Proton formation dynamics in the REMPI[2+n] process via the F $^1\Delta_2$ and f $^3\Delta_2$ Rydberg states of HCl investigated by three-dimensional velocity mapping

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HCl in the bulk gas phase at a pressure of 10$^{-5}$ mbar has been excited via selected Q-lines of the two-photon transition band systems F $^1\Delta_2 ← X 1^\Sigma^+(1, 0)$ [Q(8)], V $^1\Sigma^+ ← X 1^\Sigma^+(14, 0)$ [Q(8), Q(7)] and f $^3\Delta_2 ← X 1^\Sigma^+(0, 0)$ [Q(2–6)]. Concerning the V ← X excitation, subsequent photon absorption is known to yield HCl$^+$, H(n=2)+Cl, H$^+$+Cl$^-$ and H$+$+Cl(4s, 4p, 3d). Vibrationally excited HCl$^+$ (v$^+$≥5) can be photodissociated to H$^+$+Cl, and excited atoms can be easily photoionized by absorption of a fourth photon, respectively. Using three-dimensional velocity map imaging, the spatial proton velocity distributions resulting from these processes for these particular transitions were studied for the first time. Kvaran et al. [J. Chem. Phys. 131, 044324 (2009)].

I. INTRODUCTION

The excited states and the dynamics involved in the photodissociation and photoionization of the HCl molecule and the corresponding ion HCl$^+$ have been the subject of a large number of spectroscopic and theoretical investigations.$^{1-20}$ Studies investigating the resonance enhanced multiphoton ionization (REMPI)$^{10-20}$ have revealed fascinating dynamics involving highly excited Rydberg states. Particularly, the photodissociation and autoionization as well as the subsequent photodissociation of the highly vibrationally excited molecular ion HCl$^+$ following the two-photon excitation to the B $^1\Sigma^+$ state have been of special interest. Usually, 2+n REMPI (n=1,2) of the HCl molecule via pure low lying Rydberg states is known to lead to direct ionization only, leaving the HCl$^+$ ion in the lowest vibrational states. This cannot be photodissociated in a one-photon step at the wavelengths involved. In contrast, the B $^1\Sigma^+$ double minimum state resulting from an avoided crossing of the E $^1\Sigma^+$ Rydberg and the V $^1\Sigma^+$ state is known to undergo photodissociation in competition to the direct ionization. The V $^1\Sigma^+$ state is itself the result of an avoided crossing of a valence state and the ion-pair state asymptotically correlated with H$^+$ and Cl$^-$ (Fig. 1). A number of channels for the photodissociation has recently been identified by photoion and photoelectron imaging methods, both for the Cl$^+$ and the H$^+$ products [Eq. (1)].$^{13,14,19,20}$

$$
\begin{align*}
\text{HCl} ← & \text{HCl(B $^1\Sigma^+$)} → \quad \text{HCl}^+ (v^+ ≤ 12) + e^- \\
& \text{H$^+$ + Cl$^-$} \\
& \text{H$^+$ + Cl$^+$ + e}^- \\
& \text{H} + \text{Cl$^+$ + e}^- . \\
\end{align*}
$$

It has been shown that the speed distribution of the H$^+$ ions always shows three global features only shifting in energy and changing in their relative intensities when the wave-
potential curves of the states involved and they constitute the formation from the ionic
f 3
and three-photon energies for the two bands investigated
Morse potentials constructed from spectroscopic data in Refs. 10–12. The key role in the production of the H+ distribution showing the different channels that are thus far believed to play the
vibrational states v+=5,8. The hatched areas show the two-ground state of the ion
et al.
Photoelectron images measured by Romanescu et al. and in our group led to the conclusion that dissociation of HCl+ upon absorption of a fourth photon can only occur in the vibrational states v+≥5 through the repulsive state (2)Π of HCl+ (see Fig. 13 of Ref. 19 showing a plot of the dressed ionic ground state and its vibrational levels). The summary of this channel is given in Eq. (2).

The H(n=2) in coincidence with Cl(2P3/2) atoms [see Eq. (3)] are formed primarily by excitation of an Ω=0 Rydberg state belonging to the series with a repulsive 2Π ion core (Σ+(0), Π(0)). Ω=0 is indicated by the positive β-parameter. As usual, the β-parameter characterizes the angular distribution for a dipole transition by P(θ)=1/2(1 + βP3(cos θ))·sin θ, θ being the polar angle between the laser polarization and the recoil velocity vector.

The ion-pair channel [Eq. (4)] was first found by Yench et al.23 in one-photon processes using synchrotron radiation in the energy range 14.4–16.4 eV. Hepburn and co-workers3,24 found similar results using threshold ion-pair production spectroscopy near 14.4 eV photon energy. The analysis of the results showed that the ion-pair is formed by the predissociation of Rydberg states with an A 2Σ+ core and nσ electrons (n=4–6) by the diabatic curve of the V 1Σ+ ion-pair state. In the energy range of the REMPI process under scrutiny in this study, the formation of the ion-pair came unexpectedly when Romanescu et al. first observed it.14 It is very intriguing that in this case the ion-pair yield is highest, when the intermediate state is the ion-pair state V(1Σ+) itself. The previous results show unambiguously, and the present add strong evidence to it, that the ion-pair formation in this REMPI process is an exclusive feature of the outer well of the B 1Σ+ state at the energies involved. As pointed out by Romanescu et al., the Franck–Condon region for the excitation to the bound [A 2Σ+⋯5σ5σ4dσ]1Σ(0) states (Ω=0 again is indicated by the positive β-parameter) lies in the outer well near 2.2 Å internuclear distance and the nuclear wave functions of these states at the respective energy have a considerable overlap integral with free wave functions starting at the inner wall of the diabatic potential of the V 1Σ+ state (see Fig. 4 of Ref. 14).

In contrast with the wealth of processes described above (except one, channels leading to excited chlorine have been neglected here) for REMPI processes via pure Rydberg states in the vicinity of the B 1Σ+ state, direct ionization in a REMPI[2+1] process is by far the dominant channel. On the

length is changed.13,14,19,20 These three features are all attributed to the accessibility of the outer well of the V 1Σ+ state and they constitute the formation of (1) excited H atoms (n =2) with the partner fragment mostly in the spin orbit excited state 3P1/2, (2) dissociation into the ion-pair, and (3) photodissociation of autoionized HCl+ in the X 1Π2 state vibrationally excited to v+≥5–8,12–14. Eqs. (2)–(4) sum up the different channels that are thus far believed to play the key role in the production of the H+ distribution showing these three features. The arguments that lead to this conclusion will be discussed in detail below (see Fig. 1 for the potential curves of the states involved).

\[
\begin{align*}
HCl(1^1Σ^+) \rightarrow & HCl([1^1Π\cdots4^3s]^1Π_0) \\
& \text{hv}
\end{align*}
\]

\[
\begin{align*}
HCl^+(X^2Π, v^+≥5) & + e^- \rightarrow H^+ + Cl + e^- \\
& \text{hv}
\end{align*}
\]

\[
\begin{align*}
& H(n=2) + Cl(2P_{3/2}) \rightarrow H^+ + Cl + e^- \\
& \text{hv}
\end{align*}
\]

\[
\begin{align*}
& H + Cl(4s) \rightarrow H^+ + Cl + e^- \\
& \text{hv}
\end{align*}
\]

\[
\begin{align*}
& HCl^+(X^2Π, v^+<5) + e^- \\
& \text{hv}
\end{align*}
\]

(2)

\[
\begin{align*}
HCl(1^1Σ^+) \rightarrow & HCl([2^1Π\cdots4^3s]^3Π_0, 3Π_0) \\
& \text{hv}
\end{align*}
\]

\[
\begin{align*}
& H(n=2) + Cl(2P_{1/2}) \rightarrow H^+ + Cl + e^-, \\
& \text{hv}
\end{align*}
\]

\[
\begin{align*}
& HCl(1^1Σ^+) \rightarrow HCl[A 2Σ^+\cdots5σ5σ4dσ]^1Σ(0) \\
& \text{hv}
\end{align*}
\]

\[
\begin{align*}
& \rightarrow HCl(V^1Σ^+) \rightarrow H^+ + Cl^-. \\
& \text{hv}
\end{align*}
\]

(3)

(4)

Photoelectron images measured by Romanescu et al. showed an oscillating behavior of the photoelectron intensities in the vibrational progression for v+>3 in the autoionization process of HCl.13 They concluded that the gateway state for the autoionization to HCl+ (X 2Π(v+>3)) is most likely the purely repulsive 1Π(0) state having a 2Π ion core and a 4s 4σ Rydberg electron (see Fig. 1 for the states involved in the following discussion). The lower vibrational states of HCl+(X 2Π, v+<3) are likely to be populated by direct ionization. This gateway state converges to ground state H atoms and excited Chlorine Cl(4s) and crosses the [A 2Σ+⋯4σ4σ]1Σ+ curve that converges to H(n=2) and Cl(2P3/2). It has been estimated that ca. 5%–10% of the molecules excited to the gateway state proceed to form H(n =2) + Cl(2P3/2).14 Photoion images recorded by Romanescu et al. and in our group led to the conclusion that dissociation of HCl+ upon absorption of a fourth photon can only occur in the vibrational states v+≥5 through the repulsive state (2)Π of HCl+ (see Fig. 13 of Ref. 19 showing a plot of the dressed ionic ground state and its vibrational levels). The summary of this channel is given in Eq. (2).
other hand, recent observations by Kvaran et al. in mass resolved REMPI[2+n] (n=1,2) spectra of jet cooled HCl showed a sharp increase in the Cl− and H+ ion signals for single Q-branch lines in the transition bands F 1 Δ2 ⟷ X 1 Σ+(1,0) [Q(8)] and f 3 Δ2 ⟷ X 1 Σ+(0,0) [Q(5)]. These were ascribed to near resonance interactions with single rotational levels in the V 1 Σ+ state, i.e., v′ = 14, J′ = 8, and v′ = 8, J′ = 5, respectively. Indeed, the energy difference between the levels is 17.7 cm⁻¹ for the triplet state and 11.3 cm⁻¹ for the singlet state. This notion is summarized in Eq. (5).

$$\nu \varepsilon$$

$$\text{HCl}(B 1 \Sigma^+, v', J') \rightarrow \text{H}^+ + \text{Cl}^+ + \text{Cl}^- + \text{HCl}^+ (v^+ \leq 12)$$

(5)

$$\nu \varepsilon$$

$$\text{HCl}(f F 3 / 1 \Delta_2, v', J') \rightarrow \text{HCl}^+(v^+ < 5).$$

Here, the upper equation is a shortened version of Eq. (1). In order to shed more light on this matter, we studied the spatial proton velocity distribution of the respective transitions, since the characteristic features for the photodissociation of the V 1 Σ+ being responsible for the outer well of the B 1 Σ+ state mentioned above (Eqs. (2)–(4)) should be clearly visible in the product kinetic energy distribution. Furthermore, the proton angular distribution should be describable as the product of a distribution with a negative β-parameter and one with the β-parameter of the subsequent photodissociation, since the alignment of the molecules in the f/F Rydberg states should be according to two subsequent perpendicular (ΔΩ = 1) transitions. For the transition f 3 Δ2 ⟷ X 1 Σ+(0,0) we find a drastic change in the shape of the speed distribution for the Q(5) line compared to the neighboring transitions. The Q(1–4) and Q(6) lines are characterized by an H+ speed distribution showing the features of H(n=2)+Cl(2P 3 / 2) production and HCl+(5 ≤ v+ ≤ 8) photodissociation. In contrast, the Q(5) line shows H(n=2) + Cl(2P 1 / 2) and ion-pair production, but the HCl+ photodissociation channel has not increased in intensity. A closer look at the circumstances will reveal that the fragmentation dynamics of the absorption processes after the two-photon step can be explained by Franck–Condon factors consistent with the nuclear wave function in the B state at the energy of the f 3 Δ2 (v′ = 0) state having only a small fraction in the inner well of the double minimum state. Concerning the transition F 1 Δ2 ⟷ X 1 Σ+(1,0) we found no H+ ions for transitions other than the Q(8) line. The speed distribution emerging from this process is the same as the respective Q(8) and Q(7) lines of the transition V 1 Σ+ ⟷ X 1 Σ+(14, 0).

II. EXPERIMENTAL

The experimental setup has been described in two recent publications. Thus, here we will give only a short summary and the facts relevant to the current experiment. A homebuilt TOF spectrometer mounted to a commercial three-dimensional (3D) imaging detector consisting of a two stage micro channel plate and a delay line anode (RoentDek) in a stainless steel vacuum vessel is the heart of the 3D velocity mapping apparatus. The TOF spectrometer consists of a pulsed nozzle (General Valve, Series 9 pulsed valve) mounted to a plate, five ring electrodes comprising the acceleration region of approximately 5 cm (depending on the laser path), a tube of 10 cm length serving as a field free drift region and two meshes separating the acceleration from the drift region and the drift region from the detector. The potentials of the Einzel-lens electrode and the acceleration region were supplied by two voltage supplies (Stanford Research System, Model PS350) and measured to five digits precision by a Keithley 2000 voltmeter. The vacuum chamber is pumped by two turbo molecular pumps (Pfeiffer TMU 260 P, 220 l/s) forepumped by a rotary vane pump filled with PFPE oil. Without any gas flow, the background pressure is approximately 10⁻⁷ mbar. When the nozzle is operating, the integral pressure is of the order of 10⁻⁵ mbar.

Pure HCl with a stagnation pressure of approximately 400 mbar was expanded through the pulsed nozzle (400 μm orifice) and a dye laser [Nd:YAG (Yttrium Aluminum Garnet) pumped Scannate 2, Coherent] operating around 487.6 nm or 468.3 nm and frequency doubled by a BBO crystal was focused by an f=0.3 m lens ca. 5 mm downstream of the nozzle orifice. For the measurements reported here, the delay of the nozzle trigger was chosen such that the laser pulse came a few hundred microseconds before the gas pulse, in order to have only gas from the room temperature background making the nozzle a mere gas inlet. Cooling of the gas in a supersonic expansion must be avoided in order to maintain a significant population of HCl in rotational states up to J = 8. The repetition rate of the experiment was between 5 and 20 Hz, depending on the ion signal.

The pulses coming from the ends of the DL were differentially amplified (KSU EDL DLAS800), recorded by a four channel oscilloscope (WaveRunner 6050, Quad 5 Gs/s). The individual pulses were fitted by Gaussians in order to obtain the center of the peaks yielding the times with nearly 100 ps precision. These were used to obtain the time and position of the individual ion impacts from which the velocity vectors were computed using a forward simulation by the program SimIon® based on the dimensions of the spectrometer and the measured voltages.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the potential energy curves that are relevant to the following discussion of the experimental data. Also, keep in mind Eqs. (2)–(4) which sum up the mechanisms for the dynamics in the H+ channel. The two- and three-photon energies for the two processes studied are indicated in Fig. 1 by the hatched areas, the lower energy corresponding to the wavelength for the REMPI process through f 3 Δ2 ⟷ X 1 Σ+. The B 1 Σ+ potential has been adapted from Ref. 30 and the wave function has been calculated by the Numerov method for the eigenvalue closest to the two-photon energy. Our eigenvalue is 10.332 eV compared to 10.356 eV for the two-photon energy. The fact that the wave function has only six nodes indicates already that the outer well of the potential is not sufficient for spectroscopic purposes. Comparison with the data of Green et al. confirms this notion and work is being done to calculate an improved version of this potential.
TABLE I. Constants used in this study.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron affinity Cl⁺</td>
<td>3.613 04</td>
</tr>
<tr>
<td>E(Cl⁺(3P_{1/2}))</td>
<td>0.109 397 6</td>
</tr>
<tr>
<td>D(HCl)</td>
<td>4.4321</td>
</tr>
<tr>
<td>D(HCl⁺)</td>
<td>4.6540</td>
</tr>
<tr>
<td>E(H(n=2))</td>
<td>10.199</td>
</tr>
<tr>
<td>(\omega_c/\omega_{x,X} 2\Pi(HCl⁺))</td>
<td>2673.69/52.537 cm⁻¹</td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 32.  \(^{b}\)Reference 33.  \(^{c}\)Reference 34.  \(^{d}\)Reference 35.  \(^{e}\)Reference 36.

A. Proton formation in the \(\text{f}^3\Delta_2\rightarrow X^1\Sigma^+(0,0)\) band system

In Fig. 2 we show a meridian plot\(^{37}\) of the spatial velocity distribution of H⁺ ions emerging from the two-photon absorption \(\text{f}^3\Delta_2\rightarrow X^1\Sigma^+(0,0)\) via the Q(2) and Q(5) transitions and subsequent absorption of one or two more photons. For the Q(2) line one can clearly see two processes, the “faster” of which has a large and positive \(\beta\)-parameter. The anisotropy of the slower ions is not discernible in this figure because the points are too dense (see also Table II). In the plot of the Q(5) line the faster ions are absent but instead ions belonging to a third process are visible much closer to the “slow” ions which appear like a corona to these.

Figure 3 shows the H⁺ speed distributions for all Q-branch transitions recorded (J = 2–6). Phenomenologically, the comparison of the details for each rotational line shows three features.

(i) The “fast” channel peaking at 17 000 m/s corresponds to the photodissociation of HCl⁺ in \(v' = 5–8\) and decreases strongly in relative intensity for J = 5.

(ii) The “slow” channel at 10 000 m/s shows a gradual shift to a lower kinetic energy when J = 5 is approached, i.e., for J = 6 and J = 4 the peak positions lie in between the positions for J = 2, 3, and J = 5. The difference in kinetic energy release corresponds to the generation of electronically excited H atoms (H(n = 2)) together with ground state \(2P_{3/2}\) or spin orbit excited \(2P_{1/2}\) chlorine, respectively.

(iii) The slow peak shows a shoulder for J = 5 (the “corona”) at ca. 12 000 m/s. Its kinetic energy release corresponds to the ion-pair dissociation.

Generally, the anisotropy of these multiphoton processes can be described by \(\mathcal{P}(\theta) = 1/4\pi(1 + \sum_{j=1}^{3} \beta_{j}(\cos \theta) \cdot \sin \theta)\) for N photons. Instead of using this expression directly for the data analysis, we chose to fit the angular distribution \(d\mathcal{P}(\theta)/d\cos \theta\) by a model function that is a product of three independent dipole distributions having individual \(\beta_2\) parameters.

\[
\frac{d\mathcal{P}(\theta)}{d\cos \theta} = \text{const.} \cdot \prod_{i=1}^{3} (1 + \beta_{2i} \cdot P_2(\cos \theta)).
\]

Physically, this means that each photon contributes its own \(\beta_2\)-parameter which is of course in general a simplification.
for the two-photon step, but first, it will help to unravel some of the details of the dynamics and second, in the special case here, this description is justified by the following argument: for a two-photon transition from $\Omega=0$ to $\Omega=2$ or vice versa the only allowed spherical transition tensor components are $T_{2,2}$. Thus, the alignment of the final state for linearly polarized light is such that, assuming this state would dissociate rapidly, the photofragment distribution anisotropy would be characterized by $\beta_2=-10/7$ and $\beta_3=3/7$, which is equivalent to two individual $\beta_{2,3}=-1$ ($i=1,2$). This can be verified using Eqs. (7)–(9) setting $\beta_{2,3}=0$. Therefore, assuming that the subsequent photodissociation of the aligned state is independent of the two-photon step, the resulting photofragment angular distribution is a product of the dipole distribution for the one-photon photodissociation characterized by one $\beta_2$ and two more dipole distributions characterized by negative $\beta_2$ parameters (−1 in the limit of instantaneous dissociation). The reason that we use Eq. (6) for the fit and not the usual representation as a sum of Legendre polynomials and then calculate the individual $\beta_{2,3}$ from this is that in that latter case one has to solve the nonlinear system of equations given by Eqs. (7)–(9) for the $\beta_{2,3}$-parameters. This always yields multiple solutions of which normally all except one are complex or not in the allowed interval $-1 \leq \beta_{2,3} \leq 2$, but in some cases the result is not unique.

$\beta_2 = \frac{7}{35} \cdot \frac{7 \cdot (\beta_{2,1} + \beta_{2,2} + \beta_{2,3}) + 2 \cdot (\beta_{2,1} \beta_{2,2} + \beta_{2,1} \beta_{2,3} + \beta_{2,2} \beta_{2,3}) + 3 \cdot \beta_{2,1} \beta_{2,2} \beta_{2,3}}{5 \cdot (\beta_{2,1} \beta_{2,2} + \beta_{2,1} \beta_{2,3} + \beta_{2,2} \beta_{2,3}) + 2 \cdot \beta_{2,1} \beta_{2,2} \beta_{2,3}}$ \hspace{1cm} (7)

$\beta_4 = \frac{9}{11} \cdot \frac{22 \cdot (\beta_{2,1} \beta_{2,2} + \beta_{2,1} \beta_{2,3} + \beta_{2,2} \beta_{2,3}) + 12 \cdot \beta_{2,1} \beta_{2,2} \beta_{2,3}}{35 + 7 \cdot (\beta_{2,1} \beta_{2,2} + \beta_{2,1} \beta_{2,3} + \beta_{2,2} \beta_{2,3}) + 2 \cdot \beta_{2,1} \beta_{2,2} \beta_{2,3}}$ \hspace{1cm} (8)

$\beta_6 = \frac{90}{11} \cdot \frac{\beta_{2,1} \beta_{2,2} \beta_{2,3}}{35 + 7 \cdot \beta_{2,1} \beta_{2,2} + 7 \cdot \beta_{2,1} \beta_{2,3} + 7 \cdot \beta_{2,2} \beta_{2,3} + 2 \cdot \beta_{2,1} \beta_{2,2} \beta_{2,3}}$. \hspace{1cm} (9)

Figure 4 shows the angular anisotropy of the protons emerging from the excited H atom [case ii and the HCl$^+$ photolysis channel (case i)] for the Q(3) line. A summary of the anisotropy parameters for both representations is given in Table II. From this one can learn that for the unperturbed transitions Q(2) and Q(3) there is always a perpendicular contribution ($\beta<0$) to the H(n=2) channel that results from the alignment of the intermediate state, since, as explained above, the two-photon transition from an $\Omega^*=0$ to an $\Omega^*=2$ state can be regarded as two subsequent perpendicular transitions for which $\Delta \Omega=1$.\textsuperscript{38}

This effect decreases when J=5 is approached and for J=5 itself the angular distribution becomes isotropic. Concerning the peak for the HCl$^+$ photolysis (case i) which is very small (<5%) for the Q(5) line, the anisotropy is not altered at all for any of the rotational lines. This, together with the fact that it does not increase in intensity, means that this process is solely characteristic for the pure Rydberg state at this energy. Here, the perpendicular contribution is much smaller than for the H(n=2) channel (case ii) which suggests that the autoionization process as well as the HCl$^+$ photodissociation are dominated by parallel transitions. The fact that the density at the poles is not very much smaller than would be expected for a process with only positive $\beta$-parameters (see Fig. 4, lower panel) indicates that the duration of the process after the formation of the molecular ion is on the order of the rotational period. The H(n=2) peak is a sum of equal contributions of Cl$^2$(P$^2_{1/2}$) and Cl$^2$(P$^2_{3/2}$) for the Q(4,6) lines, while only Cl$^2$(P$^2_{1/2}$) contributes (within the given resolution) to the Q(5) line. The relative integral for the HCl$^+$ photolysis peak is lower for Q(4,6) than for Q(2,3) and reduces to approximately 1/5 for the Q(5) line (see Fig. 3), and the ratio of Cl$^+$ to HCl$^+$ ions gradually increases when the Q(5) line is approached as reported in Ref. 16. The fact that the angular distribution for the H(n=2) channel does not show the mark of the initial double perpendicular two-photon transition we think is due to interchange of angular momentum between electrons and nuclei by going from

<table>
<thead>
<tr>
<th>$\ell^3 \Delta_2 \rightarrow X^1 \Sigma^+(0,0)$</th>
<th>Q(2)</th>
<th>Q(3)</th>
<th>Q(4)</th>
<th>Q(5)</th>
<th>Q(6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(n=2)+Cl$^+$ $\beta_{2,1}/\beta_{2,2}/\beta_{2,3}$</td>
<td>$-0.71/0.84/-0.71$</td>
<td>$1.21/-0.8/-0.8$</td>
<td>$-0.4/-0.4/0.72$</td>
<td>$0.05/0.05/0.05$</td>
<td>$-0.15/-0.15/-0.2$</td>
</tr>
<tr>
<td>$\beta_{2,1}/\beta_{2,2}/\beta_{2,3}$</td>
<td>$-0.67/-0.26/0.11$</td>
<td>$-0.5/-0.58/0.2$</td>
<td>$-0.15/-0.20/0.03$</td>
<td>$0.14/0.00$</td>
<td>$-0.42/0.03/0.00$</td>
</tr>
<tr>
<td>$\beta_{2,1}/\beta_{2,2}/\beta_{2,3}$</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
<td>$-0.3/-0.3/0.05$</td>
<td>$\ldots$</td>
</tr>
<tr>
<td>$\beta_{2,1}/\beta_{2,2}/\beta_{2,3}$</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
<td>$-0.59/0.04/0.00$</td>
<td>$\ldots$</td>
</tr>
<tr>
<td>HCl$^+$</td>
<td>$1.28/0.64/-0.35$</td>
<td>$0.84/0.8/-0.5$</td>
<td>$1.28/0.3/-0.5$</td>
<td>$0.29/0.12/-0.3$</td>
<td>$1.24/-0.14/-0.14$</td>
</tr>
<tr>
<td>Photolysis</td>
<td>$1.47/-0.0/-0.07$</td>
<td>$1/-0.21/0.09$</td>
<td>$0.97/-0.3/-0.05$</td>
<td>$1.02/-0.19/-0.00$</td>
<td>$0.94/-0.17/0.01$</td>
</tr>
</tbody>
</table>
$\Omega=2$, $N=6$ to $\Omega=0$, $N=J=8$ in the nonadiabatic transition (at least two negative $\beta$-parameters should remain like for the other rotational lines as explained above). Similar effects have been described by Kable et al. for HCO when the combination of angular momenta is changed in a nonadiabatic transition prior to dissociation.\textsuperscript{39} Moreover, the H($n=2$) distribution becomes completely isotropic and the anisotropy for the ion-pair peak can be described by a single negative $\beta_2$-parameter. We see the same effect for the H($n=2$) channel in the singlet transition F$^1\Delta_2$($v'=1$, $J'=8$)$\rightarrow$X$^1\Sigma^+(v'=0$, $J'=8$), but not for the HCl$^+$ photodissociation which we interpret in terms of the time the nuclei have to react to the changing of the electronic configuration (\textit{vide infra}).

Kvaran et al. observed no spectral shifts of peak positions that could be a consequence of near resonance interactions between the $f^1\Delta_2$ and the $V^1\Sigma^+(v'=8)$ levels and they estimated the fraction $|c|^2$ of the Rydberg part of the wave function to be 0.987 for $J'=5$ from their ion intensity data.

This shows the weakness of the interaction ($\Delta E_{f,v}=-57.5$, 17.7 and 105.4 cm$^{-1}$ for $J'=4$, 5, and 6).\textsuperscript{16} However, the strong increase in the H$^+$ ion signal relative to the HCl$^+$ signal is due to the much higher dissociation probability of the V state and not to a strong coupling of the two states. This means that the HCl$^+$ photodissociation via the Rydberg state remains more or less unaltered for $J=5$ and is only seemingly diminished in Fig. 3. Also, the near resonance does not show an imprint on the Q($5$) line of the $V^1\Sigma^+(v'=8,0)$ band in the form of an enhancement of the HCl$^+$ ion signal, the main channel for all pure Rydberg states.\textsuperscript{16}

It is worthwhile to stress that while no effect is noticeable in the peak intensities of the $V^1\Sigma^+(v'=8)\rightarrow X^1\Sigma^+(v'=0)$ absorption spectrum, the dynamical picture is completely altered for the photorupture. Here, the small near resonance interaction has the drastic effect described above. This shows what sensitive tool dynamical studies are to study such small near resonance effects.

The wave function shown in Figs. 1 and 5 for the eigenvalue closest to the two-photon energy on the \textit{ab initio} potential of Bruna et al.\textsuperscript{30} explains the phenomena described above very well, since a small fraction of the nuclear wave function in the inner well of the B $^1\Sigma^+$ state will suppress further photon absorption from this region. Consequently, subsequent photon absorption must essentially occur from large internuclear distances on the right hand side of the barrier. However, the Franck–Condon factor for the transition from the right hand side of the barrier to the $[^2\Pi \cdots 4s]^3\Pi_0$ state which has been identified\textsuperscript{13,14} previously as the state that autoionizes to the higher vibrational states of HCl$^+$ is very low or vanishes completely. This explains why no extra HCl$^+$ photodissociation occurs due to the near resonance. As this $^3\Pi_0$ state is also believed to produce H($n=2$) with Cl($^2P_{3/2}$) as the partner fragment via a nonadiabatic transition to one of the bound $[^2\Pi \cdots 4s]^3\Sigma$ states, this explains why no extra H($n=2$) are generated together with ground state chlorine. In contrast, excitation of a repulsive Rydberg state having a $^2\Pi$ ion core and a 4s Rydberg electron is possible Franck–Condon-wise and explains why only Cl($^2P_{1/2}$) is formed as the hydrogen’s partner.
The formation of the ion-pair has been explained by Romanescu et al. by excitation to a bound \( \Sigma^+(0') \) Rydberg state having an \( \Sigma^+ \) ion core and a Rydberg electron and subsequent predissociation to the diabatic curve of the \( \Sigma^+ \) state at small internuclear distances (see Fig. 4 in Ref. 14). They verified this by calculating the overlap integrals using Numerov integration of the Schrödinger equation over the same \( \text{ab initio} \) \( \Sigma^+ \) potential of Bruna et al. shown in Figs. 1 and 5. Since this feature can be seen for all vibrational states, we believe that the outer well being not deep enough resulting in two vibrational quanta missing has no significant effect on this result. Here, \( \Delta \Omega=0 \) followed from the observation that for the \( \Sigma^+ \rightarrow \Sigma^+ \) (\( v' \approx 11.0 \)) Q(0) lines the \( \beta \)-parameter is 2, since in this case no alignment can occur. \( \beta \)

Since we see the dynamics connected with the outer well exclusively at the energy for the transition to the \( f^3 \Delta_2 \) state, the ion-pair channel can indeed be only accessed from large internuclear distances. We think that the observed anisotropy, which is different from that observed for higher vibrational states by Romanescu et al. and in our laboratory, is due to a perpendicular transition from the \( \Omega=1 \) state, because (i) there is no positive \( \beta \) component and (ii) it is likely that the alignment of the double perpendicular two-photon transition is lost in the nonadiabatic transition from the \( f^3 \Delta_2 \) state to the \( \Sigma^+ \) state. For the latter point see the discussion for the \( F^1 \Delta_2 \) band system below (III B). The fact that we found \( \Sigma^+/\Sigma^+ \) production for the adjacent “off-resonance” Q-lines at all needs further clarification as well. Kvaran et al. also found \( \Sigma^+ \) and \( \Sigma^+ \) and attributed this to predissociation of the triplet Rydberg states to ground state atoms, to dissociation of a superfine Rydberg state yielding excited chlorine and to photodissociation of \( \Sigma^+ \) yielding \( \Sigma^+ \) (see Fig. 1 in Ref. 16). For the first mechanism [(viii) in Ref. 16] we found no evidence (the laser power of ca. 10 \( \mu \)J/pulse is too low for ionizing \( H \) atoms nonresonantly) but we cannot rule it out either. Additionally, it may still contribute to the \( \Sigma^+ \) signal which we cannot study here due to interference from the huge \( \Sigma^+ \) signal. The \( \Sigma^+ \) from the second of these dissociation mechanisms [(ix) in Ref. 16] is not detected by us, but we believe that it is at least partly \( \Sigma^+ \) emerging from excitation of the gateway state \( \Sigma^+ \) to autoionization \( \Pi \) [process (i) in Ref. 16, \( \text{vide infra} \)]. The parameter \( \gamma \) in that study denoting the ratio of \( \Sigma^+ \) produced from photodissociation of the Rydberg state to the \( \Sigma^+ \) produced from photodissociation of the \( \Sigma^+ \) state is equal to zero (or at least negligible) for \( J'=5 \). This is what we also see for the \( \Sigma^+ \) channel, since the spatial distributions are completely different for the off-resonant rotational lines.

However, as the \( F^1 \Delta_2 \) state only shows significant fragmentation for the near-resonant Q(8) line (\( \text{vide infra} \)) and Kvaran et al. found small but significant photolysis for other triplet states as well, there could be some triplet state opening the dissociation and autoionization channel. We believe this to be due to the fact that the transition is spin allowed, since the gateway state to autoionization is supposed to be a \( \Pi \) state. However, in our case, it must be the \( \Pi \) state of the \( \Sigma^+ \) ion core group, since the observed \( \beta \)-parameter for the process is large and positive. This explains the formation of \( H(n=2) \) together with \( \Sigma^+ \) (\( n=2 \)), since the \( \Pi \) state crosses the potential curves of the bound \( \Sigma+ \) state, and the formation of \( \Sigma^+ \) atoms since it asymptotically correlates with \( H+\Sigma^+ \). These \( \Sigma^+ \) have probably been detected by Kvaran et al. as \( \Sigma^+ \) ions for the triplet states not near any resonance with the \( \Sigma^+ \) state. Since the Franck–Condon factors should be as small as for the singlet states, the direct ionization is still by far the dominating process.

The fragmentation dynamics presented in this section are summarized in Eq. (10). Note that the upper part of Eq. (10b) can be regarded as more or less unaltered by the small interaction although it looks strongly diminished in Fig. 3. This is because the small fraction transferred to the \( \Sigma^+ \) state is so effectively dissociated.

\[
\begin{align*}
2hv & \quad \text{HCl} \rightarrow \text{HCl}(f^3 \Delta_2^J \neq 5) \rightarrow \text{HCl}([^4 \Pi \cdots 4s]^3 \Pi^0) \rightarrow \\
& \quad \text{HCl}^+(v' \geq 5) \\
& \quad (H(n=2) + \text{Cl}(^2 P_{3/2})) , \\
& \quad H + \text{Cl}(4s) \\
(10a)
\end{align*}
\]

\[
\begin{align*}
2hv & \quad \text{HCl} \rightarrow \text{HCl}(f^3 \Delta_2^J = 5) \rightarrow \text{HCl}([^4 \Pi \cdots 4s]^3 \Pi^0) \rightarrow \\
& \quad (H(n=2) + \text{Cl}(^2 P_{3/2})) , \\
& \quad H + \text{Cl}(4s) \\
(10b)
\end{align*}
\]

\[
\begin{align*}
^hv & \quad \text{HCl}(V^1 \Sigma^+, v' = 8, J' = 5) \rightarrow \text{HCl}([^2 \Sigma^+ \cdots n \ell \sigma]) \rightarrow \text{HCl}(V^1 \Sigma^+) \rightarrow \\
& \quad H^+ + \text{Cl}^– \\
& \quad \rightarrow \text{HCl}([^2 \Pi \cdots 4s]) \rightarrow (H(n=2) + \text{Cl}(^2 P_{1/2})) .
\end{align*}
\]
the respective rotational level in the V state producing mechanism see Eqs. two-photon transition.

The overall positive β-parameter is clearly observable. Due to the higher photon energy as in Sec. III A, the fast ions belonging to the HCl+ photodissociation almost merge with the slower ions composed of the dissociation into the ion-pair and in H(n=2)+Cl P1/2(3/2) [for a summary of the H+ producing mechanism see Eqs. (2)–(4) in the Introduction]. This is because the latter result from a three-photon dissociation of the neutral molecule whereas the first emerge from a one-photon dissociation of the molecular ion and therefore the available energy of the latter decreases relative to the first as the photon energy increases. It should be noted that the Q(8) transition to the F 1 1/2(v′=1) state was the only one out of the Q-branch transitions for that we found an H+ signal considerably above the background level.

Figure 7 shows that the kinetic energy profile for the H+ ions emerging from the transition to the F state (v′=1, J′ =8) being in near resonance (ΔE=11.3 cm⁻¹) (Ref. 15) with the respective rotational level in the V state (v′=14, J′ =8) is the same as the one resulting from the REMPI process via the V state. Given that these fragmentation dynamics are a fingerprint for the outer well of the B 1 Σ⁺ state, this constitutes a direct observation for the resonance mediated mechanism proposed by Kvaran and co-workers who measured the relative ion intensities using mass resolved REMPI-TOF (time of flight). We do not show the H+ distribution for the Q(0) transition of the V 1 Σ⁺ ←X 1 Σ⁺(14,0) vibrational band, because the signal was not discernible against the background. This reflects the observation already mentioned by Green et al. that the v′=14 rotational progression shows unnaturally small relative line intensities not explainable by Frank–Condon factors in addition to abnormal rotational energy shifts. This is attributed to strong Rydberg-valence interactions with the nearby E 1 Σ⁺ and g 3 Σ⁻ states. Presumably, this is also why Loock et al. left out the v′=14 state in their study. However, to the best of our knowledge, this is the first time the H+ speed distribution for the REMPI process via this vibrational state of the V 1 Σ⁺ progression has been measured. Comparison with the also shown distribution resulting from the REMPI process via the Q(0) transition of the V 1 Σ⁺ ←X 1 Σ⁺(13,0) vibrational band shows that the v′=14 distributions exhibits a markedly diminished ion-pair peak. This is in accord with the trend observed by Loock et al. that the ion-pair peak diminishes strongly by going from the v′=13 to the v′=15 vibrational state of the V state.

Figure 8 depicts the angular distributions for the H(n =2) channel and the HCl+ photodissociation channel for the REMPI transition F 1 1/2 ←X 1 Σ⁺(0,1)Q(8). Table III summarizes the anisotropy parameters for the relevant transi-
tions. It is noteworthy that the anisotropy for the HCl+ photolysis remains unaltered for all three transitions, whereas the H(n=2) channel seems to lose the information about the twofold perpendicular two-photon transition completely, i.e., the negative $\beta$-parameter that should arise due to the expected alignment is absent. Above we observed the same effect for the triplet transitions in Sec. III A. We believe that the reason for this is the exchange of angular momentum of the electrons and nuclei in the nonadiabatic transition to the dissociating state from the final state of the absorption. Kable et al. 39 experimentally and theoretically described such effects for the HCO photodissociation where opposite or unexpected photodissociation anisotropies with respect to those expected by the knowledge of the electronic transition occur. Therefore, we think that the observed effect can be interpreted in the following way: the alignment of the molecular axis due the two-photon transition is destroyed in the nonadiabatic transition from the $\Omega=2$ (F 3 $\Delta_2$, f 3 $\Delta_2$) states to the $\Omega=0$ (V $\Sigma^+$) states. Regarding the observations, this means that the transition to the autoionizing $[^3\Pi\cdots4s]\Pi$ state producing vibrationally excited HCl+ is not so much affected by this as the channels producing H(n=2) and the ion pair, since it still bears the mark of the initial alignment of the two-photon excitation. We believe that the reason for this is that the ion-pair channel [not resolved for the $1\Delta_2$, $v'=1$ and $1\Sigma^+, v'=14$ transitions (Fig. 7)] and the H(n=2) channel start from larger interatomic distances with the pure ion-pair character of the V $\Sigma^+$ state (see Fig. 1). Here, the information about the initial alignment is lost when the combination of N=6 and $\Omega=2$ is switched to N=8 and $\Omega=0$. The fact that the distributions of the H+ emerging from the HCl+ photolysis, both for the F 1 $\Delta_2$ and the f 3 $\Delta_2$ transitions, still show the fingerprint of the alignment due to the two-photon transition can be interpreted such that this process is fast compared to the reaction of the nuclei to the switching of the electronic configuration. This seems reasonable, since the Franck–Condon region for the transition to the $[^3\Pi\cdots4s]\Pi$ state is close to the crossing of the potential curves of the F/f states with the B state.

IV. CONCLUSION

In extension of previous work, in this article we investigated the quantum state specific fragmentation behavior of REMPI processes in HCl through the Rydberg states F 1 $\Delta_2$ and f 3 $\Delta_2$. This has been achieved by measuring the spatial velocity distribution of the H+ ions emerging from these transitions by means of the 3D velocity map imaging technique. H+ resulting from the processes (1) HCl+3hν→H(n=2)+Cl(3P), (2) HCl+3hν→H++Cl−, and (3) HCl+3hν→HCl−+H++Cl were monitored.

Basically, the near resonance rotational states in the f 3 $\Delta_2$ and F 1 $\Delta_2$ states behave identically to the B 1 $\Sigma^+$ states in that way single rotational lines of the REMPI[2+n] (n=1,2) band systems F 1 $\Delta_2$←X 1 $\Sigma^+$, and f 3 $\Delta_2$←X 1 $\Sigma^+$ [i.e., Q(8) and Q(5), respectively] show the characteristic fragmentation dynamics of the V $\Sigma^+$←X 1 $\Sigma^+$ band system. This proved the suggested mechanism by Kvaran et al. that the vicinity in energy of the respective rotational energy levels to those in the V $\Sigma^+$ ion-pair state leads to the enhanced fragmentation of the f/F-Rydberg states that they observed by mass resolved REMPI-TOF. Additionally, a series of subtle details concerning the fragmentation dynamics in the investigated states were observed.

Concerning the f 3 $\Delta_2$←X 1 $\Sigma^+$ band our results show that the additional H+ for the Q(5) line is generated exclusively via the outer well of the B $\Sigma^+$ state belonging to the V $\Sigma^+$ part of this adiabatic potential. These consist of H(n=2) atoms with Cl+ (3P 1/2) as cofragment and H+ of the ion pair H++Cl+. Other Q-branch transitions to rotational states not in resonance with the respective rotational states in the V $\Sigma^+$ also undergo fragmentation, but the H(n=2) atoms are produced in coincidence with Cl in the spin orbit ground state.

The F 1 $\Delta_2$←X 1 $\Sigma^+$ band shows fragmentation exclusively for J=8 as the final state and the kinetic energy distribution has been shown to be the same as for the respective V $\Sigma^+$←X 1 $\Sigma^+$ transition. The anisotropy observed indicates that the HCl+ autoionization occurs from a more Rydberg-like electronic configuration as the ion-pair channel and the major part of the H(n=2) channel.

Some details manifesting themselves in spatial fragment anisotropies could not yet fully be assessed. For example the autoionizing state excited from the f 3 $\Delta_2$ state cannot be the 3$\Pi_0$ state previously reported as the gateway state for the 3$\Sigma^+$ state fragmentation. Instead, the positive $\beta$-parameter indicates that it is the respective 3$\Pi_2$ state. Moreover, the gateway state to the ion-pair dissociation at this energy has to be an $\Omega=1$ state out of the Rydberg series having an A $\Sigma^+$ ion core.

In summary, the results obtained in this work confirmed and extended the previously obtained global understanding of the HCl fragmentation process in the ($\Lambda=\Sigma=0$) 3$\Sigma^+$ manifold to Rydberg states with $\Lambda>0$ and $\Omega>0$.

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