their  $\Delta N > 0$  counterparts. For the  $P(3)$  spectrum, which is similar to the  $S(0)$  spectrum, it can be concluded that the rotational branching ratios are in good agreement with theoretical predictions. For higher members of the  $P$  branch, such calculations have not been performed and a direct comparison can consequently not be made. On the basis of the theoretical calculations of "ZEKE-PFI" ionization and "REMPI-PES" ionization,<sup>10</sup> it is, however, to be expected that the major intensity will be observed in transitions corresponding to  $|\Delta N| \leq 2$ , with a progressively larger equality of the  $\Delta N < 0$  transitions and their  $\Delta N > 0$  counterparts.

Similar considerations can be made for the series of ZEKE-PFI spectra obtained for ionization via the  $P(3)$ – $P(8)$  rotational lines associated with the  $f^3\Delta_2(v'=0)$  intermediate state (Fig. 5). Here, transitions to the  $^2\Pi_{1/2}$  ionic state are extremely weak, indicating a strong core preservation, analogous to what has been observed using REMPI-PES detection. Figure 5 shows that also for the  $f^3\Delta_2$  state, the rotational branching ratios deviate considerably from what is expected on the basis of the character of the Rydberg electron. Moreover, transitions in which the rotational angular momentum decreases are strongly favored over transitions in which it increases by an equal amount.

Summarizing, two fundamental differences are present between the results obtained with REMPI-PES and ZEKE-PFI. First, in ZEKE-PFI spectra, transitions to the  $^2\Pi_{3/2}$  state are favored over transitions to the higher-lying  $^2\Pi_{1/2}$  state, irrespective of the ionic core of the intermediate Rydberg state. In REMPI-PES, on the other hand, a strong preference for core preservation is observed. Second, in ZEKE-PFI experiments via high rotational levels in the intermediate state, unexpectedly large decreases in rotational angular momentum are observed in the ionizing step, while in REMPI-PES, these changes are limited to  $|\Delta N| < 3$  with  $\Delta N > 0$  and  $\Delta N < 0$  comparable in intensity.

Two possible explanations for these observations come to mind. First, the branching ratios could have a strong energy dependence. Second, the branching ratios observed in ZEKE-PFI could be related to the detection scheme itself.

One of the possible explanations for the observed differences in core and rotational branching ratios between the two types of experiments might be found in a strong energy dependence of these branching ratios. Our two-color experiments rule out such an explanation. The one-color REMPI-PES spectra, in which ionization is performed at high photoelectron energies, and the two-color REMPI-PES spectra, in which electrons are created with low kinetic energies, are very similar and in good agree-

ment with theoretical calculations. It can, therefore, be concluded that the branching ratios observed in the ZEKE-PFI experiments differ from those in the REMPI-PES experiments by virtue of the detection scheme employed in ZEKE-PFI.

The difference in spin-orbit branching ratios can be well explained if it is assumed that spin-orbit autoionization is of dominant importance. Spin-orbit autoionization could affect the branching ratios in several ways. First, Rydberg states converging to the higher spin-orbit state  $^2\Pi_{1/2}$  can be subject to direct spin-orbit autoionization during the delay time in ZEKE-PFI experiments, while this decay route is not possible for Rydberg states converging to the  $^2\Pi_{3/2}$  state. In REMPI-PES experiments, we have observed that the  $^2\Pi_{1/2}:^2\Pi_{3/2}$  ratio for ionization via the  $F^1\Delta_2$  state is 10:1. As there is a continuity of oscillator strength across an ionization threshold, this ratio should also hold for the high- $n$  Rydberg states accessed in ZEKE-PFI experiments. In contrast, in the ZEKE-PFI spectra, a 1:8 ratio is observed, suggesting that most Rydberg states converging to  $^2\Pi_{1/2}$  have decayed. Varying the delay time from 0.1–1  $\mu\text{s}$  does not have a visible effect on the spin-orbit ratio and presumably only for still shorter delay times will the  $^2\Pi_{1/2}$  signals increase significantly. In agreement with such an explanation, it is observed that the spin-orbit branching ratios for ionization via the  $f^3\Delta_2$  state do not show significant deviations from those obtained with REMPI-PES. Since most oscillator strength is carried by the transition to the  $^2\Pi_{3/2}$  state, in ZEKE-PFI only a small fraction of the population will be transferred to Rydberg states converging to the  $^2\Pi_{1/2}$  state. Direct spin-orbit autoionization of these states will consequently not influence the spin-orbit branching ratios as dramatically as for ionization via the  $F^1\Delta_2$  state.

Alternatively, spin-orbit autoionization could be induced by the delayed electric field pulse. A recent threshold-field-ionization study of Haber *et al.*,<sup>15</sup> in which HCl was excited under true local zero field conditions, has shown the importance of field-induced autoionization. It was concluded that a small d.c. field was already sufficient to force prompt autoionization. Since in our experiments we are exciting HCl molecules under nonzero local field conditions, it is to be expected that spin-orbit autoionization will have occurred during the delay time and the pulsed electric field will not influence the spin-orbit branching ratios.

The second important difference between the ZEKE-PFI and REMPI-PES results has been observed to occur in the rotational distribution of the ions. Above we have reasoned that spin-orbit autoionization plays a dominant role in ZEKE-PFI experiments, and one could consequently wonder whether this is also of influence on the rotational branching ratios. As similar rotational anomalies are observed for ZEKE-PFI via the  $F$  and  $f$  intermediate states, the anomalous rotational behavior cannot be induced by spin-orbit autoionization.

Previously, strong asymmetries between  $\Delta N > 0$  and  $\Delta N < 0$  transitions have been observed in several ZEKE-PFI experiments.<sup>14,22,23</sup> Of particular relevance to the

present study is the one-photon ZEKE-PFI study of HCl from the ground state,<sup>14</sup> in which similar anomalies have been observed as in the present study, in which ionization takes place via the  $F^1\Delta_2$  and  $f^3\Delta_2$  Rydberg states. It has been proposed<sup>14</sup> that field-induced rotational autoionization lies at the basis of this behavior. Briefly, simultaneous with the excitation of high- $n$  Rydberg states converging on a certain rotational ionization limit, low- $n$  Rydberg states are excited which converge to higher lying ionization limits. Although these low- $n$  Rydberg states cannot be field ionized directly since they lie too far below their respective ionization thresholds, autoionization into the continuum of the high- $n$  Rydberg states becomes a possible decay channel upon application of the pulsed external field. Since the number of low- $n$  Rydberg states that can possibly be excited is higher for  $\Delta N < 0$  than for  $\Delta N > 0$  transitions, a dominant role of field-induced rotational autoionization will lead to a strong asymmetry between  $\Delta N < 0$  transitions and their  $\Delta N > 0$  counterparts.

Apart from the asymmetry in the intensities of  $\Delta N < 0$  and  $\Delta N > 0$  transitions, the important role of field-induced rotational autoionization also becomes apparent when the changes in  $N$  are considered in the ZEKE-PFI spectra of the higher members of the  $P$  series of Figs. 4 and 5. In the ZEKE-PFI spectrum via  $P(3)$  and  $S(0)$  of the  $F^1\Delta_2$  and  $f^3\Delta_2$  states, we have seen that weak  $|\Delta N| > 2$  transitions are present, which have been reasoned to be in line with the 15%  $f$  and 0.6% higher angular momenta present in the photoelectron wave function. Consideration of, e.g.,  $P(7)$  and  $P(8)$  shows, on the other hand, that transitions in which  $N$  is subject to large negative changes have similar intensities as the rotational lines which would be expected to arise from a  $d$ -photoelectron wave. We can consequently conclude that, under the present experimental circumstances, rotational autoionization predominantly determines the intensities in the ZEKE-PFI spectra.

Recent considerations on the physics involved in ZEKE-PFI have in common that Stark-induced  $l$  mixing is considered to be an important factor.<sup>21,22</sup> Above the Inglis-Teller limit,  $l$  is essentially randomized. In the present experiments, a pulsed electric field of 20 V/cm is employed, hence  $l$  mixing is strong for Rydberg states with  $n > 38$ , which lie  $< 75 \text{ cm}^{-1}$  from their respective ionization limits. Assuming that only Rydberg states above the Inglis-Teller limit (having  $n > 38$ ) can contribute to the forced rotational autoionization mechanism, only  $\Delta N = -1$  changes in core angular momentum can be expected, given the rotational constant of the ion  $B = 9.96 \text{ cm}^{-1}$ .<sup>26</sup> However, for the  $P(8)$  transition, quite intense signals corresponding to  $N^+ = 1$  ( $\Delta N = -6$ ) are observed. From the REMPI-PES results, we can infer that from the intermediate  $f$  and  $F$  states, only transitions with  $\Delta N \leq 3$  have appreciable intensity. In the case of the  $P(8)$  transition, the lowest accessible core rotational level is, therefore,  $N^+ = 4$ . So, in order to observe  $N^+ = 1$ , several quanta have to be exchanged and hence forced rotational autoionization seems effective for Rydberg states which lie even as much as  $200 \text{ cm}^{-1}$ , significantly under the Inglis-Teller limit, below their corresponding ionization limit.

Until now we have considered the observed rotational branching ratios assuming that only rotational autoionization is of importance. ZEKE-PFI measurements via the  $A^2\Sigma^+$  state of NO show that also other factors should be taken into account. On the basis of the mechanism invoked above, we would expect that the rotational branching in the NO spectra would demonstrate even larger asymmetries, since the influence of rotational autoionization is predicted to be dependent on the rotational constants of the ionic state and on the coupling strength between Rydberg states. This is in contrast to what has been observed before by Reiser and Müller-Dethlefs<sup>23</sup> as well as in the present study (*vide supra*). A plausible explanation for this apparent contradiction can be found in the lifetimes of the Rydberg states accessed in NO. From the  $A^2\Sigma^+$  intermediate state in NO, predominantly  $np$  Rydberg series are accessed. Different from the situation in HCl, the  $np$  Rydberg series in NO are strongly predissociated. When extrapolating the lifetimes measured for low- $n$  members of the NO  $np$  series to the high- $n$  states accessed in ZEKE-PFI using a  $n^3$  lifetime dependence, one arrives at lifetimes shorter than the delay time used in ZEKE-PFI. This would suggest that this entire series could not contribute to the ZEKE-PFI signal. However, Chupka<sup>21</sup> has shown that for high- $n$  Rydberg states, the lifetime is increased by an approximate factor  $n^2$  due to  $l$  and  $m_l$  mixing. Hence, in NO, only high- $n$  Rydberg states have lifetimes longer than the delay time. The low- $n$  Rydberg states that could contribute to forced rotational autoionization have predissociated prior to the extraction pulse. From the agreement between the present results (where large d.c. voltages are used) and those of Reiser and Müller-Dethlefs<sup>23</sup> (where 50 mV/cm voltages are used), it can be inferred that only Rydberg states with high principal quantum numbers survive the delay times, despite the fact that in the present experiments  $l$  mixing is effective over a larger range of principal quantum numbers than in the experiments performed by Reiser and Müller-Dethlefs.

## V. CONCLUSIONS

This study reports the first rotationally resolved photoelectron spectra for HCl. The rotational branching ratios for ionization via the  $F^1\Delta_2(v'=0)$  state show excellent agreement with theoretical calculations. Two-color ( $2+1'$ ) REMPI experiments indicate that the ionic branching ratios are hardly dependent on the photoelectron kinetic energy.

Despite the unfavorable circumstances compared to "normal" ZEKE-PFI spectrometers, it has been shown that ZEKE-PFI measurements can be performed reliably in the magnetic bottle spectrometer. The ionic state branching ratios observed in ZEKE-PFI show large differences from those observed with REMPI-PES. The ZEKE-PFI results can be understood qualitatively on the basis of both spin-orbit and rotational autoionization mechanisms. As the branching ratios depend critically on several factors, a more quantitative understanding is out of reach at present.

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