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Photofragmentations, state interactions, and energetics of Rydberg and ion-pair states: Resonance enhanced multiphoton ionization via E and V (B) states of HCl and HBr

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$(2 + n)$ resonance enhanced multiphoton ionization mass spectra for resonance excitations to diabatic $E^1\Sigma^+$ (v') Rydberg and $V^1\Sigma^+$ (v') ion-pair states (adiabatic $B^1\Sigma^+$ (v') states) of H^{*i*}Cl ($i = 35, 37$) and H^{*i*}Br ($i = 79, 81$) were recorded as a function of excitation wavenumber (two-dimensional REMPI). Simulation analyses of ion signal intensities, deperturbation analysis of line shifts and interpretations of line-widths are used to derive qualitative and quantitative information concerning the energetics of the states, off-resonance interactions between the E states and V states, closest in energy as well as on predissociation channels. Spectroscopic parameters for the $E^1\Sigma^+$ (v') ($v' = 1$) for H³⁵Cl and $v' = 0$ for H⁷⁹Br states, interaction strengths for $E - V$ state interactions and parameters relevant to dissociation of the E states are derived. An overall interaction and dynamical scheme, to describe the observations for HBr, is proposed. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4776260>]

INTRODUCTION

VUV (vacuum ultraviolet)^{1,2} and REMPI^{3–10} spectroscopic studies of the hydrogen-halides have revealed and led to characterization of large number of electronically excited states. It is customary to group these into valence and Rydberg states. The former group of states consists of low energy repulsive states correlating with the ground atomic and spin-orbit excited halogen species $H + X(^2P_{3/2})/X(^2P_{1/2})$ and the ion-pair state $V^1\Sigma^+$ which correlates with the ground ionic species $H^+ + X^-$. The dominant configuration of the ion-pair state is $\sigma\pi^4\sigma^*$.¹¹ The Rydberg states, which have been observed, have ground and/or spin-orbit excited ion cores ($^2\Pi_{3/2,1/2}$) and electronic configurations $\sigma^2\pi^3 n l \lambda$. Perturbations observed in spectra as line shifts or intensity anomalies^{3,4,7,9,12–18} are indicative of state interactions and state mixings which vary largely in nature and magnitude. These are mostly due to Rydberg to repulsive valence state interactions, seen as line-width broadenings due to predissociations or as line shifts and/or intensity alterations due to interactions between Rydberg and ion-pair vibrational states.^{3,4,7,9,12–16,18} Rydberg to Rydberg state interactions are also observed.^{7,13,18}

The strongest state interactions are observed between the diabatic $E^1\Sigma^+(4p\pi)$ Rydberg states and the diabatic $V^1\Sigma^+(\sigma\pi^4\sigma^*)$ ion-pair states which merge together to give the lowest energy $B^1\Sigma^+$ adiabatic potential curves in calculations.^{11,19} The B states show double minima closely corresponding to the average internuclear distances of the E and the V states. This shows as dramatic alterations in energy quantum levels, hence vibrational and rotational parameters,

from that for unperturbed states.²⁰ Thus, quantum energy levels of the Rydberg vibrational states are compressed, whereas those for the ion-pair states expand to give lower and higher rotational parameters, respectively.¹⁴ Dynamic studies, by use of photofragment imaging techniques coupled with REMPI for HCl and HBr have revealed various photoionization processes for these states.²¹

Recently, we have used the two-dimensional (2D) REMPI technique to study photofragmentation processes and state interactions for HCl and HBr,^{12,15,16,18} which show as signal line shifts, intensity alterations, and line-width broadenings, depending on the total angular momentum quantum numbers (J'). Quantitative analyses based on level-to-level interactions have allowed determinations of interaction strengths and parameters relevant to photofragmentation processes. These analyses revealed that Rydberg states, both interacting with repulsive valence states and ion-pair states, play central role as gateway states for ion-pair state dissociations.¹⁸ Such interaction patterns could be important for molecular photodissociation processes in general. Main emphasis, so far, has been on weak to medium strong near-resonance state interactions between Rydberg and ion-pair states, but stronger off-resonance, homogeneous state interactions, such as those between the $E^1\Sigma^+$ and the $V^1\Sigma^+$ states, are likely to be of more importance for fragmentation processes.

In this paper, we present data and analysis relevant to interactions between $E^1\Sigma^+$ and $V^1\Sigma^+$ states, predissociation processes involved, as well as energetics of the states, both for HCl and HBr.

EXPERIMENTAL

Following laser excitations ion yield signals were recorded as a function of mass and laser radiation

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wavenumber to obtain two-dimensional REMPI data for jet cooled HCl and HBr samples. The apparatus used is similar to that described in Refs. 12, 18, and 22. Experimental parameters are given in the supplementary material.²³ Tunable excitation radiation in the 460–520 nm wavelength region was generated by an excimer laser pumped dye laser system, using a Lambda Physik COMPex 205 excimer laser and a Coherent ScanMatePro dye laser. Frequency doubled radiation was focused into an ionization chamber between a repeller and extractor plates. We operated the jet in conditions that limited cooling in order not to lose transitions from high rotational levels. Thus, undiluted, pure gas samples were used. Ions formed were extracted into a time-of-flight tube and focused onto a MCP detector. Signals were fed into a LeCroy WaveSurfer 44MXs-A, 400 MHz storage oscilloscope and stored as a function of flight time. Average signal levels were evaluated and recorded for a fixed number of laser pulses (typically 100 pulses) to obtain mass spectra. REMPI spectra for certain ions as a function of excitation wavenumber (1D REMPI) were obtained by integrating relevant mass signal intensities. Care was taken to prevent saturation effects as well as power broadening by minimizing laser power. Laser calibration was performed by recording an optical galvanic spectrum, obtained from a built-in neon cell, simultaneously with the recording of the REMPI spectra. Line positions were also compared with the strongest hydrogen chloride rotational lines reported by Green *et al.*⁵ The accuracy of the calibration was found to be about $\pm 2.0 \text{ cm}^{-1}$ on a two-photon wavenumber scale. Intensity drifts during the scan were taken into account, and spectral intensities were corrected accordingly.

RESULT AND ANALYSIS

Spectra and energy levels

Mass-resolved ($2 + n$) REMPI spectra are shown for the excitation regions 83 200–84 250 cm^{-1} and 85 600–86 440 cm^{-1} for H^{35}Cl in Figs. 1(a) and 1(b), respectively. Peaks due to two-photon resonance transitions from the ground state $X^1\Sigma^+$ to $E^1\Sigma^+(v' = 0, 1)$ (hereafter named $E(0)$ and $E(1)$) and $V^1\Sigma^+(v' = 10, 11, 14, 15)$ (named $V(10)$ – $V(15)$) as well as $g^3\Sigma^-(v' = 1)$ are assigned. The spectra intensities for $V(10)$ and $V(14)$ are noticeably weaker than those for $V(11)$ and $V(15)$. The spectrum for $V(10)$ has been amplified in Fig. 1(a) for clarification. Mass-resolved ($2 + n$) REMPI spectra are shown for the excitation region 77 540–78 480 cm^{-1} for H^{79}Br in Fig. 1(c). Peaks due to the transitions from the ground state $X^1\Sigma^+$ to $E^1\Sigma^+(v' = 0)$ ($E(0)$) and $V^1\Sigma^+(v' = m + 4, m + 5)$ ($V(m + 4)$ and $V(m + 5)$) are assigned. The spectra intensities for $V(m + 5)$ are noticeably weaker than those for $V(m + 4)$.

Rotational level energies were derived from the line positions and the rotational level energies of the ground state^{24,25} (see Fig. 2). When more rotational lines have been observed by others,^{2,5,8} these were added to our data. To a first approximation an unperturbed state will show linear behaviour for the energy spacing between neighbour energy levels, $\Delta E_{J',J'-1} (=E(J') - E(J'-1))$, as a function of J' with a slope of $2B_{v'}$, where $B_{v'}$ is the v' -dependent rotational constant. Observed

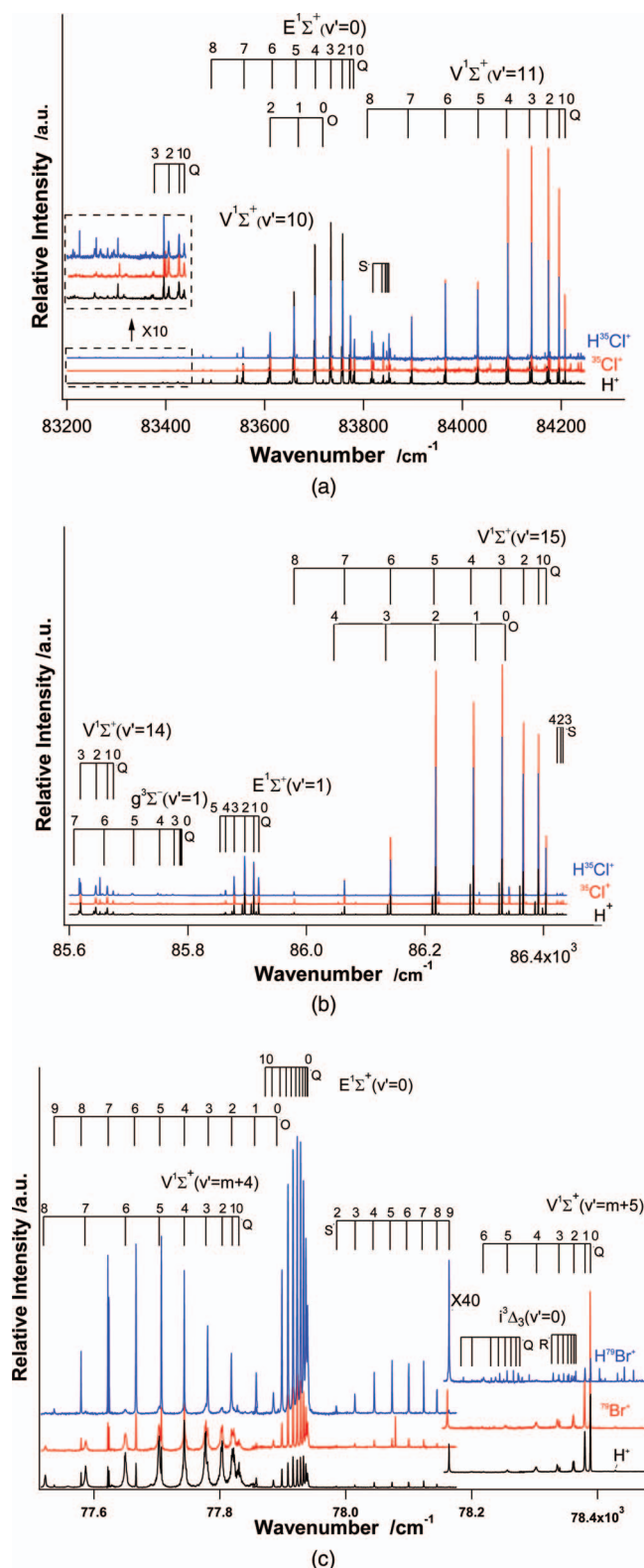


FIG. 1. (a) and (b) HCl: 1D REMPI spectra for H^+ , $^{35}\text{Cl}^+$, H^{35}Cl^+ and J assignments for rotational peaks corresponding to two-photon resonance excitations to the $E^1\Sigma^+(v' = 0, 1)$, $V^1\Sigma^+(v' = 10, 11, 14, 15)$ and $g^3\Sigma^-(v' = 1)$ states for the excitation regions 83 200–84 250 cm^{-1} (a) and 85 600–86 440 cm^{-1} (b). (c) HBr: 1D REMPI spectra for H^+ , $^{79}\text{Br}^+$, H^{79}Br^+ and J assignments for rotational peaks corresponding to two-photon resonance excitations to the $E^1\Sigma^+(v' = 0)$, $V^1\Sigma^+(v' = m + 4, m + 5)$ and $i^3\Delta_3(v' = 0)$ states for the excitation region 77 520–78 450 cm^{-1} .

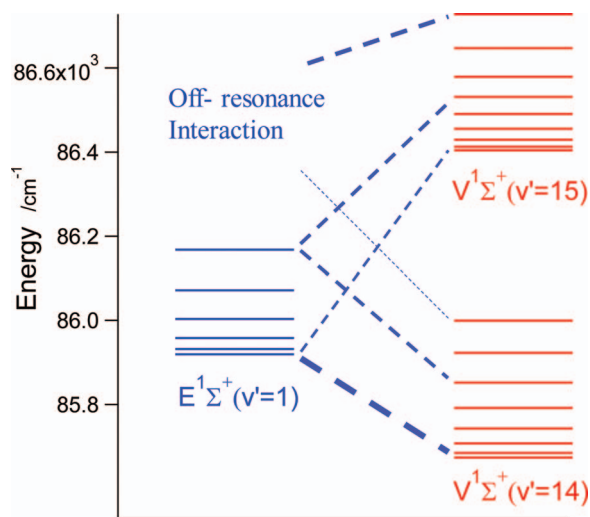


FIG. 2. HCl: Rotational energy levels, derived from the observed REMPI rotational peaks for the $E^1\Sigma^+(v'=1)$ and $V^1\Sigma^+(v'=14, 15)$ states. Level-to-level off-resonance interactions between the $V(v')$ ion-pair states and the $E(v')$ Rydberg states are indicated by broken lines. Strength and alterations in state mixings are indicated, roughly, by varying thickness of broken lines.

curvatures or irregular shapes of $\Delta E_{J',J'-1}$ as a function of J' (Fig. 3) indicate strong homogeneous off-resonance state interactions, of which those between the E and the neighbour V states will dominate. The interaction is “repulsive” in nature, showing as an increase in spacing between energy levels with same J' quantum numbers, $\Delta E_{J'}(E, V)$ ($=E_{J'}(E) - E_{J'}(V)$), where $E_{J'}(E)$ and $E_{J'}(V)$ are the energy levels for the E and the V states, respectively (see Table I). The repulsion effect depends on the degree of state mixing which decreases as $\Delta E_{J'}(E, V)$ increases. Therefore, since the spacing between neighbour energy levels ($\Delta E_{J',J'-1}$) in ion-pair states are smaller than the corresponding spacings in Rydberg states, the repulsion effect, hence the mixing, increases with J' for an interaction between a Rydberg state and a higher energy ion-pair state (V_H) but decreases with J' for a corresponding interaction with a lower energy ion-pair state (V_L). This is indicated in Fig. 2 by varying thickness of broken lines in the case of the interactions between $E(1)$ and $V(14)/V(15)$. This effect explains the positive curvatures seen in the $\Delta E_{J',J'-1}$ vs J' plots for the V_H states $V(15)$ and $V(11)$ for HCl and negative curvatures seen for the V_L states $V(14)$ and $V(10)$ for HCl

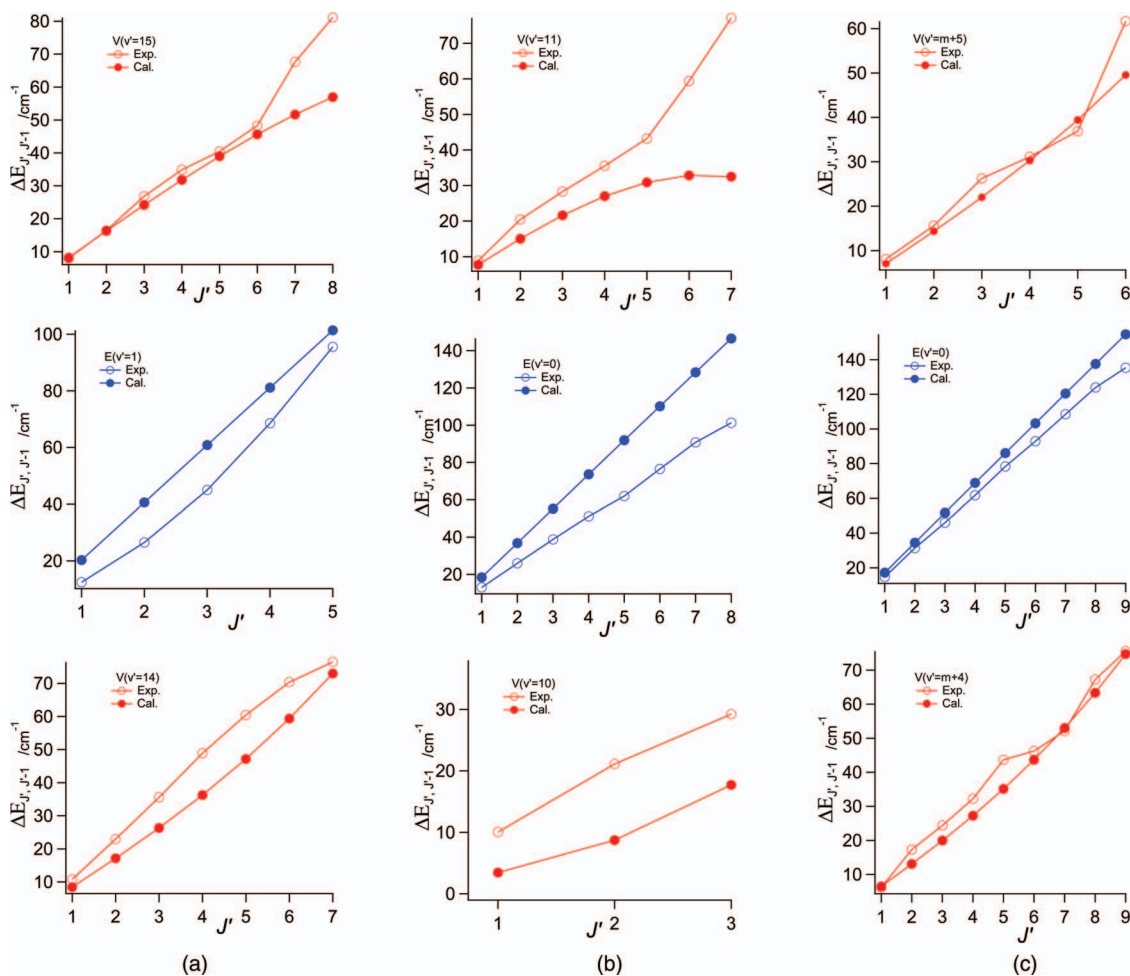


FIG. 3. (a) and (b) $H^{35}Cl$: Spacings between rotational levels ($\Delta E_{J',J'-1}$) as a function of J' for $V^1\Sigma^+(v'=15)$ ((a), top), $E^1\Sigma^+(v'=1)$ ((a), middle), $V^1\Sigma^+(v'=14)$ ((a), bottom), $V^1\Sigma^+(v'=11)$ ((b), top), $E^1\Sigma^+(v'=0)$ ((b), middle) and $V^1\Sigma^+(v'=10)$ ((b), bottom). (c) $H^{79}Br$: Spacings between rotational levels ($\Delta E_{J',J'-1}$) as a function of J' for $V^1\Sigma^+(v'=m+5)$ ((c), top), $E^1\Sigma^+(v'=0)$ ((c), middle) and $V^1\Sigma^+(v'=m+4)$ ((c), bottom). Open circles are derived from observed Q lines (this work and Refs. 2, 5, and 8). Filled circles are derived from deperturbation calculations (see text).

TABLE I. $\Delta E_{J'}$ relevant to off-resonance interactions between $E^1\Sigma^+(v' = 1)$ and $V^1\Sigma^+(v' = 14,15)$ states (H^{35}Cl) (left), $E^1\Sigma^+(v' = 0)$ and $V^1\Sigma^+(v' = 10,11)$ states (H^{35}Cl) (middle) and $E^1\Sigma^+(v' = 0)$ and $V^1\Sigma^+(v' = m + 4, m + 5)$ states (HBr) (right).

J'	H^{35}Cl		H^{35}Cl		H^{79}Br	
	$\Delta E_{J'}(E(1)-V(14))$	$\Delta E_{J'}(V(15)-E(1))$	$\Delta E_{J'}(E(0)-V(10))$	$\Delta E_{J'}(V(11)-E(0))$	$\Delta E_{J'}(E(0)-V(m+4))$	$\Delta E_{J'}(V(m+5)-E(0))$
0	246.0	485.1	346.4	427.7	110.8	447.8
1	247.7	480.7	348.8	423.6	119.3	441.2
2	251.4	470.6	354.2	418.1	133.4	425.4
3	260.7	452.5	363.5	407.7	155.1	405.6
4	280.3	418.8	377.9 ^a	392.1	184.6	375.0
5	315.4	363.8	398.2 ^a	373.3	219.3	333.5
6			430.8 ^a	356.2	266.0	302.2
7			479.0 ^a	342.6	322.3	266.0 ^b
8			542.9 ^a		379.0	235.0 ^b
9					438.8	200.0 ^b

^aValues estimated by use of spectroscopic parameters for $V(10)$.^bValues estimated by extrapolation.

(Fig. 3). The clear positive curvature seen in the $\Delta E_{J',J'-1}$ vs J' plot for the $E(1)$ state (Fig. 3(a)) is indicative of a larger repulsion interaction (hence larger mixing) with $V(14)$ compared to that with $V(15)$ due to less energy difference (see Table I and Fig. 2). The “close to linear” shape of the $\Delta E_{J',J'-1}$ vs J' plot (Fig. 3(b)) for $E(0)$, on the other hand, suggests that a decreasing repulsion with J' due to mixing with $V(10)$ closely matches an increasing repulsion with J' due to $V(11)$. This is what might be expected from inspection of the energy differences (Table I).

Signal intensities and interpretations

It has been shown that ion signal intensities in one-color REMPI differ largely depending on the resonance excited states of HCl ^{3,12,15,16} and HBr .^{8,18} “Pure” unperturbed Rydberg states mostly result in parent ion signals whereas ion-pair states, mixed with Rydberg states, give both fragment and molecular ions with an increasing contribution of the fragment ion signals as the mixing decreases. Rydberg states mixed with ion-pair states, show fragment ion signals depending on the degree of mixing and interaction strength. Accordingly, ion signal ratios, $I(\text{X}^+)/I(\text{HX}^+)$ ($\text{X} = \text{Cl}, \text{Br}$), are found to vary with J' . In addition, J' -independent contributions to the signal ratios have been found for some Rydberg state excitations. These are believed to be due to dissociation channels.¹⁶

Figures 4(a) and 4(b) show $I(^{35}\text{Cl}^+)/I(\text{H}^{35}\text{Cl}^+)$ as a function of J' for H^{35}Cl , $E(1)$ and $E(0)$, respectively. Similar graphs were obtained for H^{37}Cl . The sharply decreasing intensity ratio with J' for $J' \geq 1$, observed for $E(1)$ (Fig. 4(a)) indicates decreasing overall mixing of the $E(1)$ state with ion-pair states as J' increases. This fits with a dominating mixing with the $V(14)$ state in agreement with the conclusion from the energy level shifts, mentioned above. The “close to constant” or “slightly decreasing” intensity ratio vs. J' observed for $E(0)$ (Fig. 4(b)) suggests analogous total mixing of $E(0)$ with $V(10)$ and $V(11)$, also in agreement with the conclusion above. Figure 4(c) shows $I(^{79}\text{Br}^+)/I(\text{H}^{79}\text{Br}^+)$ as a function of J' for H^{79}Br , $E(0)$. Similar graph was obtained for H^{81}Br . The intensity ratio shows a decrease with J' for J'

= 1–5, a minimum near $J' = 5$ –8 and significant increase for $J' = 9$. This is a clear indication of a decreasing mixing of $E(0)$ with $V(m+4)$ but an increasing mixing with $V(m+5)$ as J' increases.

Intensity ratios vs. J' have been expressed as a function of fractional contributions to the state mixing, derived for two-level interactions.¹⁷ The assumption is made that the ion intensity ratio is a sum of contributions due to interactions between a Rydberg state (1) and two ion-pair vibrational states ($2H$ and $2L$), such as those between the $E(v')$ and the $V(V_H$ and $V_L)$ states. Thus, an expression for $I(\text{X}^+)/I(\text{HX}^+)$ ($\text{X} = \text{Cl}, \text{Br}$), depending on the fractional contributions of the V_I ($I = H, L$) states to the state mixing (c_{2I}^2 ($I = H, L$)) as well as on parameters which depend on relative rates of ionizations (α_I and γ_I ; $I = H, L$) is derived.^{12,23} The state mixings depend on the energy spacings between levels with same J' quantum numbers for the Rydberg state (1) and the $2H$ and $2L$ states, respectively, ($\Delta E_{J'}(1,2H)$ and $\Delta E_{J'}(1,2L)$) as well as the corresponding interaction strengths (W_L and W_H). The energy spacings can easily be derived from energy levels (Table I). To a first approximation $W_L = W_H = W$, $\alpha_L = \alpha_H = \alpha$ and $\gamma_L = \gamma_H = \gamma$ is assumed. α measures the rate of the X^+ formation for excitation from the ion-pair states to the HX^+ formation from the Rydberg state, whereas γ represents the rate of X^+ formation via the Rydberg state to that of its formation from the ion-pair states.

The intensity ratios shown in Fig. 4 were fitted to derive the contributions due to the E vs. V_L and E vs. V_H state mixings as well as the α and γ values in the following way.

Careful investigation of the ion intensity ratio for H^{35}Cl , $E(1)$ (Fig. 4(a)) revealed that the values for $J' = 0$ and 1, where mixing with $V_L(V(14))$ is dominant, are equal within experimental error. This suggests that the mixings, c_1^2 and c_{2L}^2 are equal, i.e., $c_1^2 = c_{2L}^2 = 0.5$. This corresponds to a value of $W(E(1), V_L) = \Delta E_{J'}/2$ ¹⁵ which gives $W \approx 123 \text{ cm}^{-1}$ (see Table I). This allows to estimate the fractional contributions to the mixing as a function of J' . A fit shown in Fig. 4(a), for the parameters listed in Table II, was obtained. This shows that the drop in the intensity ratio for $J' > 1$ is mostly due to the decreasing mixing of $E(1)$ and $V(14)$ as J' increases whereas the contribution due to the $E(1)$ and $V(15)$

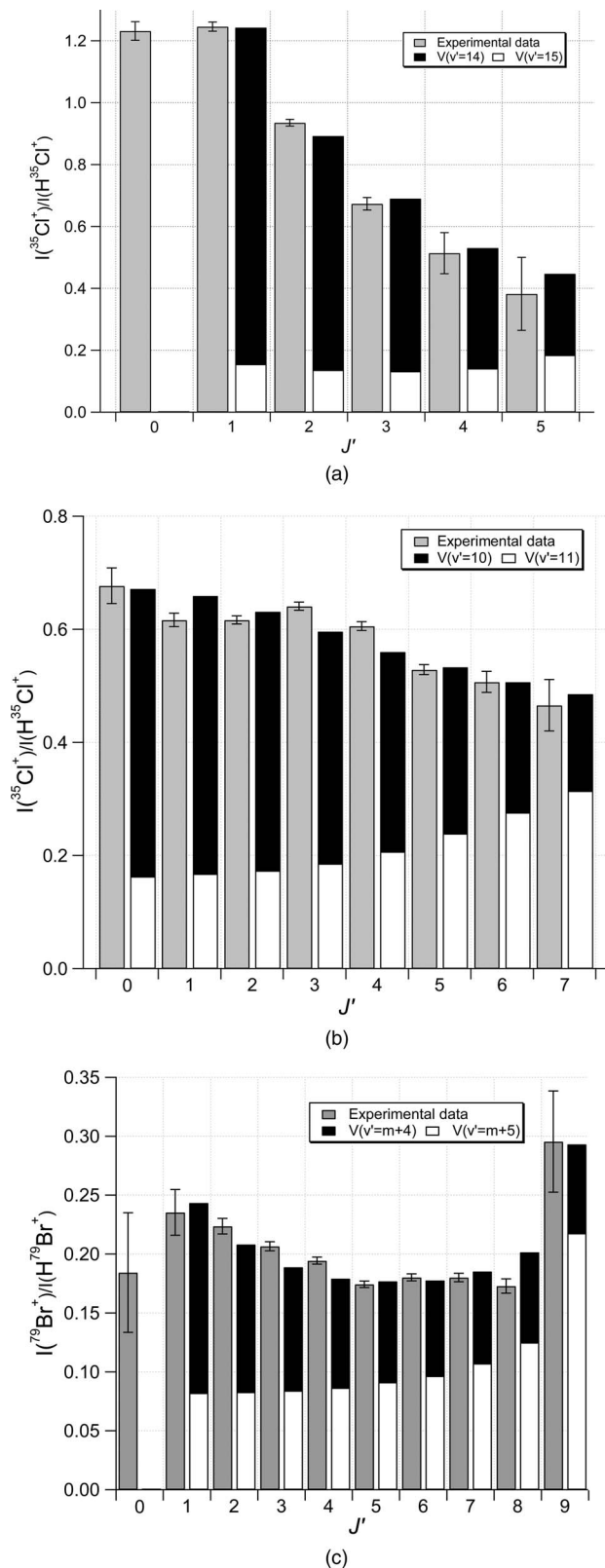


FIG. 4. (a) and (b) H^{35}Cl : Relative ion signal intensities, $I(^{35}\text{Cl}^+)/I(\text{H}^{35}\text{Cl}^+)$ vs. J' derived from Q rotational lines of REMPI spectra due to two-photon resonance excitations to the Rydberg states $E^1\Sigma^+$ ($v'=1$) (a) and $E^1\Sigma^+$ ($v'=0$) (b). (c) H^{79}Br : Relative ion signal intensities, $I(^{79}\text{Br}^+)/I(\text{H}^{79}\text{Br}^+)$ vs. J' derived from Q rotational lines of REMPI spectra due to two-photon resonance excitations to the Rydberg state $E^1\Sigma^+$ ($v'=0$). Gray columns are experimental values. The black and white columns are calculated values for the contributions due to the interactions of the $E(v')$ states with the lower energy V states (V_L) and the higher energy V states (V_H), respectively.

TABLE II. Parameters used in analysis if relative ion signal intensities $I(^X\text{X}^+)/I(\text{H}^X\text{X}^+)$ ($X = ^{35}\text{Cl}, ^{79}\text{Br}$) as a function of J' for $(2+n)$ REMPI of $E^1\Sigma^+(v')$ Rydberg states (see definitions in text).

	$E(v'=1)$ HCl	$E(v'=0)$ HCl	$E(v'=0)$ HBr
W_L (cm^{-1})	123	152	57
W_H (cm^{-1})	123	152	100
α	1.1	0.9	0.2
γ	~ 0	~ 0	0.4

mixing is almost unchanged with J' . The value for γ of about zero suggests that dissociation of $E(1)$ is negligible.

The monotonically decreasing intensity ratio as a function of J' observed for $E(0)$, HCl, did not allow an unique solution of all the variables to be derived. Deperturbation analysis of HCl spectral data by Liyanage *et al.*²⁰ revealed interaction strength of about 187 cm^{-1} for the interaction between $E(0)$ and $V(10)$. An improved fit for the ion intensity ratio vs. J' was obtained by lowering the interaction strength, but accurate value for W could not be determined. Figure 4(b) shows fit of the intensity ratio for $E(0)$ vs. J' for the parameters listed in Table II. Clear decrease in the contribution due to the $E(0)$ and $V(10)$ mixing and increase in the contribution due to the $E(0)$ and $V(11)$ mixing is seen as J' increases. This shows a resemblance with results given by Liyanage *et al.*^{20,26} derived from deperturbation analysis for $E(0)$, $V(10)$, and $V(11)$, where percentage mixing of the $V(10)$ and $V(11)$ states with $E(0)$ are found to decrease and increase with J' , respectively. The results presented by Liyanage *et al.*²⁶ on the other hand show a decreasing diabatic character of the $E(0)$ state with J' considering also mixing with the Rydberg states $g^3\Sigma_0^-$ and $g^3\Sigma_1^-$ whereas our intensity ratios, which only represent Rydberg to ion-pair state mixing, show close to constant mixing of $E(0)$ as J' increases.²³ A value for γ of about zero suggests that dissociation of $E(0)$ is minor, analogous to that found for $E(1)$.

Analysis of the intensity ratio data for HBr, $E(0)$ revealed decrease in the contribution due to the $E(0)$ and $V(m+4)$ mixing and increase in the contribution due to the $E(0)$ and $V(m+5)$ mixing as J' increases as shown in Fig. 4(c). These results were obtained for the parameters listed in Table II. The nonzero value for γ differs from that derived for HCl and suggests that photodissociation via $E(0)$ excitation is of important. This is further supported by line-width analysis (see below).

Line shifts and deperturbations

In cases of weak near-resonance level-to-level interactions, localized line shifts, hence energy level shifts, from regular patterns, can be used to evaluate deperturbed energy levels and interaction strengths. In cases of stronger off-resonance interactions, such as between E and V states, where gradually changing state mixing, is observed, more sophisticated treatment of state interactions needs to be performed. As an attempt to evaluate deperturbed energy levels and spectroscopic constants, as well as interaction strengths, for $E(1)$ for HCl and $E(0)$ for HBr, we performed simplified

TABLE III. Spectroscopic parameters derived from direct analysis of observed spectral lines (Obs.) and from deperturbation analysis (Dep.) (see text), (a) for $E^1\Sigma^+(v' = 1)$, $V^1\Sigma^+(v' = 14, 15)$ (H^{35}Cl) by using interaction strengths $W_L = 124 \text{ cm}^{-1}$ and $W_H = 126 \text{ cm}^{-1}$. Observed values are from this work (above) and from Ref. 3 (below). (b) For $E^1\Sigma^+(v' = 0)$, $V^1\Sigma^+(v' = 10, 11)$ (H^{35}Cl) by using interaction strengths $W_L = 191 \text{ cm}^{-1}$ and $W_H = 194 \text{ cm}^{-1}$. Observed values are from this work and from Ref. 3 (below). (c) For $E^1\Sigma^+(v' = 0)$, $V^1\Sigma^+(v' = m + 4, m + 5)$ (H^{79}Br) by using interaction strengths $W_L = 57 \text{ cm}^{-1}$ and $W_H = 97 \text{ cm}^{-1}$. Observed values are from this work (top) and from Refs. 8 (middle) and 2 (bottom).

(a) For $E^1\Sigma^+(v' = 1)$, $V^1\Sigma^+(v' = 14, 15)$ (H^{35}Cl)						
	$E(v' = 1)$		$V(v' = 14)$		$V(v' = 15)$	
	Obs.	Dep.	Obs.	Dep.	Obs.	Dep.
v^0	85 919.7	85 843	85 674	85 773	86 405	86 374
	85 919.8		85 671.7		86 404.6	
B'	6.18	10.1	...	4.2	3.99	4.1
	6.028		6.126		4.01	
$D' \times 10^3$	-69.9	0.12	...	-10	-6.66	12
	-79.55		4.529		-3.648	
(b) For $E^1\Sigma^+(v' = 0)$, $V^1\Sigma^+(v' = 10, 11)$ (H^{35}Cl)						
	$E(v' = 0)$		$V(v' = 10)$		$V(v' = 11)$	
	Obs.	Dep.	Obs.	Dep.	Obs.	Dep.
v^0	83 780.4	83 696	83 434.5	83 609	84 207.66	84 125
	83 780.0		83 434.0		84 208.0	
B'	6.40	9.2	5.27	1.6	4.41	3.9
	6.6257		5.05		4.348	
$D' \times 10^3$	0.29	0.39	19.45	-76	-7.58	16
	3.1134		-24.1		-6.872	
(c) For $E^1\Sigma^+(v' = 0)$, $V^1\Sigma^+(v' = m + 4, m + 5)$ (H^{79}Br)						
	$E(v' = 0)$		$V(v' = m + 4)$		$V(v' = m + 5)$	
	Obs.	Dep.	Obs.	Dep.	Obs.	Dep.
v^0	77 940.8	77 927	77 830	77 865	78 389	78 369
	77 939.5		
	77 940		77 832		78 389.5	
B'	7.78	8.6	4	3.2	3.8	3.5
	7.721		
	7.6		3.9		3.79	
$D' \times 10^3$	0.8	0.16	0.4	-6	-10.7	-9
	0.3		
	-1.7		-2.1		-1.4	

deperturbation calculations. To a first approximation, we assumed that the perturbation effects on an $E(v')$ state is only due to homogeneous ($\Delta\Omega = 0$) interactions with the V states closest in energy (V_L and V_H). The diagonal matrix elements (unperturbed energy levels) are expressed in terms of the spectroscopic parameters (v_X^0 , B'_X , D'_X ; $X = E, V_L, V_H$).²³ The off-diagonal matrix elements are the interaction strengths W_L and W_H . The perturbed energy levels were derived from observed spectral lines and known energy levels for the ground state. The spectroscopic parameters for the E and V states were searched for in the deperturbation procedure. An emphasis was placed on the derivation of the rotational constants B'_E and corresponding energy levels for unperturbed E states. In order to evaluate the B'_E 's the number of unknown parameters needed to be lowered. This was done, based on the following criteria:

- (i) $0 < D'_E < 0.001$ was assumed. The unperturbed $E(v')$ states belong to a series of Rydberg states, which converges to the ground ionic states $X^2\Pi$. We, there-

fore, assume that the Rydberg states resemble the ionic states as well as the ground neutral states in terms of centrifugal distortions. The D_e values for H^{35}Cl^+ and H^{81}Br^+ are $5.47 \times 10^{-4} \text{ cm}^{-1}$ and $3.48 \times 10^{-4} \text{ cm}^{-1}$, respectively.^{24,25} The corresponding values for the neutral ground states are $5.3194 \times 10^{-4} \text{ cm}^{-1}$ (H^{35}Cl) and $3.457 \times 10^{-4} \text{ cm}^{-1}$ (H^{81}Br), respectively.^{24,25} Assuming the D 's for the $E(v')$ states to be of the same order of magnitude, it is realistic to assume $0 < D'_E < 0.001$.

- (ii) $W_L \leq W_H$ was assumed for W_L and W_H close to the W values derived from the intensity ratio analysis, mentioned earlier. In the diabatic approximation, the state interaction strength (W) is proportional to the vibrational wavefunction overlap^{11,20} for the Rydberg vs. the ion-pair states. For a fixed $E(v')$ state, this corresponds to an increasing value of W as a function of v' for the ion-pair state, hence $W_L \leq W_H$.

As a test of this method, we calculated B' of $E(0)$ ($B'_{E(0)}$) for HCl as a function of W_L and W_H .²³ A value of $B'_{E(0)} = 8.6 \text{ cm}^{-1}$ was obtained by using equal interaction strengths

of 187 cm^{-1} , corresponding to the W_L derived by Liyanage *et al.*²⁰ in a more detailed deperturbation analysis. This is close to their value of $B'_{E(0)} = 8.37\text{ cm}^{-1}$. These B'_E values are significantly larger than those derived from the perturbed energy levels ($B'_{E(0)} = 6.6257\text{ cm}^{-1}$)³ but smaller than B_e values for the ground ionic state (9.9566 cm^{-1}) and the ground neutral state (10.59341 cm^{-1})²⁴ as well as B'_v values of unperturbed Rydberg states of HCl, which are typically $B'_v = 9\text{--}10.5\text{ cm}^{-1}$.³ Considering the criteria (i) and (ii), on the other hand, values of $B'_{E(0)} = 9.2 \pm 0.3\text{ cm}^{-1}$ and $D'_{E(0)} = 3.9 \times 10^{-4}\text{ cm}^{-1}$ were obtained for $W_L = 191\text{ cm}^{-1}$ and $W_H = 194\text{ cm}^{-1}$ (see Table III).

Analogous analysis of the data for $E(1)$ (HCl) and $E(1)$ (HBr) gave $B'_{E(1)} = 10.1 \pm 0.2\text{ cm}^{-1}$ for $W_L = 124\text{ cm}^{-1}$ and $W_H = 126\text{ cm}^{-1}$ (HCl) and $B'_{E(0)} = 8.6 \pm 0.2\text{ cm}^{-1}$ for $W_L = 57\text{ cm}^{-1}$ and $W_H = 97\text{ cm}^{-1}$ (HBr) (see Table III). The latter value is an increase from the value of 7.721 cm^{-1} for the perturbed state.⁸ It can be compared to the B_e values of 8.072 cm^{-1} and 8.46488 cm^{-1} for the ground ionic and neutral states of HBr, respectively,²⁴ as well as values of B'_v for unperturbed Rydberg states ($B'_v \approx 7.6\text{--}8.7\text{ cm}^{-1}$).^{2,8,10}

Further conclusions, which can be drawn from the deperturbation analysis (see Table III and Fig. 3), are as follows: (a) Term values (band origins), ν^0 , for all the E states and the higher energy V states (V_H) decrease from the observed ν^0 -values whereas an increase is observed for the V_L 's. Therefore, the energy spacing between the vibrational states, V_L and V_H , which has been found to be unusually large,^{9,14} is found to decrease. The energy spacing between the HCl, $E(0)$ and $E(1)$ states increases slightly to about 2147 cm^{-1} . (b) Rotational constants (B'), hence rotational energy level spacing ($\Delta E_{J',J'-1}$), for all the V_I ($I = L, H$) states lower (or stay unchanged) compared to values observed for the perturbed states, in agreement with expectations.¹⁴ (c) The second order rotational constants, D' , increase on an absolute scale for all V_H states and lower for all the V_L 's as a result of deperturbation. For HCl the D' values in fact switch sign from negative to positive values for V_H and from positive to negative values for V_L , which corresponds to a change in $\Delta E_{J',J'-1}$ vs J' plots from showing positive to negative curvatures for V_H and vice versa for V_L (see Fig. 3). These observations are clear indications of further perturbations due to interactions of the V states with other Rydberg states, not taken account of in the deperturbation calculations.

Line-widths

Rotational line-widths of the $E(\nu')$ ($\nu' = 0, 1$) and $V(\nu')$ ($\nu' = 10, 11, 14$, and 15) states REMPI spectra for H⁷⁹Br are all close to our detection limit of about $0.3\text{--}0.4\text{ cm}^{-1}$ which suggests that predissociation is not of major importance for these states^{18,27} (see Figs. 1(a) and 1(b)). This agrees with the derivation of $\gamma \approx 0$ values, hence negligible dissociation, for the E states according to the intensity ratio analysis mentioned before. The lifetime (τ), being inversely proportional to the line-width as^{18,27,28}

$$\tau(\text{ps}) = 5.3 / \Gamma(\text{cm}^{-1}) \quad (1)$$

gives the lower limit value for τ of about 13 ps.

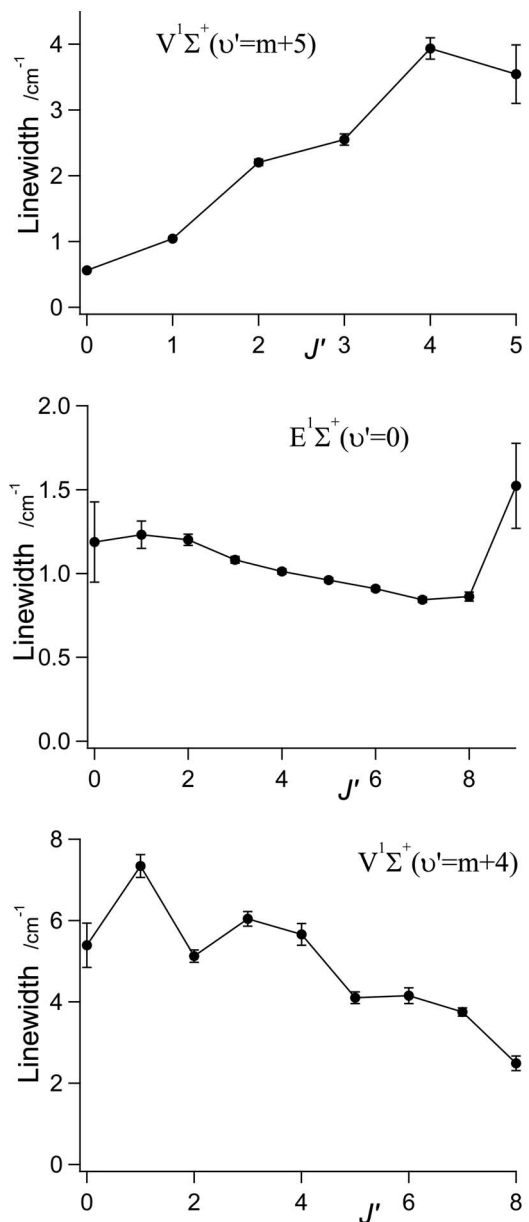


FIG. 5. HBr: Rotational line-widths vs J' derived from Q lines of H⁷⁹Br REMPI spectra for $V^1\Sigma^+(\nu' = m + 5)$ (top), $E^1\Sigma^+(\nu' = 0)$ (middle) and $V^1\Sigma^+(\nu' = m + 4)$ (bottom).

Line-widths of the $E(0)$ and $V(m+i)$ ($i = 4$ and 5) state spectra for H⁷⁹Br, on the other hand, are larger, suggesting that predissociation processes are significant in agreement with the conclusion derived from the intensity ratio analysis which gave $\gamma \neq 0$. Furthermore, the line-widths vary significantly depending on the rotational levels as seen in Figs. 1(c) and 6. Those for the Q lines of the $V(m+5)$ spectrum increase with J' whereas those for the $V(m+4)$ spectrum decrease with J' (Figs. 5(a) and 5(c)). The line-widths for the Q lines of the $E(0)$ spectrum (Fig. 5(b)), generally are smaller and show close correspondence to the intensity ratios as a function of J' (Fig. 4(c)) previously explained to reflect interactions with $V(m+4)$ as well as $V(m+5)$. Because of the inverse relationship between τ and Γ (Eq. (1)), the lifetimes of the $E(0)$ state rotational levels generally are longer than those for the $V(m+4)$ and $V(m+5)$ state levels

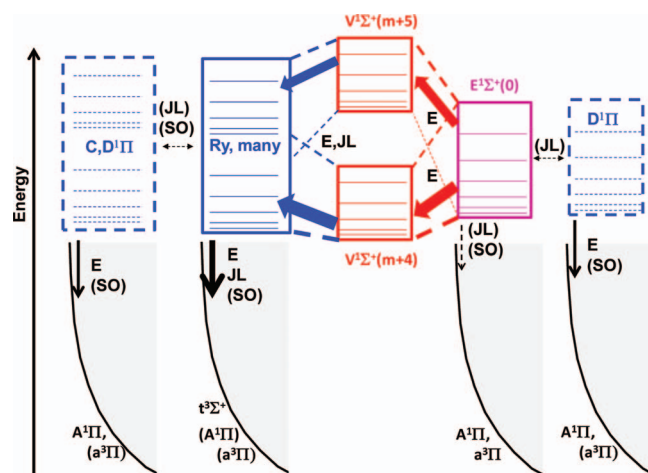


FIG. 6. Schematic figure, showing the HBr energetics, state interactions and energy transfers of relevance to the data presented (see text). Electrostatic, rotational and spin-orbit couplings are marked E , JL and SO , respectively. Red boxes represent the ion-pair states. Blue and purple boxes are Rydberg states and black curves are repulsive states. The blue box with solid lines represents a manifold of many Rydberg states, which couple with the ion-pair states. The blue boxes with broken lines are gateway states with respect to predissociation of other states. Relative importance of couplings and transfers are indicated by different boldness of arrows and broken lines as well as by use of brackets or not. The colored arrows indicate the major paths towards predissociation for the V and E states.

and the lifetimes of the rotational levels for the $V(m+5)$ and $V(m+4)$ decrease and increase with J' , respectively. The alteration in lifetimes, hence line-widths, with J' and the dependence on electronic states reflects different rates of predissociation. This observation suggests that the predissociation of the $E(0)$ state is primarily determined by that of the $V(m+5)$ and $V(m+4)$ states following the state interactions described earlier. Large average internuclear distance of the V state makes crossing to repulsive states, hence direct predissociation, highly improbable.¹⁸ The Rydberg states, on the other hand, are either in close vicinity of, or crossed by, repulsive states to make predissociation processes more probable. Possible interactions involved in indirect predissociations of the $E(0)$, $V(m+4)$, and $V(m+5)$ states are presented semi-schematically in Fig. 6.^{28,29} These involve strong electrostatic interactions (E) between the $E(0)$ and the V states, electrostatic (E) and rotational (JL) couplings of the V states with a manifold of a large number of Rydberg states, such as $g^3\Sigma_0^-$, $g^3\Sigma_1^-$, $e^3\Sigma_0^+$, $e^3\Sigma_1^+$, $f^3\Delta$, $F^1\Delta$ ^{28,29} as well as predissociations of the Rydberg states or gateway-Rydberg states due to state couplings of different nature (E , JL , SO) and strengths. Generally, the E -interactions are the strongest, whereas the JL - and SO -interactions are weak-to-intermediate (Hunds cases (a)-(b)).²⁸ Furthermore, the Franck-Condon-overlap of the Rydberg states with the $f^3\Sigma^+$ states exceeds that of the overlap with the $A^1\Pi$ and $a^3\Pi$ states.²⁹ The major direct predissociation channels, therefore, are believed to be those involving E -interactions between Rydberg states, such as the $e^3\Sigma_0^+$ and $e^3\Sigma_1^+$ states, and the repulsive $f^3\Sigma^+$ states. C and $D^1\Pi_1$ state spectra for HBr (as well as for HCl) all show diffuse structures,^{2,3} which suggests that these states could act as gateway states by strong E -interactions with the $A^1\Pi$ state following weaker JL (and SO) couplings with other Rydberg

states. All in all, this shows that quantum interference effects, involving several states, play important role in the overall interaction process and that the major paths of indirect predissociations of the $E(0)$, $V(m+4)$ and $V(m+5)$ states are likely to be as indicated by the arrows shown in Fig. 6.

CONCLUSIONS

$(2+n)$, 2D REMPI spectra of $H^1Cl(i=35,37)$ and $H^1Br(i=79,81)$ for resonance transitions to $E^1\Sigma^+(v')$ Rydberg states and $V^1\Sigma^+(v')$ states, close in energy, have been recorded and analysed in terms of state interactions, energetics, and photofragmentations. Spectra show large perturbation effects due to J' dependent Rydberg-to-ion-pair state interactions as line broadenings for HCl and HBr as well as line broadenings for HBr. The data are analysed in terms of off-resonance interactions between the $E^1\Sigma^+(v')$ states and two $V^1\Sigma^+(v')$ states, closest in energy, one higher (V_H) and one lower (V_L) in energy. Variation in ion signal intensity ratios ($I(H^1X^+)/I(H^1X^+)$) as a function of J' are shown to be due to altering contributions of the two Rydberg-to-ion-pair state mixing depending on energy differences between quantum levels for the same J' quantum numbers. In cases when different observations depend on the same dynamical properties (state interactions and/or photofragmentations) analysis results are found to be supportive in nature. Thus, simulation calculations of ion signal intensity ratios and deperturbation analyses of line positions as a function of J' reveal interaction strengths as well as deperturbed spectroscopic parameters for the $E^1\Sigma^+(v'=1)$ state of HCl and the $E^1\Sigma^+(v'=0)$ state of HBr. Analysis of both intensity ratios and line-widths are indicative of predissociation processes being negligible for the HCl, $E^1\Sigma^+(v'=0,1)$ states but of significant importance for the HBr, $E^1\Sigma^+(v'=0)$ state. An overall interaction and dynamical scheme, to describe the observations for HBr is proposed, where the ion-pair states play central role in the dissociation of the E states via off-resonance interactions followed by predissociation of Rydberg states.

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- S. G. Tilford, M. L. Ginter, and A. M. Bass, *J. Mol. Spectrosc.* **34**, 327 (1970); S. G. Tilford, M. L. Ginter, and J. T. Vanderslice, *ibid.* **33**, 505 (1970); S. G. Tilford and M. L. Ginter, *ibid.* **40**, 568 (1971); J. B. Nee, M. Suto, and L. C. Lee, *J. Chem. Phys.* **85**, 4919 (1986); **85**, 719 (1986).
- D. S. Ginter, M. L. Ginter, and S. G. Tilford, *J. Mol. Spectrosc.* **90**, 152 (1981).
- D. S. Green, G. A. Bickel, and S. C. Wallace, *J. Mol. Spectrosc.* **150**, 303 (1991).
- D. S. Green, G. A. Bickel, and S. C. Wallace, *J. Mol. Spectrosc.* **150**, 354 (1991); D. S. Green and S. C. Wallace, *J. Chem. Phys.* **96**, 5857 (1992); Á. Kvaran and H. Wang, *J. Mol. Spectrosc.* **228**, 143 (2004).
- D. S. Green, G. A. Bickel, and S. C. Wallace, *J. Mol. Spectrosc.* **150**, 388 (1991).
- E. d. Beer, B. G. Koenders, M. P. Koopmans, and C. A. d. Lange, *J. Chem. Soc. Faraday Trans.* **86**, 2035 (1990); E. d. Beer, W. J. Buma, and C. A. d. Lange, *J. Chem. Phys.* **99**, 3252 (1993); T. A. Spiglanin, D. W. Chandler,

- and D. H. Parker, *Chem. Phys. Lett.* **137**, 414 (1987); Á. Kvaran, H. Wang, and Á. Logadóttir, *Recent Research Development in Physical Chemistry* (Transworld Research Network, 1998), vol. 2, p. 233; Á. Kvaran, H. Wang, and B. G. Waage, *Can. J. Phys.* **79**, 197 (2001); H. Wang and Á. Kvaran, *J. Mol. Struct.* **563-564**, 235 (2001); Á. Kvaran and H. Wang, *Mol. Phys.* **100**, 3513 (2002); S. A. Wright and J. D. McDonald, *J. Chem. Phys.* **101**, 238 (1994); S. T. Pratt and M. L. Ginter, *J. Chem. Phys.* **102**, 1882 (1995); K. Matthiasson, H. S. Wang, and A. Kvaran, *J. Mol. Spectrosc.* **255**, 1 (2009).
- ⁷Y. Xie, P. T. A. Reilly, S. Chilukuri, and R. J. Gordon, *J. Chem. Phys.* **95**, 854 (1991).
- ⁸R. Callaghan and R. J. Gordon, *J. Chem. Phys.* **93**, 4624 (1990).
- ⁹Á. Kvaran, H. Wang, and Á. Logadóttir, *J. Chem. Phys.* **112**, 10811 (2000).
- ¹⁰J. Long, H. Wang, and A. Kvaran, *J. Mol. Spectrosc.* **282**, 20 (2012).
- ¹¹H. Lefebvre-Brion, H. P. Liebermann, and G. J. Vazquez, *J. Chem. Phys.* **134**, 204104 (2011).
- ¹²K. Matthiasson, J. Long, H. Wang, and A. Kvaran, *J. Chem. Phys.* **134**, 164302 (2011).
- ¹³D. S. Ginter and M. L. Ginter, *J. Mol. Spectrosc.* **90**, 177 (1981).
- ¹⁴Á. Kvaran, Á. Logadóttir, and H. Wang, *J. Chem. Phys.* **109**, 5856 (1998).
- ¹⁵Á. Kvaran, K. Matthiasson, H. Wang, A. Bodi, and E. Jonsson, *J. Chem. Phys.* **129**, 164313 (2008).
- ¹⁶S. Kauczok, C. Maul, A. I. Chichinin, and K. H. Gericke, *J. Chem. Phys.* **133**, 024301 (2010).
- ¹⁷A. Kvaran, K. Matthiasson, and H. Wang, *J. Chem. Phys.* **131**, 044324 (2009).
- ¹⁸J. Long, H. R. Hrodmarsson, H. Wang, and A. Kvaran, *J. Chem. Phys.* **136**, 214315 (2012).
- ¹⁹M. Bettendorff, S. D. Peyerimhoff, and R. J. Buenker, *Chem. Phys.* **66**, 261 (1982); D. M. Hirst and M. F. Guest, *Mol. Phys.* **41**, 1483 (1980); C. Maul, A. I. Chichinin, and K.-H. Gericke, *J. At., Mol., Opt. Phys.* **2011**, 410108 (2011).
- ²⁰R. Liyanage, R. J. Gordon, and R. W. Field, *J. Chem. Phys.* **109**, 8374 (1998).
- ²¹A. I. Chichinin, C. Maul, and K. H. Gericke, *J. Chem. Phys.* **124**, 224324 (2006); A. I. Chichinin, P. S. Shternin, N. Godecke, S. Kauczok, C. Maul, O. S. Vasyutinskii, and K. H. Gericke, *ibid.* **125**, 034310 (2006); C. Romanescu and H. P. Loock, *Phys. Chem. Chem. Phys.* **8**, 2940 (2006); *J. Chem. Phys.* **127**, 124304 (2007); C. Romanescu, S. Manzhos, D. Boldovsky, J. Clarke, and H. Loock, *ibid.* **120**, 767 (2004).
- ²²A. Kvaran, K. Sveinbjornsson, J. Long, and H. Wang, *Chem. Phys. Lett.* **516**, 12 (2011); A. Kvaran, H. Wang, K. Matthiasson, and A. Bodi, *J. Phys. Chem. A* **114**, 9991 (2010).
- ²³See supplementary material at <http://dx.doi.org/10.1063/1.4776260> for intensity ratio analysis, typical experimental parameters, Hamiltonian matrix elements, contour plots showing $B'E$ as a function W_L and W_H , $I(^{35}\text{Cl}^+)/I(\text{H}^{35}\text{Cl}^+)$ vs. J' for H^{35}Cl , $E(0)$, fractional state mixing of $E(0)$, $V(10)$, and $V(11)$ for H^{35}Cl .
- ²⁴NIST (National Institute of Standards and Technology) Chemistry Web-Book, online at <http://webbook.nist.gov/chemistry/form-ser.html.en-us.en>.
- ²⁵K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand-Reinhold, New York, 1979).
- ²⁶See supplementary material in Ref. 20.
- ²⁷K. Matthiasson, H. Wang, and A. Kvaran, *Chem. Phys. Lett.* **458**, 58 (2008).
- ²⁸H. Lefebvre-Brion and R. W. Field, *The Spectra and Dynamics of Diatomic Molecules* (Elsevier Academic, 2004).
- ²⁹M. H. Alexander, X. N. Li, R. Liyanage, and R. J. Gordon, *Chem. Phys.* **231**, 331 (1998).