I. INTRODUCTION

The hydrogen halides, particularly HCl (Refs. 1–13) and HBr,14–19 are perhaps the most studied diatomic molecules in the field of photodissociation and photoionization dynamics. The HX ground electronic state, \(X^1\Sigma^+(0^+)\), arises from a \([\ldots]σ^2\pi^1\sigma^0\) valence-electron configuration and removal of an electron from the nonbonding \(π\) molecular orbital gives rise to the \(X^2\Pi\), ground state of the molecular ion. In onephoton ionization HX\(^+\) is hence formed with its vibrational population largely in the \(X^2\Pi\) [\(υ=0\)] state. By comparison, removal of an electron from the \(σ\) bonding orbital leads to weakening of the H–X bond and consequent formation of the first excited state of the ion, \(A^2Σ^+\), with considerable vibrational excitation.3,13

One-photon ionization has also been observed in the energy gap between these two states of the HX\(^+\) ion and was attributed to autoionization of superexcited states.1,4 The autoionization process results in the formation of a long vibrational progression of the molecular ion, where the vibrational distributions can be modeled using the product of two overlap integrals, i.e., the overlap integral between the corresponding nuclear wave functions of the ground state and superexcited states as well as between the superexcited states and the molecular ion.20 In addition to autoionization, the superexcited states were also found to dissociate into electronically excited atomic photofragments or the \(H^+X^+\) ion pair. The neutral dissociation products were detected using fluorescence and were assigned mostly to electronically excited halogen atoms, with only small contributions from excited hydrogen atoms.3,21

For HCl the competition between the autoionization and predissociation processes was quantified by Lefebvre-Brion and Keller.5 It was shown that 4\(ρ\pi\), 4\(π\rho\), 4\(σ\rho\), and 3\(π\rho\) superexcited states with an \(A^2Σ^+\) ionic core acted as gateway states by coupling to (1) the ionization continuum of the \(X^2\Pi\) state leading to autoionization and (2) to the dissociation continuum of Rydberg states with an \(4\Pi\) \((α^1\pi^3α^{-1})\) ionic core leading to dissociation into excited photofragments. For example, it was proposed that the \([A^2Σ^+\cdot3\pi\rho\cdot4ρ\pi]^{1}Π\) superexcited states couple electronically to the ionization continuum of the \(X^2\Pi\) state and autoionize, while the \([A^2Σ^+\cdot4σ\rho]^{1}Σ(0^+)\) superexcited states are predissociated by the unbound \([4\Pi\cdot3\pi\rho\cdot4σ\rho]^{1}Π(0^+)\) superexcited states, which correlate to the excited halogen atoms. This predissociation was attributed to the spin-orbit coupling. In subsequent studies on HCl, superexcited states based on the \(A^2Σ^+\), \(2^2Π\),...
or \(^4\)II ion cores and with low-\(n\) outer electrons were also proposed to be gateway states for electronic autoionization, and for dissociation into excited atomic fragments.\(^{11,12,18,22}\)

In addition to predissociation and subsequent formation of the Cl\(^-\) photofragments, the \(^3\Sigma^+\) superexcited states of HCl were also found to form the ion pair, H\(^+\)+Cl\(^-\), following electronic coupling with the continuum of the V \(^1\Sigma^+(0^+)\) ion-pair state.\(^{11,23-25}\)

As expected, the spin-orbit interactions responsible for the formation of the excited halogen, X', fragments are stronger in the case of the Br or I, and the dissociation into excited atomic fragments then prevails over autoionization and ion-pair dissociation.\(^5\)

The use of \((2+1)\) resonance enhanced multiphoton excitation at similar total photon energies allows for studying the ionization and dissociation dynamics from a different angle. Since the two-photon intermediate states are \((n, \nu, J)\) quantum state selected, the excitation process occurs from a single parent state and complete state-to-state correlation is possible. The measured ionization/dissociation branching ratios, the product state distribution, and the angular distributions of photofragments all carry the signature of both the two-photon intermediate states as well as of the superexcited states.\(^{11,16,18,23}\)

For example, ionization of the \((\Omega>0)\) Rydberg states with a \(\chi^2\) II core configuration was found to form the HBr\(^+\) or HCl\(^+\) ion mostly in its vibrational ground state and with the conservation of the total angular momentum of the ion core.\(^{24,25}\) When, on the other hand, the V \(^1\Sigma^+(0^+)\) ion-pair state or any \((\Omega=0^+)\) Rydberg state in its vicinity is the intermediate state, direct ionization may become a minor process, and excitation of superexcited states is favored by one-electron excitation rules. The deviation from the Rydberg character through perturbations with the V \(^1\Sigma^+(0^+)\) state manifests itself in the photodissociation and photoionization dynamics following \(2+1\) photon excitation, mainly by the minor contribution that direct ionization now plays compared to dissociation and autoionization.

The V \(^1\Sigma^+(0^+)\) state itself is the result of an avoided crossing between the ion-pair state with configuration \([\cdot \cdot \cdot \sigma^2 \pi^4 \sigma^0]\) and the valence state \([\cdot \cdot \cdot \sigma^1 \pi^4 \sigma^1]\).\(^{26}\) The avoided crossing leads to a shallow minimum at large internuclear distance. For HCl a second avoided crossing of the V \(^1\Sigma^+(0^+)\) state with the \(E^1\Sigma^+(0^+)\) produces a new set of adiabatic curves,\(^{27}\) of which the lower one, the \(B^1\Sigma^+(0^+)\) state, has two minima and an electronic configuration that changes with the internuclear distance.\(^{28}\) Previous studies have shown that in HCl the \(B^1\Sigma^+(0^+)\) state interacts strongly with \(^1\Sigma^+(0^+)\) Rydberg states with a \([\cdot \cdot \cdot \sigma^2 \pi^4 \sigma^0 - 4 \pi^4 \sigma^0]\) configuration.\(^{6-9,23}\)

For HBr a similar double minimum state is formed by an avoided crossing of the respective V \(^1\Sigma^+(0^+)\) state with the \(E^1\Sigma^+(0^+)\) state. Perturbations of the resulting \(B^1\Sigma^+(0^+)\) state by Rydberg states belonging to the \(5 \rho \pi\) and \(4 \delta \pi\) manifolds were observed.\(^{16}\)

Previous photoelectron imaging studies on HCl (Ref. \(^{11}\)) or HBr (Ref. \(^{18}\)) have shown that a long vibrational progression of ground state ions is formed when the V \(^1\Sigma^+(0^+)\) state or one of the perturbed Rydberg states is used as two-photon intermediate. In addition, formation of electronically excited hydrogen atoms H\(^+(n=2)\), in coincidence with, both, ground state and spin-orbit excited halogen atoms, as well as formation of electronically excited halogen atoms was observed. With this paper we expand on our previous work\(^{11,18,22}\) and on the recent studies by Chichinin et al.\(^{12,29}\) by using proton velocity map imaging to (1) identify a pathway by which the H\(^+\)+X\(^-\) ion pair may be formed, (2) use the alignment of the intermediate state following two-photon excitation to identify excitation and dissociation pathways, (3) identify the superexcited states responsible for the formation of H\(^+(n=2)\), and (4) quantify the quantum yield for dissociation of HX\(^+[\nu^+>0]\) into H\(^+\)+X.

II. EXPERIMENT

The experimental setup and analysis procedure have been described in detail previously,\(^{11}\) and only a brief summary is given here. An excimer laser operating at 308 nm pumped a dye laser (both Lambda Physik) using a Coumarin dye (C460, C480, or C500). The dye laser pulse was frequency doubled in a beta-barium borate crystal to produce 200–250 \(\mu\)J/pulse and focused onto the molecular beam with a f.l.=30 cm lens. The laser wavelength was calibrated with respect to the previously reported spectra of HCl (Ref. \(^9\)) or HBr.\(^{16}\) The energy resolution of the excitation spectra was limited by the laser bandwidth and was less than 1.0 \(\text{cm}^{-1}\) at the two-photon level.

A molecular beam containing rotationally cold HCl or HBr was generated by expansion of a gas mixture containing 10\%–20\% gas (HCl or HBr, Mathesson 99.9\%, used without further purification) in helium at a stagnation pressure of 760 Torr through a pulsed valve (600 \(\mu\)m nozzle diameter) and a 500 \(\mu\)m skimmer located 20 mm downstream of the valve. The molecular beam was aligned along the time-of-flight (TOF) axis and directed at the center of a position sensitive charged particle detector (diameter of 76 mm). The vertically polarized laser beam was at right angle to the TOF axis and crossed the molecular beam 70 mm downstream of the valve in the region between the repeller and extractor electrodes. The ion images were recorded by a 12 bit charge-coupled device camera (1280 \times 1024 pixels). The gain of the detector was gated to select for the \(m/\ell\) of the ion of interest, in this case the protons. The backing pressure and time delay between the opening of the pulsed beam valve and the firing of the laser were chosen in such a way that no molecular clusters were detected.

The images were averaged on a computer (\(\sim 8000\) images, 16 bits). A background image, which was recorded “off resonance,” was subtracted, and the radial and angular distributions of the charged-particle cloud were determined from the averaged image using either the BASEX software\(^{30}\) or the GLASSONION software.\(^{31}\) which is based on the onion-peeling algorithm by Winterhalter et al.\(^{32}\) Due to a nonuniform sensitivity over the detection area of our detector, the integrated intensities of the different quadrants of the proton images were slightly different. However, we found that there were only minor differences between the radial distributions or the angular distributions of the photoions collected in the different quadrants of the detector. Spatial anisotropy param-
eters were obtained from an expansion of the angular distributions into even Legendre polynomials.

From the inverted images the photoion yields were determined by Gaussian fitting to the radial profiles. The yields were then referenced to previously recorded photoelectron images as described below.

III. RESULTS AND DISCUSSION

A. Proton formation pathways

Proton ion images were recorded for HCl with excitation wavelengths between 231.4 and 242.7 nm, corresponding to the 2+1 photon excitation of the $V^1\Sigma^+(v=9, 11-13, 15, 17, 19)$, $g^1\Sigma^-(v=0)$, and $E^1\Sigma^+(v=0)$ states. For HBr proton images were recorded following multiphoton excitation via ground vibrational levels of the $g^1\Sigma^+(0^+)$, $E^1\Sigma^+(0^+)$, and $H^1\Sigma^+(0^+)$ Rydberg states as well as for the vibrationally excited $V^1\Sigma^+(v=m+3, m+5 to m+8)$ state, where $m=0$ or possibly 2.

The processes that can lead to the formation of protons in the multiphoton excitation of HX (X=Cl or Br) can be summarized as follows.

1. Dissociation of the lowest ion-pair state
   \[ \text{HX} + 3h\nu \rightarrow \text{H}^* + X^{-} (1s) \]  

2. Dissociation of superexcited HX** and ionization of excited H^* photofragments
   \[ \text{HX} + 3h\nu \rightarrow \text{HX}^{**} \rightarrow \text{H}^*(n=2) + X(2P_{3/2,1/2}), \]
   \[ \text{H}^*(n=2) + h\nu \rightarrow \text{H}^* + e^- \]  

3. Formation of HX* by (2+1) resonance enhanced multiphoton ionization (REMPI) and subsequent dissociation
   \[ \text{HX} + 3h\nu \rightarrow \text{HX}^*(\Omega^*, \nu^*) + e^- \]  
   \[ \text{HX}^*(\text{2P}_{3/2,1/2}) + h\nu \rightarrow \text{H}^* + X(2P_{3/2}), \]
   \[ \text{HX}^*(\text{2P}_{1/2,3/2}) + h\nu \rightarrow \text{H}^* + X(2P_{1/2}), \]
   \[ \text{HX}^*(\text{2P}_{1/2,3/2}) + h\nu \rightarrow \text{H}^* + X(2P_{3/2}), \]

4. Dissociative ionization of superexcited HX**
   \[ \text{HX} + 3h\nu \rightarrow \text{HX}^{**}, \]
   \[ \text{HX}^{**} + h\nu \rightarrow \text{H}^* + X(2P_{3/2,1/2}) + e^- \]  

Energy conservation applied to the dissociation processes (1)–(3) necessarily gives a linear dependence of the kinetic energy release (KER) on the total photon energy, which, in turn, scales with the total number of photons absorbed in the dissociation. The expressions of the KER for the first three processes are

Channel 1:
   \[ \text{KER} = 3h\nu - D_0(\text{HX}) - \text{IP(H)} + \text{EA(X)}, \]
   \[ \text{KER} = 3h\nu - D_0(\text{HX}) - \text{IP(H)} - \text{EA(X)} \]  

The KER for channel (4) is also dependent on the photon energy but in a less straightforward manner, since it includes the photoelectron kinetic energy as a variable that depends on the potential energy curves of the states involved in the dissociation step and, ultimately, on the projection of the wave function of the lower state on the potential curve of the unbound ionic curve. The photoelectron yield spectra obtained for HCl and HBr do not contain features to support a contribution of dissociative ionization and, for simplicity, we assume that channel (4) has, at best, a minor contribution to the formation of protons.

In Eqs. (5)–(7) \[ D_0(\text{HCl}) = 35.748.2 \text{ cm}^{-1} \] and \[ D_0(\text{HBr}) = 30.210 \pm 40 \text{ cm}^{-1} \] are the dissociation energies of HCl (Ref. 35) and HBr, \[ \text{IP(H)} = 109.677.6 \text{ cm}^{-1} \] is the ionization potential of the hydrogen atom, \[ \text{EA(Cl)} = 29.138.3 \text{ cm}^{-1} \] and \[ \text{EA(3Br)} = 27.129.1 \text{ cm}^{-1} \] are the electron affinities of chlorine and bromine. \[ E[H^*(n=2)] = 82.258.95 \text{ cm}^{-1} \] is the electronic energy of the electronically excited H atom, \[ G_6(\text{HX}^*) \] are the vibrionic energies of HX** ions with respect to the ground state of neutral HX. \[ \text{KER} \] of the proton formed in the multiphoton excitation of HCl and HBr J. Chem. Phys. would be

Channel 2:
   \[ \text{KER} = 3h\nu - D_0(\text{HX}) - E[\text{H}^*(n=2)] - \text{EA(X)} \]  

Channel 3:
   \[ \text{KER} = h\nu + G_6(\text{HX}^*) - D_0(\text{HX}) - \text{IP(H)} - \text{EA(X)}. \]
TABLE I. Anisotropy parameters for the protons formed in coincidence with Cl\(^-\). The parallel contribution to last excitation step \(|M(0)|^2\), was calculated from \(b_2\). The values for the \(V^1 \Sigma^+(v=9)\) and \(E^1 \Sigma^+(v=0)\) are considered less reliable because of the weak ion-pair signal. The branching ratio is given with respect to the proton signal arising from the \(H^+ + Cl\) channel and is defined as \(BR=\frac{|H^+ + Cl^-|}{|H^+ + Cl|}\).

| \(V^1 \Sigma^+ [v=9]\) | \(Q(0)\) | \(Q(1)\) | \(\beta_2\) | \(\beta_4\) | \(|M(0)|^2\) |
|---|---|---|---|---|---|
| \(\beta_2\) | \(0.30(6)\) | \(-0.17(8)\) | 0.05(1) |
| \(\beta_4\) | \(1.32(3)\) | \(-0.64(5)\) | 0.025(5) |
| \(E^1 \Sigma^+ [v=0]\) | \(Q(0)\) | \(1.21(5)\) | \(0.85\) | \(-0.05(6)\) | 0.015(10) |
| \(Q(1)\) | \(0.62(12)\) | \(0.89\) | \(-0.38(18)\) |
| \(V^1 \Sigma^+ [v=11]\) | \(Q(0)\) | \(1.88(4)\) | \(0.98\) | \(0.12(6)\) | 0.11(1) |
| \(Q(1)\) | \(1.16(3)\) | \(0.98\) | \(-0.48(3)\) |
| \(V^1 \Sigma^+ [v=12]\) | \(Q(0)\) | \(1.95(5)\) | \(0.99\) | \(0.12(6)\) | 0.29(5) |
| \(Q(1)\) | \(1.30(2)\) | \(1.00\) | \(-0.71(3)\) |
| \(V^1 \Sigma^+ [v=13]\) | \(Q(0)\) | \(1.89(9)\) | \(0.98\) | \(-0.20(7)\) | 0.14(4) |
| \(Q(1)\) | \(1.48(2)\) | 1.02 | \(-0.49(3)\) |

\(^a\)The branching ratios for the \(Q(0)\) lines are qualitatively similar to those calculated for the \(Q(1)\) lines, but have much larger errors, due to the poorer resolution of the respective proton images.

\(^b\)The peak overlaps with the peaks corresponding to the one-photon dissociation of \(HCl^+ [v^*=5]\). For the calculation of the BR we subtracted an area equal to the area of the second \(v^*=5\) dissociation peak.

B. Alignment of the intermediate states

Following two-photon excitation with linearly polarized light, the rotationally excited \(1 \Sigma\) states are aligned in the lab frame. The rotational alignment of the intermediate \(E^1 \Sigma^+(v^=0)\) state of HCl and the \(H^1 \Sigma^+(v^=0)\) state of HBr by respective two-photon transitions through the \(Q(1)\) lines was observed previously by our group and described by a first principle calculation by Manzhos et al.\(^{22,43}\) The effect was also observed recently by Chichinin et al.\(^{29}\) for the \(E^1 \Sigma^+(v^=0)\) and \(V^1 \Sigma^+(v^=12)\) intermediate states of HCl through a characteristic change in the relative intensities of the \(O, Q, S\) rotational branches. Chichinin et al. introduced the complex parameter \(b\) to quantify the contribution of the perpendicular and parallel excitation.\(^{29}\)

\[
b = \frac{D_{\perp} - D_{||}}{2D_{\perp}}
\]

(8)

Here, the two-photon transition moments for the parallel \((\Sigma \rightarrow \Sigma \rightarrow \Sigma)\) and perpendicular \((\Sigma \rightarrow \Pi \rightarrow \Sigma)\) pathways are

\[
D_{\parallel} = \sum_{\eta} \frac{R^{(2)}_{\eta,0} R^{(1)}_{\eta,0}}{E_{\eta,0,J} - E_{\eta,0} + i\Gamma_{\eta,0,J}/2} \langle \eta |v| \eta \rangle \langle \eta |v| \eta \rangle
\]

(9)

where \(D_{\perp}\) is the denominator in Eq. (9). With this expression one can specify the parallel \((\Sigma \rightarrow \Sigma \rightarrow \Sigma)\) contribution by the value \(|R^{(2)}_{\eta,0} R^{(1)}_{\eta,0}|^2/D_{\perp}\). Here, \(\eta=1-\eta_{\perp}\) is the fractional contribution of the \(\Omega_{\perp}=0\) states to the one-photon absorption cross section. Correspondingly, the perpendicular \((\Sigma \rightarrow \Pi \rightarrow \Sigma)\) contribution is given by \(\eta_{\perp}\). Note that there is also a phase difference between the parallel and perpendicular excitation processes which is reflected in the interference terms of the form \(i b^{(2)}_{\eta,0} b^{(1)}_{\eta,0}\).

Chichinin et al.\(^{29}\) measured \(|b_{\eta=\eta_{\perp}}|^2=2.01\pm0.15\) and \(|b_{\eta=\eta_{\perp}}|^2=1.06\pm0.22\) for HCl, and thereby confirmed that the two-photon excitation is described largely by the perpendicular pathway \((\Sigma \rightarrow \Pi \rightarrow \Sigma)\). This is consistent with what had been observed previously.\(^{22}\)

Excitation of any aligned intermediate state to the final state (with \(\Omega=0\) or 1) may again be by a parallel \((q=0)\) or perpendicular \((q=1)\) process. The contribution of the parallel and perpendicular dissociation channels to the incoherent excitation of multiple dissociation continua was expressed by means of the dynamical parameter \(|M(q)|^2\), where \(0 < |M(q)|^2 < 1\).\(^{22}\) With known radial integrals \(|R^{(2)}_{\eta,0} R^{(1)}_{\eta,0} D_i|\) and \(|M(q)|^2\) it is straightforward to calculate the spatial anisotropy parameters \(\beta_2\) and \(\beta_4\) [see Eq. (11) of Manzhos et al.\(^{22}\)]. For example, the limiting values of the anisotropy parameters are \(\beta_2=1.30\) and \(\beta_4=-0.94\) for the parallel dissociation, \(|M(0)|^2=1\), of a rotationally excited intermediate.
state populated in $J=1$ via $\Omega=1$ virtual states ($\eta_2=1$). Conversely, $|M(q)|^2$ is readily determined if $\beta_2$ and $\beta_4$ are obtained from experiments and may be used to identify the excited state symmetry.

C. Proton kinetic energy distributions of HCl

The contribution of the dissociation channels 1–3 to the formation of protons is illustrated in a typical proton image (Fig. 1) obtained though two-photon resonant excitation of HCl via the $V^1\Sigma(0^+) \left[ v=12 \right] \leftarrow X^1\Sigma(0^+) Q(1)$ line transition. The right half shows the inverted image; (b) associated proton kinetic energy release spectrum with anisotropy parameters $\beta_2$ (solid circles) and $\beta_4$ (empty circles) given for each of the peaks.

FIG. 1. (a) Proton image following 2+1 resonance enhance multiphoton excitation of HCl via the $V^1\Sigma(0^+) \left[ v=12 \right] \leftarrow X^1\Sigma(0^+) \left[ v=0 \right] Q(1)$ line transition. The right half shows the inverted image; (b) associated proton kinetic energy release spectrum with anisotropy parameters $\beta_2$ (solid circles) and $\beta_4$ (empty circles) for each of the peaks.

state populated in $J=1$ via $\Omega=1$ virtual states ($\eta_2=1$). Conversely, $|M(q)|^2$ is readily determined if $\beta_2$ and $\beta_4$ are obtained from experiments and may be used to identify the excited state symmetry.

1. Ion-pair dissociation

Dissociation of HCl into the $H^+\text{Cl}^{-}$ ion pair was first observed in 1993 by Yencha et al. in one-photon excitation using synchrotron radiation. The excitation spectrum of Cl$^-$ was compared to the one-photon ionization and dissociation spectra of HCl and the ion-pair formation in the 14.4–16.4 eV excitation energy range was explained as a two-step process consisting of excitation of electronically superexcited states with $A^2\Sigma^+$ ion cores and $nl\sigma$ ($n=4,5,6$ and $l=s,p,d$) Rydberg electrons, followed by predissociation by the $V^1\Sigma(0^+)$ ion-pair state. Ion-pair formation via predissociation of superexcited states with similar electronic configurations was studied by Hepburn and co-workers in high-resolution threshold ion-pair production spectroscopy experiments at 14.4–14.55 eV excitation energies. At excitation energies above the first ionization potential only those transitions of similar images which were recorded following 2+1 photon excitation of a number of electronic transitions of HCl.

The “slow” protons can be formed either by 2+1 photon dissociation of HCl into the $H^+\text{Cl}^{-}$ ion pair (see Sec. III C 1) or they can result from the dissociation of a superexcited state (Sec. III C 2) and subsequent one-photon ionization of electronically excited hydrogen atoms, $H^*$. The latter process is further divided into two dissociation channels, i.e., formation of the correlated chlorine atom in the ground state or in the spin-orbit excited state.

The “fast” protons are formed following one-photon dissociation of vibrationally excited HCl$^+$ ions (Sec. III C 3).
superexcited states with an $A^2\Sigma^+$ ion core can be excited from the ground state in a one-photon excitation process.

In our experiments observation of the $H^++Cl^-$ ion pair came unexpectedly. Note that the strongest contribution of the ion-pair dissociation pathway (Fig. 2) is found when the two-photon intermediate state, i.e., the lower state in the final dissociation step, was the ion-pair state $V^1\Sigma(0^+)$ $[v=12]$ itself! Furthermore, the nuclear wave function of any of the two-photon intermediate states is rather spread out to long internuclear distance and does not have appreciable values near the repulsive wall of the ion-pair state at 15.5–16.1 eV. Clearly, a plausible mechanism must involve a neutral gateway state that can be accessed in a single photon transition from the $V^1\Sigma(0^+)$ state at large internuclear distance but must also have overlap with the repulsive wall of the ion-pair state at short internuclear distance.

The $\beta_2$ anisotropy parameters for the excitation of the rotationless intermediate states have values close to the limiting values for a parallel transition ($\beta_2=2.00$) for all intermediate states, which suggests that the gateway states have $\Omega=0^+$ symmetry (Table I). Similarly the limiting value of $\beta_2=1.30$ is approached, when the intermediate state is rotationally excited ($J=1$) and aligned. Exceptions are found for those intermediate states with a low ion-pair dissociation yield, where the experimental values are probably underestimated. For a given electronic state it is expected that the values for $|M(0)|^2$ are identical when calculated from $\beta_2$ of the $Q(0)$ line or from $\beta_2$ of the $Q(1)$ line. The small differences apparent in Table I are indicative of the experimental error.

Polar plots of the intensity distributions, which were calculated assuming $\eta_i=0$ and $|M(0)|^2=1$, are shown in Fig. 3 for $J=0$ and $J=1$ along with the respective experimental proton distributions for the ion-pair dissociation of the $V^1\Sigma(0^+)$ $[v=12]$ state.

The experimental $\beta_2$ values for the $Q(0)$ and $Q(1)$ lines are all higher than the limiting value of $\beta_2=0$ and $\beta_2=-0.94$, respectively. This deviation is likely not due to an incomplete alignment but rather indicative of a small systematic error in the expansion of Legendre polynomials, which is caused by the center line noise.

The spatial anisotropy parameters are influenced by the degree of alignment of the two-photon intermediate state, as expressed through the parameter $\eta_i$. For HCl it was found that $\eta_i=1$ meaning that a ($\Sigma\rightarrow\Pi\rightarrow\Sigma$) pathway is dominant. This was expected, since it is well known that the $\Pi(1)$ state is a dominant contributor to the one-photon absorption of HCl around 240 nm.\(^{48-51}\)

The most probable gateway states for the ion-pair dissociation channels are the $[A^2\Sigma^+\cdot 5sx, 4dx, or 5px]^1\Sigma(0^+)$ bound superexcited states, which were described previously by Lefebvre-Brion et al.\(^{3}\) and by Hepburn and co-workers.\(^{46,47}\) As shown in Fig. 4, the Franck-Condon region for the excitation is located in the outer well of the double minimum state and centered around 2.2 Å, i.e., near the attractive wall of the gateway state potential. Predissociation is then aided by considerable overlap integrals of the $A^2\Sigma^+\cdot nlsx$ states with the wave function of the dissociation continuum of the $V^1\Sigma(0^+)$ state at short internuclear distance.

In Fig. 4 the two-photon intermediate state is the double minimum $B^1\Sigma(0^+)$ state potential,\(^{10}\) while the dissociation continuum is represented by the diabatic curve of the $V^1\Sigma(0^+)$ ion-pair state. The latter curve was optimized by Yencha et al.\(^{10}\) to obtain good agreement between their experimental spectrum and the theoretical spectrum calculated from the overlap integrals. Figure 4 also illustrates why the

![Image](https://via.placeholder.com/150)

**FIG. 3.** (Color online) Symmetrized polar plots of the proton angular distributions obtained by excitation of the $V^1\Sigma(0^+)[v=12]$ intermediate state and subsequent dissociation into the $H^++Cl^-$ ion pair. The angular distributions (solid lines) for the $Q(0)$ and $Q(1)$ line transitions were calculated for the limiting case of $\eta_2=1$ and $|M(0)|^2=1$.

**FIG. 4.** (Color online) Potential energy curves illustrating the proposed mechanism for the dissociation of HCl into $H^++Cl^-$. The potential of the $V^1\Sigma(0^+)$ state was adapted from the RRK curve of Yencha et al. (Ref. 10). The bound superexcited state was estimated by translating the ab initio potential curve of the $A^2\Sigma^+$ ionic state (Ref. 61) using the quantum defects values reported by Lefebvre-Brion and Keller (Ref. 5). The curve of the $B^1\Sigma(0^+)$ double minimum potential was adapted from the ab initio curves published by Peyerimhoff and co-workers (Refs. 27 and 62). The Numerov wave function is shown for the $V^1\Sigma(0^+)[v=0]$ state.
E \( ^1\Sigma^+(v^* = 0) \) state does not dissociate appreciably into the H\(^+\) + Cl\(^-\) ion pair upon excitation. The nuclear wave function is located primarily in the inner well of the double minimum potential, and excitation of the attractive wall of the \( A^2\Sigma^+ \cdot \cdot \cdot n\ell\sigma \) gateway states is not favored by Franck-Condon arguments.

2. H\(^+(n=2)\) formation

Electronically excited H\(^+(n=2)\) atoms can be formed in either 1s2s \( (2^3S_{1/2}) \) or 1s2p \( (2^3P_{3/2,1/2}) \) states and the assignment of the electronic configuration cannot be done solely based on the kinetic energy release in the fragmentation since the two states are almost degenerate.\(^{41}\) In principle, the angular momentum of the H\(^+\) frontier orbital can be determined by measuring the angular distribution of the photoelectron that is released by ionization. The spatial anisotropy parameters \( (\beta_2 = 1.1\) – 1.3) obtained, e.g., using Fig. 4 in Ref.\(^{11}\) allow us to conclude that most of the photoelectrons are formed in a \( p \) wave, i.e., by ionization of 1s2s \( (2^3S_{1/2}) \) excited hydrogen atoms. The deviation from the limiting value may indicate a small contribution of 1s2p \( (2^3P_{1/2,3/2}) \) or may be due to overlap with the rings corresponding to the (auto)ionization into HCl\(^+\) \([v^*]\) for which the respective \( \beta_2 = 0 \).

Formation of 1s2s \( (2^3S_{1/2}) \) is also consistent with the observed proton recoil, which is along the polarization axis of the laser beam. Only a photoelectron \( p \) wave results in a split of the “polar caps” of the proton rings,\(^{51}\) as seen in Fig. 1(a) for the dissociation of the V \( ^1\Sigma^+ \) \([v = 12]\) intermediate state. The propensity for the detection of H\(^+(2^3S)\) is likely due to the short radiative lifetime of H\(^+(1s2p, 2^3P)\), \( \tau = 1.6 \) ns.\(^{52}\) While H\(^+(2^3P)\) may be formed and quickly decay, we have no experimental evidence for its formation.

We note that at the laser fields in this study \((200–800 \mu J/\text{pulse}, 10 \text{ ns}, 30 \text{ cm focal length})\) Stark mixing between the nearly degenerate \( 2^3S \) and \( 2^3P \) states is expected to be extensive. We therefore also need to consider that H\(^+(2^3S)\) may be formed not only by dissociation of the respective field free states but also from H\(^+(2^3P)\). In fact, the distinction between states that correlate to H\(^+(2^3S)\) and those that correlate to H\(^+(2^3P)\) but differ only by the angular momentum of the Rydberg electron may be a moot point in even a moderate laser field as in our study.

The arguments and spectroscopic data leading to the proposed mechanism for H\(^+\) formation are given in detail in a document deposited in the Electronic Physics Auxiliary Publication Service (EPAPS) and only the conclusion is given here.\(^{53}\)

1. Between 60% and 90% of the H\(^+(n=2)\) fragments are formed in coincidence with spin-orbit excited chlorine atoms, Cl\(^+(2^3P_{1/2})\). According to the Wigner-Witmer rules the superexcited electronic states that form H\(^+(n=2)\) + Cl\(^+(2^3P_{1/2})\) are likely \( n = 4 \) Rydberg states converging to the unbound \( 2^3\Pi \) ionic state, i.e., \([2^3\Pi \cdot \cdot \cdot 4\ell\alpha]\) \( ^1\Sigma^+ \) \((0), 3\Pi(0)\) states (Fig. 5). This assignment encompasses the mechanisms proposed by Chichinin \( et \) \( al.\) who only considered pathways leading to H\(^+(1s2p, 2^3P)\).\(^{12}\)

2. Excitation of the \([4\Pi \cdot \cdot \cdot 4\ell\alpha]\) \( 3\Pi(0)\) state is responsible for the previously observed formation of electronically excited chlorine atoms, Cl\(^+(4s)\).\(^{5,11}\) The state is crossed by the \([A(2^3\Sigma^+) \cdot \cdot \cdot 4\ell\alpha]\) \( ^1\Sigma^+ \) state and using the simple Landau-Zener model at the respective excitation energies one can estimate that about 5%-10% of the excited molecules proceed to form H\(^+(n=2)\) + Cl\(^+(2^3P_{1/2})\) in agreement with our experimental observations. Repulsive \([4\Pi \cdot \cdot \cdot n\ell\alpha]\) superexcited states with higher angular momentum correlate to Cl\(^+(4p)\) and \((3d)\), respectively, and will also contribute to the formation of H\(^+(n=2)\) through nonadiabatic interactions.

3. Dissociation of HCl\(^+\)

The proton kinetic energy spectra for HCl (Fig. 2) show that most of the fast H\(^+\) ions can be assigned to the dissociation of only four vibrational levels of HCl\(^+\) \([v^* = 5–8]\), irrespective of the excitation energy. Similar imaging experiments using two-photon excitation of the E \( ^1\Sigma^+ \) \([v = 0]\) and V \( ^1\Sigma^+ \) \([v = 12]\) states were performed recently by Chichinin \( et \) \( al.\) who also reported the formation of H\(^+\) following the dissociation of HCl\(^+\).\(^{12}\) From their HCl\(^+\) images it was concluded that the “surviving” HCl\(^+\) was left in lower vibrational states \( v^* = 0–4\), whereas their proton image showed that \( v^* = 5–11 \) had dissociated.

In addition, we observed here a second group of peaks, with even higher kinetic energy and assigned those to the dissociation of higher vibrational levels of HCl\(^+\) ions \([v^* \geq 10]\). For all HCl\(^+\) dissociation processes \( \beta_2 = 2 \) indicat-
ing that for this excitation process $\Delta \Omega = 0$. In the adiabatic limit, the parallel dissociation pathways leading to formation of $H^+$ ions are

$$\text{HCl}^+ (X^2\Pi_{3/2}) + h\nu \rightarrow \text{HCl}^+ (2^2\Pi_{3/2}) \rightarrow H^+ + \text{Cl}(2P_{3/2}),$$

(3b')

$$\text{HCl}^+(X^2\Pi_{1/2}) + h\nu \rightarrow \text{HCl}^+(A^2\Sigma_{1/2}) \rightarrow H^+ + \text{Cl}(2P_{3/2}),$$

(3d')

$$\text{HCl}^+(X^2\Pi_{1/2}) + h\nu \rightarrow \text{HCl}^+(2^2\Pi_{1/2}) \rightarrow H^+ + \text{Cl}(2P_{1/2}).$$

(3e')

The value of the spin-orbit constant of HCl$, A_{SO} = 644 \text{ cm}^{-1}$, is similar to the value of SO$(\text{Cl}) = 881 \text{ cm}^{-1}$, and contributions from channels (3b') and (3e') are difficult to distinguish, since the difference in proton kinetic energy is close to the resolution of our velocity map imaging apparatus. On the other hand, the faster protons are clearly attributable to the process (3d'). The best fit of the experimental values of the kinetic energies (Fig. 1) favors a dissociation pathway in which the chlorine atoms are formed exclusively in their ground electronic states, i.e., channels (3b') and (3d') dominate.

Two dissociation channels [(3b') and (3e')] involve direct excitation into the dissociation continuum of the $2^2\Pi$ states. The peak in the quantum yield at $v^+ = 5-6$ is a result of favorable Franck-Condon integrals (Fig. 5). This was already illustrated by Chichinin et al.\textsuperscript{12}

A closer look at the potential energy curves in Fig. 5 (or Fig. 13 in the paper of Chichinin et al.)\textsuperscript{12} indicates that dissociation pathway (3d') is also energetically allowed for all vibrational levels of spin-orbit excited HCl$^+$ with $v^+ \gg 1$. Franck-Condon factors were calculated for the excitation of vibrationally excited $X^2\Pi$, $[v^+ = 1-12]$ into the dissociation continuum of the $A^2\Sigma^+$ state. They indicate that at energies similar to those used in these experiments the ground state wave functions with $v^+ = 5$ overlap favorably with the continuum wave functions. Excitation of the $A^2\Sigma^+$ state is consistent with formation of the Cl atoms in their lower spin-orbit state, corresponding to the second, higher energy peak in the fine-structure doublets of $5 \leq v^+ \leq 8$ in Fig. 2. While this contribution was originally discounted by Chichinin et al.,\textsuperscript{12} we believe that it is the only parallel dissociation pathway that explains the observed formation of Cl$(2P_{3/2})$ from excitation of $X^2\Pi_{1/2}$.

Finally, we are able to quantify an observation that was made previously by Chichinin et al., i.e., that only low vibrational levels of HCl$^+$ “survive,” whereas the remainder is subjected to further excitation and dissociation. Figure 6 shows the relative photoelectron and proton yields following autoionization into $X^2\Pi\ [v^+]$. Both yields were referenced to the photoelectrons and protons formed by the ionization process $H^+ (n=2) \rightarrow H^+ + e^-$. The quantum yield to fragmentation is found to peak at about 40% for the dissociation of the $v^+=6$ state formed by 2+1 photon excitation via the $E^1\Sigma(0^+)$ intermediate state. Clearly, the yield depends strongly on the laser power and focusing conditions, but still illustrates that even at moderate laser powers the dissociation step can become largely saturated.

### D. Proton kinetic energy distributions of HBr

Similar to HCl, the velocity map images of the proton formed by 2+1 excitation via $1\Sigma(0^+)$ intermediate states show “slow protons” attributed to the formation of $H^+(1\Sigma) + \text{Br}(2P_{3/2}, 2P_{1/2})$ and fast protons formed by one-photon dissociation of HBr$^+$ (Figs. 7 and 8). Contrary to HCl, the perturbed $1\Sigma$ Rydberg states and the $V^1\Sigma_{1/2}(v=(m+3), (m+5)-(m+8))$ ion-pair state show similar photofragment angular distributions and branching ratios. There was no evidence for the formation of $H^+ + \text{Br}^{-}$.

#### 1. Angular distributions

As shown above, rotational alignment of HCl is consistent with a perpendicular ($\Sigma \rightarrow \Pi \rightarrow \Sigma$) excitation pathway followed by largely parallel dissociation into $H^+(n=2) + \text{Cl}(2P_{3/2,1/2})$ in the axial recoil limit. By comparison, the alignment of HBr is less complete since triplet virtual states also contribute to the two photon excitation$^{22,24}$

$$X^1\Sigma(0^+) \xrightarrow{h\nu} A^1\Pi_{1/2}, a^3\Pi_{1/2}, A^3\Sigma(1) \xrightarrow{h\nu} 1\Sigma(0^+),$$

(11)
angular distributions can be modeled well by assuming that the resonant excitation process follows to 20% a parallel excitation route ($\eta_1=0.8$), while the excitation to the dissociative state is almost entirely parallel, $|M(0)|^2=1$. Similar contributions for the parallel and perpendicular excitation pathways were found by Regan et al. $^{36}$ and by Smolin et al. $^{54}$ for the one-photon photodissociation of HBr at around 250 nm.

Since the photodissociation of molecules in rotationless electronic states, i.e., $Q(0)$ lines, does not depend on the nature of the one-photon intermediate (virtual) states, it is possible to calculate the $|M(0)|^2$ dynamical parameters from experimentally obtained $\beta_2$ values. Then, by assuming that $|M(0)|^2$ for excitation of the dissociative states are the same for rotationless and aligned ($J=1$) intermediate states, these dynamical parameters can be used to determine $\eta_1$. This assumption seems valid, since for HCl the values for $|M(0)|^2$ were found to be approximately constant for $Q(0)$ and $Q(1)$ lines of the same transition.

The calculated values for $|M(0)|^2$ and $\eta_1$ are presented in Table II. As for HCl, rotational alignment of the intermediate $^1\Sigma$ ($J=1$) states is apparent. For most states the value for $\eta_1$ is consistent with a contribution of about 20% of the parallel ($\Sigma\rightarrow \Sigma\rightarrow \Sigma$) excitation pathway. As indicated by $|M(0)|^2$, the third photon absorption to the dissociative state(s) is a parallel process at higher excitation energies and perpendicular at lower excitation energies.

The $V^1\Sigma(0^+)\ [v=m+6]$ and $[v=m+7]$ states show a marked deviation from this trend, and also the proton images display positive $\beta_4$ parameters and an increase of $\beta_2$ with rotational excitation. All three observations are in contradiction with what is expected by the angular momentum algebra developed by Manzhos et al. $^{22}$ While we have no explanation for this deviation we note that some of the rotational

---

**FIG. 7.** (a) Proton image following 2+1 resonance enhance multiphoton excitation of HBr via the $H\,^1\Sigma(0^+), [v=0]\rightarrow X\,^1\Sigma^+, [v=0]$ transition. The right half shows the inverted image for the $Q$ transition. The right half shows the inverted image with anisotropy parameters $\beta_2$ (solid circles) and $\beta_4$ (empty circles) given for each of the peaks.

\[
X\,^1\Sigma(0^+) \xrightarrow{hv} a\,^1\Pi(0^+) \xrightarrow{hv} X\,^1\Sigma(0^+) .
\]  

Here, the one-photon “virtual” states of HBr have a considerable excitation probability at around 250 nm. They lead to dissociation into H+Br where the bromine atomic photo-fragments may be spin-orbit excited. $^{36,48,55}$

Previous calculations of the anisotropy parameters of the protons for the $Q(1)$ line of the $H\,^1\Sigma^+, [v=0]\rightarrow X\,^1\Sigma^+, [v=0]$ transition have shown that the experimental proton
of the \( V^\Sigma [v=0] \) states to dissociation limit. Consequently, there is a reversal of the dissociation limits. We can assume that the relevant superexcited states that correlate to \( H^+(n=2) \) states, thereby leading to the \( H^+(n=2) \) formation.

Previously published photoelectron images following 2+1 photon excitation of any of the \( \Omega=0 \) intermediate states show a highly anisotropic contribution, \( \beta_2 \geq 1.3 \), from the ionization of \( H^+(n=2) \), i.e., a large contribution of an electron \( p \) wave. From this observation and the vertical displacement of the “slow” proton rings apparent in Fig. 7, it can be concluded that—as for HCl—the \( H^+(n=2) \) fragment is detected predominantly in its \( ^2S \) state. Again, we suggest that this may be due to the fast decay of the \( H^+(2P) \) photofragment. As described above, the \( ^2S \) and \( ^2P \) states of the hydrogen atom, and, to some extent, the potentials that correlate to these limits are Stark mixed in the laser field.

Due to the large spin-orbit coupling constant of the bromine atoms (\( A_{SO}=3685.24 \text{ cm}^{-1} \)),\(^{37,38} \) the dissociation pathways leading to formation of \( H^+(n=2) \) in coincidence with both \( Br(2P_{3/2}) \) and \( (2P_{1/2}) \) can be easily distinguished, as shown in Fig. 7 for the photoexcitation of HBr via the \( H^1\Sigma [v^*=0] \), \( [v^*=0] \) intermediate state. For \( H^+(n=2) \) forming processes, the \( Br(2P_{3/2})/[Br(2P_{1/2})+Br(2P_{3/2})] \) branching fraction (Table II) increases in a remarkably consistent manner with increasing excitation energy from about 35% to over 95%. Also it appears as if both \( H^++Br \) channels are associated with a predominantly parallel excitation, i.e., \( |M(0)|^2 > 0.5 \). The \( H^+(n=2)+Br(2P_{1/2}) \) photodissociation channel is not observed for the transitions via the \( g^3\Sigma^+(0^+) \) and \( V^\Sigma (0^+) [v=m+3] \) states because the three-photon excitation energies are below the respective dissociation threshold.

To quantify the formation of \( H^+(n=2) \) a discussion of the potential energy curves of \( HBr^+ \) is in order. The potential energy curves of \( HBr^+ \) are similar to those of the \( HCl^+ \) discussed above (Fig. 6), with the difference that for \( HBr^+ \) the bound \( A^2\Sigma \) state correlates \( H(n=1)+Br(1D_2) \). Consequently, the associated \( [A^2\Sigma^+ \cdot \cdot \cdot n\ell \cdot \cdot \cdot] \) superexcited states of \( HBr \) do not form electronically excited \( H \) atoms.\(^{60} \) The electronic states of \( HBr^+ \) that correlate adiabatically to the \( H^++Br(2P_{3/2;1/2}) \) channels are the repulsive \( B^2\Sigma^+ \) state with a \( \sigma^2 \pi^2 \sigma^{-1} \) configuration and the repulsive \( (3)^2 \Pi \) state with a \( \sigma^4 \pi^3 \sigma^{-1} \) configuration.\(^{60} \) According to the \( ab \) \textit{initio} calculations of Banichevich et al.,\(^{27} \) the \( B^2\Sigma^+ \) state of \( HBr^+ \) correlates diabatically to the spin-orbit excited bromine atoms while both spin-orbit states of the \( (3)^2 \Pi \) state correlate to the ground state bromine atoms. In the adiabatic limit the two \( \Omega=1/2 \) curves form an avoided crossing and, consequently, there is a reversal of the dissociation limits.

We can assume that the relevant superexcited states that correlate to \( H^+(n=2) \) are low-\textit{n} Rydberg states with \( B^2\Sigma^+ \) and \( (3)^2 \Pi \) ion cores. Table II shows that \( |M(0)|^2 > 0.5 \) for the majority of states probed and, consequently, only parallel \( \Delta\Omega=0 \) transitions will be considered.

For example, the \( 1^5\Sigma(0) \) and \( 3^3\Pi(0) \) states of the type \( [B^2\Sigma^+\cdot\cdot\cdot n\ell \cdot\cdot\cdot] \) with \( 5p\sigma, 5p\pi, \) or \( 5\sigma \) frontier orbitals will diabatically correlate to spin-orbit excited \( Br \) atoms, whereas the respective \([3)^2\Pi \cdot\cdot\cdot n\ell \cdot\cdot\cdot] \) states correlate to ground state bromine. Avoided crossings between these two sets of curves will again lead to a reversal of dissociation limits and in the adiabatic approximation the \([B^2\Sigma^+\cdot\cdot\cdot n\ell \cdot\cdot\cdot] \) and \([3)^2\Pi \cdot\cdot\cdot n\ell \cdot\cdot\cdot] \) states correlate to \( Br(2P_{3/2}) \) whereas the \([3)^2\Pi \cdot\cdot\cdot n\ell \cdot\cdot\cdot] \) states correlate to \( Br(2P_{1/2}) \). The potential energy curves of the superexcited states of \( HBr \) are shown in Fig. 9.

It appears reasonable that with increasing excitation energy the higher lying \([3)^2\Pi \cdot\cdot\cdot n\ell \cdot\cdot\cdot] \) states are excited preferentially over the \([B^2\Sigma^+\cdot\cdot\cdot n\ell \cdot\cdot\cdot] \) states, thereby leading to the
oberved increase in the Br(2P_{1/2}) branching fraction. The minor perpendicular dissociation channel may be explained as excitation of either the 3Σ_g or 1Π_h superexcited states. This proposed pathway assumes that the dissociation process remains adiabatic at all excitation energies and that the change in branching fraction with increasing energy is solely due to preferential excitation of a higher lying state with a different adiabatic correlation limit.

On the other hand, it is difficult to exclude the possibility of a pathway that consists of (direct) excitation of the [B 3Σ^+ ·· nlξ] superexcited states, followed by nonadiabatic interactions due to the spin-orbit coupling with the [(3) 2Π_{1/2} ·· nlξ] superexcited states. In the limits of the Landau-Zener theory, the measured branching fractions are consistent with an interaction strength of ~700 cm^{-1}. Here, the ab initio potential energy curves of Banichevich et al. were used to estimate the potential energy gradients (~6200 cm^{-1} Å^{-1}) at the curve crossing point (3.1 Å).

3. Dissociation of HBr^+

Previously HBr^+ was found to be formed in a large number of vibrational states, presumably by autoionization via one or more superexcited gateway states. Figure 7 shows that the highest lying vibrationally excited states can then dissociate to form protons and bromine atoms in either spin-orbit state. For instance, when HBr^+ has been formed by REMPI through the H 2Σ state, the X 2Π_{1/2} [v^+ = 10] state is the lowest vibrational state that dissociates (Fig. 7). From the potentials calculated by Banichevich et al. it is also apparent that this is the lowest vibrational state for which vertical excitation of the (3) 2Π state is possible (Fig. 9). Both 2Π spin-orbit states with (v^+ ≥ 10) dissociate including the highest bound vibrational levels. This is also observed when HBr^+ is formed through excitation via other intermediate states.

The spatial anisotropy parameters included in Fig. 7 illustrate that HBr^+ dissociates in a direct and parallel process. The kinetic energies and the anisotropy parameters are then consistent with only two dissociation pathways, i.e., pathways (3b) and (3e).

Here it is implied that the dissociation process follows the adiabatic potentials at the avoided crossing of the (3) 2Π_{1/2} with the (2) 2Π_{3/2} state (Fig. 6). The ab initio potentials by Banichevich et al. show that both (3) 2Π spin-orbit states cross the B 2Π_{1/2} state at short internuclear distance. For the Ω=1/2 states this results in an avoided crossing and an excitation of the (3) 2Π_{1/2} followed by adiabatic dissociation will yield excited bromine atoms. This is indeed observed to be the dominant process—as is expected from a simple Landau-Zener-type calculation using the ab initio curves and an estimated interaction term of 700 cm^{-1}. With an interaction term >500 cm^{-1} a diabatic dissociation process for the Ω=1/2 component is negligible for all proton kinetic energies used in this study.

It is conceivable that direct excitation of the B 3Σ^+ state also contributes to the formation of H^+ + Br(2P_{1/2}), but by Franck-Condon arguments lower vibrational states of HBr^+ would then also be expected to dissociate. Also, the electron configuration of the (σ^2 π^2 σ^−1) B 3Σ^+ state differs by two spin orbitals from the HBr^+ ground state configuration, whereas the (σ^2 π^2 σ^−1) (3) 2Π state can be excited in a “one-electron” transition.

IV. SUMMARY AND CONCLUSIONS

Molecular beam cooled HCl and HBr samples were laser excited using 2+1 resonance enhanced multiphoton excitation via a number of (Ω=0) states. The proton kinetic energy and angular distribution were determined using velocity map imaging. The images show that—for both halogen halides—protons are formed by two major mechanisms.

Protons with low kinetic energy were formed by dissociation of the excited hydrogen halide,HX^*, into H^+(n=2) + X(2P). Depending on the intermediate state between 60% and 95% of the chlorine was formed in 2P_{1/2}, while H^+(n=2) was detected largely as 2S—a consequence of the short radiative lifetime of the 2P state. We identified parallel excitation of the repulsive [(2) 2Π ·· 4ξ] superexcited states as the dominant dissociation pathway for HCl. For HBr an increase of the Br(2P_{1/2})/Br(2P_{3/2}) branching ratio is observed with increasing excitation energy. Here, it is likely that at high photon energy the higher lying [(3) 2Π_{1/2} ·· nlξ] Ω=0 superexcited states are excited preferentially over the [B 3Σ^+ ·· nlξ] states.

Protons with higher kinetic energy were formed by one-photon excitation and dissociation of HX^*. Previous work had identified the distribution of HX^*[v^+] vibrational states formed by 2+1 resonance enhanced multi-photon (auto-)ionization. The combination of this distribution with the present measurements of proton kinetic energy distributions results in a quantum yield for dissociation that, e.g., in
case of excitation at 238 nm, peaks at 40% for HCl$^*$(v=6).
Based on the spin-orbit components in the kinetic energy spectrum and the near limiting spatial anisotropy of the protons, an argument is made for the parallel excitation and dissociation of both $A^1S^2_{1/2}$ and (2) $^3H^2$ states. For HBr the data are more ambiguous, but also indicated that predominantly HBr$^*$(v=8) dissociates, peaking at a quantum yield of close to 100% for HBr$^*$(v=12). The spatial anisotropy of the protons and their kinetic energy is consistent with photodissociation of both spin-orbit components of the repulsive (a1dπd2r1) (3)$^3H^2$ state. This work has demonstrated that by selection of the intermediate state one can create molecular ions in highly excited vibrational states. Subsequent one-photon dissociation combined with velocity map imaging allows for the characterization of the ions’ repulsive excited states.

Because of the restrictions imposed by the one-color excitation scheme, only “snapshots” of the branching ratios and quantum yields could be obtained. Potential parameters and quantum yields for dissociation may be obtained by a two-color excitation scheme similar to that used by Webb et al. combined with proton and photoelectron imaging.

For HCl a third process was observed to contribute to the formation of protons. The photodissociation of rotationally selected two-photon excited states was observed to form the H$^+$-Cl$^-$ ion pair. Interestingly, this process had a particularly large contribution when the lower state was the $V^1S^2$(0) [v=12] state with a nominal ion-pair electron configuration, $\sigma^2\pi^2\sigma^0$. A mechanism is proposed by which a bound state $\Sigma^+$ superexcited state is excited at its attractive wall, but subsequently predissociated through interactions with the ion-pair state near its repulsive wall. The process contributes a surprising 23% to the total proton signal and may be a source for state-selected Cl$^-$ ions with a well-defined velocity in future collision studies.

Complete state-to-state correlation is one of the major goals in molecular dynamics. With this work we exploit the fact that the lower state can be rotationally selected prior to dissociation into the H$^+$-X($^2P$) photofragments. Two-photon excitation further permits rotational alignment of the intermediate state. Comparison of the proton spatial anisotropy parameters that were measured when exciting through a rotationless intermediate state and through a rotating intermediate state is fully consistent with previous theoretical and experimental studies.

ACKNOWLEDGMENTS

The authors thank Dr. Sergei Manzhos for many insightful comments, especially regarding the intermediate state alignment. They also thank Dr. Scott W. Hopkins for proofreading the manuscript. This work was financially supported by the Natural Sciences and Engineering Research Council of Canada.

(2003).
53 See EPAPS Document No. E-JCPSA6-127-021731 for a detailed analysis of the mechanisms by which H*(n=2) may be formed. This document can be reached through a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).