(2+1) REMPI spectra of \( \Omega=0 \) states of the hydrogen halides: Spectroscopy, perturbations and excitation mechanisms

Ágúst Kvaran, Áshildur Logadóttir, and Huasheng Wang
Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavík, Iceland

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(2+1) REMPI spectra of HX (X=Cl, Br and I) have been recorded and analyzed by simulation calculations to derive rotational constants, band origins and isotope shift values for a number of vibrational bands of \( \Omega=0 \) states. Our data for HCl compare nicely with those derived by Green et al. by conventional analysis methods [D. S. Green et al., J. Mol. Spectrosc. 150, 303, 354, 388 (1991); D. S. Green and S. C. Wallace, J. Chem. Phys. 96, 5857 (1992)]. New spectroscopic parameters were derived for eight vibrational bands which are assigned to the \( V^1\Sigma^- \) state, for \( \Omega'=4 \) of the \( E^1\Sigma^- \) state, as well as for five new bands in HBr. New spectroscopic parameters were derived for four vibrational bands which are assigned to the \( V^1\Sigma^- \) state and for \( \Omega'=1 \) of the \( E^1\Sigma^- \) state in HI. Anomalies observed in energy level spacings, rotational parameters and isotope shift values are interpreted as being largely due to homogeneous interactions between the \( V \) and the \( E \) states. It is argued that the interaction causes a compression of rovibrational levels in the \( E \) state manifold but an expansion of levels in the \( V \) state manifold, something which might be expected for a Rydberg to ion-pair interaction. Variations observed in the intensity ratio of \( O \) and \( S \) lines series to \( Q \) line series in vibrational bands of the \( E \) and \( V \) states for HCl and HBr are discussed and mechanisms of two-photon excitation processes are proposed. © 1998 American Institute of Physics. [S0021-9606(98)01326-2]

INTRODUCTION

A wealth of spectroscopic data has been derived on electronically excited states of the hydrogen halides by conventional single-photon spectroscopic methods. However, only limited information has been obtained on the rotational structure by these means.

Resonance enhanced multiphoton ionization (REMPI) spectroscopy, on the other hand, has proved to be a more successful technique in this respect. The largest amount of information has been obtained on HCl, while limited data are available on HBr and HI. Rotational spectroscopic constants have been derived for a number of Rydberg states and for the \( V^1\Sigma^- \) ion-pair states for HCl, HBr, and HI. Most of this spectroscopic information has been derived from analysis of spectra recorded under jet-cooled conditions, restricting its validity to low rotational energies. Rotational and vibrational perturbations due to state interactions have been observed in high resolution REMPI spectra of HCl and HBr. Thus intensity, linewidth and line position anomalies have been observed in spectra of Rydberg and/or ion-pair states of HCl, HBr, and HI.

In this paper we present rotational REMPI analysis of the \( E^1\Sigma^- \) Rydberg states, the \( V^1\Sigma^- \) ion-pair states for HCl, HBr, and HI, as well as for some new \( \Omega=0 \) states for HBr. Spectra were recorded at room temperature and analyzed by simulation calculations in order to derive information on (i) spectroscopic parameters, (ii) state interactions, as well as (iii) the resonance excitation processes. The analysis of the HCl spectra serves as a comparison of our analysis technique with the more conventional technique used by others. Furthermore, the HCl data are used as a basis for interpretation of somewhat analogous trends observed in vibrational energy level spacings and rotational constants with energy for all HX (X=Cl, Br and I).

EXPERIMENT AND METHOD OF ANALYSIS

Experiment

The REMPI spectra were recorded by total current detection at room temperature, which is a sensitive method, suitable for detecting low as well as moderately high rotational energy levels. The experimental setup has been described elsewhere and only a brief description is given here. Tunable ultraviolet (UV) laser pulses were generated by a dye laser pumped by an excimer laser. For wavelengths less than about 330 nm, the output from the dye laser was frequency doubled by suitable SHG crystals (KDP or BBO crystals). The frequency doubled beam was separated from the fundamental one by means of a Pellin Brocca prism. The radiation was focused into an ionization cell between two stainless steel electrodes which were kept at a fixed voltage difference by batteries. The cell contained gas samples at low pressure (typically 1 Torr). Current pulses due to multiphoton ionization caused voltage drops across the electrodes which were amplified by a balanced bias differential amplifier. The signal was integrated by a conventional integration circuit and fed through a linear amplifier before...
entering a multichannel analyzer for voltage peak height measurement and recording. Finally, average pulse heights for a fixed sampling time were recorded to produce the spectrum. The various equipment units were computer controlled.

The laser was typically run at a 20 Hz repetition rate for a sampling time of 5 s. The bandwidth of the laser beam from the dye laser was about 0.05 cm\(^{-1}\). The dye laser output was usually scanned in 0.2 or 0.4 cm\(^{-1}\) steps. Calibration of the wavelength was either achieved by recording atomic (neon and iodine) lines\(^{22}\) or by comparison of the strongest hydrogen chloride rotational lines with those reported by Green et al.\(^{20}\) The accuracy of the calibration, as judged from the position of the atomic lines in the spectral region studied, was found to be \(\pm 2\) cm\(^{-1}\) on the two-photon wave number scale.

**Spectra analysis**

As a first guide toward analyzing \(v'\) bands in terms of estimating first order rotational constants \((B')\), it turned out to be useful to plot wave number spacings between neighboring rotational lines in the \(Q\) series \(\Delta v_{J',J-1}(Q) = v_{J'}(Q) - v_{J}(Q)\) against integer numbers. Since the relationship

\[
\Delta v_{J',J-1}(Q) = 2(B' - B^0)J + 2(B' - B^0)
\]

holds as a first approximation \((D' = 0, D^0 = 0)\), consistency in slope and intercept values could be used to assign rotational lines followed by estimation of \(B'\).

Simulations of rotational structure of vibrational bands require evaluations of rotational line positions as well as line strengths (absorption cross sections).\(^{30,33,34}\)

Rotational line positions are determined by the energy difference between rovibrational energy levels of concern \([v(J',v' = v,J',v')\)]. These are formulated in a standard way, based on first and second order vibrational \((\omega_v,\omega_r,\) or \(v',\psi_r)\) and rotational \((B,D)\) constants for the excited \((u'^+)'\) and ground \((u')\) electronic states

\[
v(u',\psi'; v',\psi') = F_{u'}(\psi' + \frac{1}{2} - \omega_r\psi')^2 - \frac{1}{2}(\omega_v^2(u' - 1/2) - \omega_r^2(\psi' + 1/2)^2),
\]

and \(\Delta E(J',v')\) is the difference in rotational energies (in cm\(^{-1}\)) for the two states

\[
\Delta E(J',v') = (J + \Delta J)(J + \Delta J + 1)B'(J + \Delta J + 1)^2 - (J + \Delta J + 1)(J + \Delta J + 1)^2D'^2 - (J + \Delta J + 1)B'^2 + (J + \Delta J + 1)^2D'.
\]

where \(J = J'\) and \(\Delta J = J' - J\).

Relative intensities of vibrational lines are proportional to the products of cross sections for the two major steps, (i) resonance excitation \((\sigma_1)\) and (ii) photoionization \((\sigma_2)\). For two-photon resonance excitation followed by single-photon ionization, i.e., \((2 + 1)\) REMPI (see Fig. 1), the cross section for the first step \((\sigma_1)\) can be expressed as\(^{30,35}\)

\[
\sigma_1 = \sum_i \frac{|\langle \psi' | \mu_i | \psi \rangle|^2}{\Delta E_{ni} - \hbar \nu + C(\Gamma_i)}.
\]

where the transition occurs from a ground rovibronic state \((\psi)\) to the absorbing state \((\psi')\) by simultaneous absorption of two photons, each having energy \(\hbar \nu\). \(\mu_i\) is the operator representing the interaction between the electric field component of the electromagnetic wave and the molecular charge dipole moment. The intermediate rovibronic states \((\psi)\) are separated from the ground state by \(\Delta E_{ni}\) and from the laser photon energy by \((\Delta E_{ni} - \hbar \nu)\). The cross section for the photoionization step \((\sigma_2)\) commonly is a slowly varying function with photon energy. Hence, in such cases (for narrow excitation frequency range), the total cross section \((\sigma_{tot})\) can be assumed to vary proportionally to the resonance excitation cross section only, in which case the ionization simply acts as a “detection step.” Explicit forms for two-photon absorption cross sections for rotating diatomic molecules have been developed further from expression \((5)\) by Bray and Hochstrasser.\(^{37}\) \(\sigma_{tot}\) is found to be proportional to a function \(S_{\nu',\nu}\) (“the two-photon absorption strength”), which depends on the difference in the angular momentum quantum numbers, \(\Delta I\) and \(\Delta J\), of the two states as well as on the parallel \((\mu_\parallel)\) and perpendicular \((\mu_\perp)\) transition dipole moments corresponding to transitions to virtual/nonstationary intermediate states \((\psi)\).

\[
\sigma_{tot} = S_{\nu',\nu}(\Delta I,\Delta J,\mu_\parallel,\mu_\perp),
\]

where

\[
\mu_{\parallel} = \langle \Omega | \sigma | \Omega \rangle,
\]

\[
\mu_{\perp} = \langle \Omega | e | \sigma | \Omega \rangle.
\]

Eventually, after specifically taking account of the population distribution and the degeneracy \([g(J)]\) of the ground state rotational energy levels \([E(J)]\), the relative rotational line strength takes the form

\[
I_{ni} = C(u',\psi')g(J)S_{\nu',\nu}\exp(-E(J)/kT)
\]

in the case of a Boltzmann distribution. \(C(u',\psi')\) is a factor (“constant”) assumed to be independent of \(J'\) and \(J\) which can be expressed as\(^{30,37}\)

\[
C(u',\psi') = KE(u',\psi')\int P'(u')\sigma_1(u'),
\]

(9)
where $F(v', v'')$ is the Franck-Condon factor for the transition $v' \rightarrow v''$ and $K$ is a parameter dependent on the electronic structure of the molecule, geometrical factors and sample concentration. $C(v', v'')$ also depends on the laser power ($P$) as $P^n$, where $n$ depends on the number of photons involved in the overall ionization process [thus $n \approx 3$ for (2 + 1) REMPI].

In order to simulate measured REMPI spectra, rotational lines are displayed as Gaussian-shaped functions. A simulation procedure involves comparison of measured and calculated spectra for different bandwidths of rotational lines and for different values of rotational parameters ($B'$ and $D'$) for the excited state. Known rotational parameters for the ground state ($B''$ and $D''$) are used, derived from

$$B = B'' - \alpha_c (v + 1/2),$$

$$D = 4B'' \omega_c^2.$$  \hspace{1cm} (10)

This procedure is performed until best fit is obtained to give rotational parameters as well as band origins [$v''(v'', v'')$].

Rotational perturbations due to state interactions can be interpreted in terms of deviations of rotational constants from standard behavior with $v'$ [equations such as (10) and (11)] as well as in terms of deviations of line positions and intensities from expressions (2) and (8). \hspace{1cm} 25,38 Vibrational perturbations, on the other hand, can be viewed in terms of deviations of $v'$ dependent parameters, such as band origins [$v''(v', v'')$] from Eq. (3). \hspace{1cm} 26 Isotope shifts ($\Delta v''_u$), i.e., difference between band origins for two isotopomers H CX and H2X (i.e., H13C1 and H23C1 as well as H32Br and H33Br) for an unperturbed system can be approximated by Eq. \hspace{1cm} 25

$$\Delta v''_u = (w''(i) + 1/2) - w''(i)/(v' + 1/2)] [1 - \rho],$$  \hspace{1cm} (12)

where

$$\rho = \frac{\mu(i) \mu(j)}{\mu(i) \mu(j)}.$$  \hspace{1cm} (13)

Unusual isotope shift values obtained by comparison of observed isotope shifts and calculated values by (12) based on estimated vibrational frequencies for the excited states and known values for the ground states can give indications of state interactions.

Effects of intermediate states on the resonance excitation mechanism can be analyzed in terms of relative contributions of parallel ($\mu_\perp$) and perpendicular ($\mu_\parallel$) transitions/translation dipole moments for $\Delta \Omega = 0$ transitions. This can be estimated by simulation of relative intensities of rotational line series, which depend on the transition dipole moments $\mu_\parallel$ and $\mu_\perp$. \hspace{1cm} 25

RESULTS AND INTERPRETATIONS

Spectroscopic and perturbation effects

Figure 2 shows typical spectra simulations of vibrational bands of the $\Delta \Omega = 0$ and $\Delta \Omega = 1$ states for the hydrogen halides, HX (X = Cl, Br). Only $O$, $Q$ and $S$ band series are observed as expected for a $\Delta \Omega = 0$ two-photon transition. \hspace{1cm} 18,35 All series for the $V$ state spectra are degraded to the red, indicative of a large difference in rotational constants and average internuclear distances for the ground ($B''$, $r''$) and the excited states ($B'$, $r'$) and $B'' - B' < 0$, $r'' > r' > 0$. For the $E$ state, on the other hand, the $S$ series are degraded to blue, while the $O$ series are degraded to red. The $Q$ series show only slight degradation to the red, indicative of an analogous trend in relative magnitude of rotational constants and average internuclear distances to that for the $V$ state (see above) ($B'' - B' < 0$, $r'' > r' > 0$), except smaller differences. Ground state vibrational and rotational parameters form the basis for the simulations of the bands. \hspace{1cm} 40 These are listed in Table I. Rotational parameters for the excited states, as well as band origins derived from the simulation procedures as described above, are summarized in Table II, along with values derived by others.

![Figure 2](image.png)

FIG. 2. Simulations of (2 + 1) REMPI vibrational band for HX, X = Cl and Br. Experimental spectra above, calculated spectra below. Rotational line numbers are $J$, and $v'' = J(J+1)$ of the state. $v''(v'')$ are peak positions.

<table>
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<th>State</th>
<th>$B'' / \text{cm}^{-1}$</th>
<th>$D'' / \text{cm}^{-1}$</th>
<th>$B' / \text{cm}^{-1}$</th>
<th>$D' / \text{cm}^{-1}$</th>
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<td>6.3419 35</td>
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*Reference 40.*
### TABLE II(a) HCl

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### TABLE II(c) HI

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\(^a\)Ry: Rydberg states
\(^b\)LP: Assigned as ion-pair state bands, based on observed isotopes shifts.
HCl

First and second order rotational parameters ($B'$ and $D'$) as well as band origins were derived from simulation analysis of the vibrational bands ($v',v''=0$); $v'=8-13$ and $15-18$ for the $V''(\Sigma^+)$ state of HCl (Table II). Large rotational perturbations observed in the (14,0) band made the simulation analysis too difficult to determine rotational parameters precisely, although the band origin could be estimated fairly accurately. Furthermore, the analogous parameters for the vibrational bands ($v',v''=0$); $v'=0,1,1$ for the $E'(\Sigma^+)$ state were derived. In Fig. 3, energy levels as well as the first order rotational constants ($B'$) and spacings between "neighbor" vibrational levels/vibrational origins ($\Delta v''(v''+1,v''=0)=v''(v''+1,0)-v''(v''=0)$) are plotted for $E(v',v''=0); v''=0-3$ and for $V(v',v''=0); v''=3-26$.

Our values, both for rotational constants and band origins/band spacings, compare nicely with those determined by Green et al.\textsuperscript{19-21} who used a conventional rotational analysis method. The major characteristics of the combined data will now be considered and interpreted.

In terms of the spacing between vibrational levels in the $V$ state, an overall decrease is observed with energy, while peaks (with larger spacings) are observed between vibrational levels 10 and 11, 14 and 15, 18 and 19, as well as near $v''=22$ and 23. These match with the vibrational levels $v''=0,1,2$ and 3 in the $E$ state. Both on the high and the low energy sides of these gaps, some lowering in the separations is observed. This is particularly clear for the spacing between $v''=13$ and 14, but also a small but significant drop in spacing is observed between $v''=15$ and 16 as well as between $v''=17$ and 18. The same holds true for the spacing between $v''=19$ and 20 as well as between $v''=21$ and 22. The spacing between vibrational levels $v''=0-3$ in the $E$ state, on the other hand, is found to increase with energy, contrary to what one would expect for an unperturbed system.

The first order rotational constant ($B''$) for the $E$ state shows a characteristic decrease with vibrational quantum numbers, although its behavior deviates strongly from linear dependence [Eq. (10)], which is to be expected for an unperturbed system. The $B''$ values for the $V$ state show irregular behavior with vibrational quantum numbers. First, a steady increase in the values is observed for $v''=3-8$. In the region $v''=9-26$, maxima in $B''$ values are observed for those vibrational levels which are closest in energies to the vibrational levels in the $E$ state, i.e., $v''=10$ (nearest to $v''=0$ in the $E$ state; $\Delta E=345.9$ cm$^{-1}$), $v''=14$ (near $v''=1$; $\Delta E=243.9$ cm$^{-1}$), $v''=18$ (near $v''=2$; $\Delta E=200$ cm$^{-1}$) and $v''=23$ (near $v''=3$; $\Delta E=197.4$ cm$^{-1}$). Notice that all $B''$ values in the high vibrational level region ($v''=6-26$) are relatively large compared with those for the lowest levels ($v''=3-5$).

These findings are consistent with a homogeneous inter-
action between the $E(^1\Sigma^+)$ and the $V(^3\Sigma^+)$ states as the major cause of the observed perturbations.

Thus, the various peaks or increases in energy gaps between vibrational levels in the $V$ state (the vibrational perturbation) can be viewed as being due to repulsive type shifts of zero approximation vibrational energy levels due to interactions with the vibrational levels in the $E$ state. Such an interaction will be inversely dependent on vibrational level separations. The appearance of localized peaks and troughs in the energy gap structure suggests that the interaction strength falls rapidly with energy. The strongest interactions are by $a=0$ and $\tilde{l}$ in the $E$ state, suggesting that the crossing point of the two states $\Delta E$ is at an energy between those (i.e., 83,780 cm$^{-1}$ < $\Delta E$ < 85,920 cm$^{-1}$). Linear extrapolation of the $\Delta E$ vs $v_0^*$ curve for the lowest vibrational levels (say $v_0^*=3$; assuming vibrational interaction between the states to be negligible in this region) to higher energy region, suggests that the majority of the observed vibrational spacings in that region are larger than expected for an unperturbed system. This suggests that an overall expansion of vibrational spacings in the $V$ state is occurring due to the interaction.

The $v'$ level spacing values for the $E$ state (2137.2–2266.0 cm$^{-1}$) are significantly lower than corresponding values for the ground states of the neutral and the ion species $\omega_s(X(3\Pi\text{Cl})) = 2990.946_j$ cm$^{-1}$ and $\omega_s'(X(3\Pi\text{Cl}^+)) = 2673.69$ cm$^{-1}$). The $E$ state electron configuration corresponds to a promotion of a single $\pi$ electron to a $5p\pi$ Rydberg orbital (a $2p^3\pi5p\pi$; $0^+$ state) and belongs to a series of Rydberg states which correlate with the ground ionic state, $\omega'_s(X(3\Pi\text{Cl}^+))$ or band spacing for an unperturbed state therefore might be expected to be in the range between those for the ground states, i.e., 2673.69–2990.946 cm$^{-1}$.

Hence we believe that the lower values show an effect of overall compression of the zero order vibrational levels due to interactions with the $V$ state energy level manifold. The irregular behavior in the first order rotational constants ($B'$) for the vibrational states both in the $V$ and the $E$ state can be interpreted as being due to repulsive type shifts of equal value $J$ levels where the interaction strength is inversely dependent on the level separations. This is demonstrated in Fig. 4(a) for the case where the vibrational state for the $E$ state ($E(\tilde{l}=1)$) is higher in energy than the one for the $V$ state, and in Fig. 4(b) for the case where the vibrational state for the $E$ state is lower in energy than the one for the $V$ state.

FIG. 4. Schematic figure showing rotational repulsive type interaction in the $V$ and the $E$ states. Spacings between "neighbor" rotational levels in the $V$ state are shorter than the corresponding ones in the $E$ state. Hence $J\rightarrow J$ interactions (a) weaken with $J$ if the vibrational state of $E$ is higher in energy than that for the $V$ state (i.e., $E(\tilde{l}=1) < E(\tilde{l}=0)$) but (b) increase with $J$ if the vibrational state of $E$ is lower (i.e., all rotational levels in $E$ of concern are lower in energy) in energy than that for the $V$ state (i.e., $E(\tilde{l}=1) > E(\tilde{l}=0)$). This will cause vibrational levels in the $E$ state to become compressed, but levels in the $V$ state to expand.
TABLE III. Isotope shift values for E-X bands in HCl (a) and for V - X bands in HBr.

<table>
<thead>
<tr>
<th>Compound</th>
<th>i</th>
<th>j</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>Δνᵦᵦ⁻¹⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>35</td>
<td>37</td>
<td>Σ₄⁺</td>
<td>0.00</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>37</td>
<td>Σ₄⁻</td>
<td>1.00</td>
<td>3.8</td>
</tr>
<tr>
<td>HBr</td>
<td>79</td>
<td>81</td>
<td>Σ₄⁺</td>
<td>m + 15.0</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>81</td>
<td>Σ₄⁻</td>
<td>m + 19.0</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>81</td>
<td>Σ₄⁻</td>
<td>m + 22.0</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>81</td>
<td>Σ₄⁺</td>
<td>0</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>81</td>
<td>Σ₄⁺</td>
<td>m + 91.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

State. In both cases B'L > B'', hence, effectively rovibrational levels in the V state expand, while those in the E state compress. Thus the gradually increasing B' values in the V state for v' = 3 to 10 can be understood as being due to interaction of the type in Fig. 4(a), i.e., zero order J levels in a particular v' state in V(Σ⁺) (i.e., v') experience decreasing downward repulsion due to interactions from higher lying levels in the E state (mainly v'' = 0) since the energy spacing between interacting levels increases with J. This will cause an effective expansion of the zero order rotational levels in v' and, so increasing rotational constants are observed. The peaks in the B' vs v' plots [Fig. 3(a)] for v' = 14 and 18 similarly could be explained as being mainly due to analogous effects from v'' = 1 and 2 in the E state. These rovibrational levels will also experience similar effects due to repulsive interactions from lower lying v'' states according to the case demonstrated in Fig. 4(b). In fact the relatively large B' values observed for all the vibrational levels in the perturbation region (compared with those for the lowest observed ones) suggest that an overall expansion of vibrational levels is occurring in the interaction region. The irregular changes in the B' values for the V state for v' > 10 is most probably due to combinations of repulsion effects of this type of varying magnitude both from higher and lower lying v'' states.

We also believe that the irregularity in the B' values for the v' = 0 states can be explained as being due to analogous repulsion effects due to interactions with the v'' = 0 states. The rotational constants for the E state (B'' = 6.6 cm⁻¹) for v'' = 0 is a lot lower than those for the ground state of the neutral and the ion species BE(X[ClX]) = 10.4 and 9.5 cm⁻¹ and B[Cl(X[ClX])] = 9.8 to 8.8 cm⁻¹ for v'' = 0 to 3, which suggests that rotational levels (hence vibrational levels) effectively 'experience' compression due to interaction with the V state manifold.

Considering both the variation in interaction strengths between J levels with energy difference (inverse dependence) and the vibrational contribution (overlap) to the perturbation function, the effect described above for J-J interaction (Fig. 4) can cause compression of the whole vibrational state manifold in the E state but an expansion of those in the V state, as observed.

The observed isotope shifts for v' = 0 and 1 in the E states [κ(35Cl⁺) = ω'(HCl) - ω'(HδCl)] = 1.8 and 3.8 cm⁻¹, respectively; see Table III] are larger than values calculated with Eq. (12) by using ω'(E) = 2137.2 cm⁻¹ (= spacing between v' = 0 and 1) (−0.3 and +1.3 cm⁻¹, respectively). This suggests that the spacing value (2137.2 cm⁻¹) is an underestimate of ω'(E) as concluded before (see above). The opposite effect is found for the V state according to Green et al., 19, 21, who observe a decreasing isotope effect for those vibrational levels in the V state which are closest to the interacting v'' states. Our suggestion is that this opposite effect (in V vs E states) in terms of isotope shift is also associated with the opposite repulsion interaction discussed above (compression in E vs expansion in V).

HBr

Band origins were evaluated for the V state, v'' = m + 3 to m + 11, m + 19, m + 19 and m + 22, of which values for m = 4, m = 9, m = 11, m = 15, m = 19 and m = 22 have not been determined before (see Table II). Furthermore, rotational constants were determined for all these states except for m = 5 and m = 10, of which values for m = 4, m = 6, m = 7, m = 9, m = 11, m = 15, m = 19 and m = 22 have not been determined before. Band origin values as well as rotational constants were evaluated for the E state, v' = 0, for which v'' = 0 has not been detected or analyzed before. In addition, five new bands of Rydberg states and two new bands of ion-pair states were detected and analyzed (see Table II). HBr-HδBr isotope shifts were observed for high vibrational ion-pair bands only (Table III), while no isotope splitting was detected for the Rydberg states or lower v' levels (v' < m + 15) in the V state. Available data on energy levels as well as the first order rotational constants (B') and the spacing between vibrational levels are plotted in Fig. 5 for E(v', v'' = 0); v' = 0 to 4 and for V(v', v'' = 0); v'' = m + 3 to m + 22.

Good agreement is found between our results and those determined by Callaghan and Gordon 24 in terms of band origins for the V and E states and in terms of the rotational constants for the V state (v'' = m + 3 and m + 8) (see Table II and Fig. 5). The only slight discrepancy is found between our values for rotational constants (both B' and D') for the E state, v' = 1 - 3 and corresponding values determined by Callaghan and Gordon. The major characteristics of the combined data will now be considered and interpreted by reference to the analogous results for HCl described before.

In terms of the spacing between vibrational levels in the V state, similar behavior is observed as for HCl. Enhanced spacings are observed between neighbor vibrational levels on both (energy) sides of vibrational levels in the E state due to repulsive type shifts/homogeneous interactions between the E and the V state, i.e., between v' = m + 4 and m + 5 (due to interaction with v'' = 0), between v' = m + 8 and m + 9 (due to v'' = 1), between v' = m + 11 and m + 12 (due to v'' = 2) and between v' = m + 15 and m + 16 (due to v'' = 3). Judging from the gradual increase in these spacings with energy, the interaction strength increases as v'' = 0 < v'' = 1 < v'' = 2 < v'' = 3. The v' = m + 18 band could not be detected because it was going beyond v'' = 3. This suggests that the two states (E and V) cross near or above v' = 3.

The spacing between vibrational levels in the E state decreases gradually with vibrational quantum numbers (Fig.)
5). Conventional analysis of this data, assuming the $E$ state to be a Morse potential, gives $\omega_v(E) = 2339.4$ cm$^{-1}$ and $\omega_{v0}(E) = 58.28$ cm$^{-1}$ to be compared with the corresponding values for the ground states of the neutral and ionic species, $\omega_v(X(\text{H}^4\text{Br})) = 2648.975$, $\omega_{v0}(X(\text{H}^4\text{Br})) = 45.217$, $\omega_v(X(\text{HBr}^-)) = 2441.52$, and $\omega_{v0}(X(\text{HBr}^-)) = 47.41$ cm$^{-1}$. We believe that the lower value of $\omega_{v0}(E) = 2339.4$ cm$^{-1}$ shows an effect of compression of the zero order vibrational levels due to interactions with the $V$-state energy level manifold, similar to that found for HCl.

Both rotational constants for the $E$ and the $V$ states show irregular behavior with vibrational quantum numbers. Similar to what is found for HCl, maxima in $B'$ values for the $V$ state are observed for $v'$ levels close in energy to vibrational levels in the $E$ state, i.e., for $v'_v = m + 8$ near $v'_v = 1$, for $v'_v = m + 11$ near $v'_v = 2$, for $v'_v = m + 15$ near $v'_v = 3$, and for $v'_v = m + 19$ near $v'_v = 4$. This effect we believe is due to a dominating downward shift of levels due to interactions with higher lying rotational levels in the $E$ state which will cause an expansion in rotational level spacings [Fig. 4(a)], hence an effective increase in $B'$ values, as described for HCl.

The "zig-zag" pattern in the $B'$ vs $v'$ plot for the $E$ state can be explained as being due to a combination of increasing overall interaction strength with $v'_v$ and an alternating change in relative (energy) distance between neighbor vibrational bands in the two states. Thus the $v'_v$ levels nearest to the $v'_v = 0$ and 1 states (i.e., $v'_v = m + 4$ and $v'_v = m + 8$) are just below the $v'_v$ levels ($\Delta E = 116$ and $140$ cm$^{-1}$, respectively), while $v'_v = m + 12$ is just above $v'_v = 2$ ($\Delta E = 145$) and $v'_v = 3$ is near midway between $v'_v = m + 15$ ($\Delta E = 473$) and $v'_v = m + 16$ ($\Delta E = 382$ cm$^{-1}$). Generally, the rotational constants for the $E$ state ($B' = 7.72 - 7.53$ cm$^{-1}$ for $v' = 0 - 3$) are slightly lower than the corresponding ones for the ground states ($B(X(\text{H}^4\text{Br})) = 8.35 - 7.65$ and $B(X(\text{HBr}^-)) = 7.95 - 7.3$ cm$^{-1}$), further suggesting the effect of compression interaction.

The perturbation effects described above could be further complicated by possible effects of the other $\Omega = 0$ Rydberg $v'$ states found and listed in Table II. Thus the Rydberg state bands at $v'' = 83$ 087.1 and $v'' = 83$ 657.5 cm$^{-1}$ are close to where $v'_v = m + 14$ is expected to be found. The reason why $v'_v = m + 14$ has not been detected could be associated with near resonance interactions caused by either one or both of these states. Similarly, interaction effects caused by the x$' = 83$ 463.9 cm$^{-1}$ Rydberg state could be the reason why the $v'_v = m + 18$ band has not been detected. The bands at $v'' = 83$ 657.5, $x'' = 85$ 463.9, and $x'' = 87$ 385.2 cm$^{-1}$ (with spacings 1808 and 1919 cm$^{-1}$) could belong to the same Rydberg state, in which case the most probable assignment would be $v' = 0$, 1 and 2, respectively. The relatively low
spacing values, as well as rotational constants \( B' = 5.78 \) (\( v' = 0 \)), \( 6.32 \) (\( v' = 1 \)) and \( 6.88 \) cm\(^{-1} \) (\( v' = 2 \)), could then be due to analogous compression effects due to interactions with the \( V \) state as that observed for the \( E \) state.

The spectral regions 84 100–84 800 and 86 850–87 380 cm\(^{-1} \) show complicated structure, which could not be analyzed in detail. On the high energy side of about 88 090 cm\(^{-1} \), several bands with \( Q \) branches, which degrade to blue, hence correspond to states with \( B' \) values greater than that for the ground state, are observed. The \( v' = 83 \) 105.8 cm\(^{-1} \) band is the only one which could be analyzed.

Isotope shift values observed for ion-pair bands vary significantly (see Table III). By comparison with the analysis for HCl mentioned above, there is a reason to believe that low isotope shift values for an ion-pair state go with large expansion effects (hence large rotational constants). Although there is some tendency in that direction to be found [low isotope shift values for the bands at \( v' = 85 \) 644 and \( v' = 85 \) 911 cm\(^{-1} \), with rather high \( B' \) values (7.1 and 5.0 cm\(^{-1} \), respectively) are observed], the data are too limited to tell if this is generally the case.

**HI**

Band origins were evaluated for the \( V \) state, \( v' = m + 4 \) to \( m + 9 \), for which a value for \( v' = m + 7 \) has not been determined before (see Table II). Rotational constants were determined for \( v' = m + 5 \) to \( m + 7 \) and for \( v' = m + 9 \), all of which have not been determined before. Band origins and rotational constants were evaluated for the \( E \) state, \( v' = 0 \) and 1. Rotational constants for \( v' = 1 \) have not been determined before. Energy levels, first order rotational constants \( (B') \) and spacings between vibrational levels are plotted in Fig. 6 for both states.

Reasonably good agreement is found between our data and those derived by Pratt and Ginter\(^ {26} \) in terms of band origins except for \( v' = m + 9 \). They assign band at \( v' = 72 \) 022 cm\(^{-1} \) to \( v' = m + 9 \) but a band at \( v' = 72 \) 506 to \( v' = m + 10 \). The spacing between the \( v' = m + 8 \) and \( m + 9 \) bands according to Pratt and Ginter is only 102 cm\(^{-1} \), compared with the average spacing between levels \( v' = m + 4 \) to \( m + 8 \) of about 500 cm\(^{-1} \), which makes us believe that the band at \( v' = 72 \) 022 cm\(^{-1} \) is some other system, but that the band at \( v' = 72 \) 506 cm\(^{-1} \) is \( v' = m + 9 \). The only available data from rotational analyses of these systems are those given by Wright and McDonald for the \( v' = 0 \) of the \( E \) state.\(^ {27} \) Their \( B' \) value is slightly lower, while their second order rotational constant \( (D') \) is very large and a lot larger than ours. This mainly causes a difference in the evaluation of high rotational energy levels, but since their data are based on REMPI spectra recorded under jet cooled conditions, we believe that our values are more reliable in the high energy level range.
The data for HCl are less complete than those for HCl and HBr discussed above, which make them more difficult to interpret. Based on the knowledge derived from the analysis of HCl and HBr, however, we conclude the following. The “zig-zag” variation in vibrational spacings observed for the V state \(v' = m + 4\) to \(m + 9\); Fig. 6(a) cannot be explained solely as being due to interaction with the E state, and there is a reason to believe that it shows effects of interactions with other \(\Omega = 0\) states as well. The spacing between \(v'\chi = 0\) and \(v'\chi = 1\) (1801 cm\(^{-1}\)) is significantly less than corresponding values for the ground states of the neutral and the ion species \(\omega_0(X(1\Sigma^+)) = 2539.01\), \(\omega_0(X(1\Sigma^+) = 2170 \text{ cm}^{-1}\)).\(^{40}\) suggesting that a “compression interaction” with the V-state manifold is occurring.

The largest of the four rotational constants (\(B'\)) derived for the V states are those of the \(v'\chi\) levels closest in energy to the vibrational levels of the E state, i.e., for \(v'\chi = m + 6\) near \(v'\chi = 0\) and for \(v'\chi = m + 9\) near \(v'\chi = 1\). This could be due to a dominating rotational interaction with the \(v'\chi\) states to cause rotational level expansions in the \(v'\chi\) states. The rotational constants for the E state \([B' = 5.81 \text{ cm}^{-1} (v'\chi = 0)\) and \(B' = 5.01 \text{ cm}^{-1} (v'\chi = 1)\)] are lower than those for the ground state \([B(X(1\Sigma^+)) = 6.34 \text{ and } 6.17 \text{ cm}^{-1} \text{ for } v'\chi = 0 \text{ and } 1, \text{ respectively. rotational constants for the ground ion species are not available}, \text{ which might also suggest a “compression interaction” with the V state.}]

**Resonance excitation mechanism**

The intensity ratio of \(O\) and \(S\) line series to \(Q\) line series \((I(O,S)/I(Q))\) is found to vary in the HX spectra in the following way. HCl: All line series (\(O, Q\) and \(S\)) were detected in the vibrational bands recorded and studied for the \(E\) and \(V\) states for HCl (see above and Table II). No large significant variation in the \([I(O,S)/I(Q)]\) ratio from one \(v'\chi\) band to another could be observed. HBr: \(Q\) branch lines were observed for all \(v'\chi\) bands in the \(V\) and \(E\) states of HBr, while \(O\) and \(S\) lines could only be detected in the \(v'\chi = 0\) and \(1\) bands and in \(v'\chi = m + 3\) and \(m + 8\). In the case of the \(V\) state, the main reason could be due to low signal intensity of other \(V\)-state bands and or large overlap of other band systems. For the \(E\) state bands, on the other hand, the ratio \(I(O,S)/I(Q)\) was found to drop as \((v'\chi = 0) > (v'\chi = 1) > (v'\chi = 2)\), \((v'\chi = 3)\) (see Fig. 7). These findings will now be interpreted in terms of the effect of intermediate states on the two-photon resonance excitation process.

The “two-photon absorptions strength” functions, \(S_{v'\chi}(\Delta \Omega, \Delta \Omega, \mu, \mu, \mu, \mu, \mu, \mu)\) for the \(O, Q\) and \(S\) lines, for linearly polarized light, are listed in Table IV.\(^{35}\) \(\mu_1\) and \(\mu_2\) represent the collective effect of all one-photon transition moments and energy denominators that give rise to parallel or perpendicular transitions, respectively (see Fig. 8). There are several limiting cases to be considered. (i) First, if \(\mu_1^2\) is very small \((\mu_1^2/\mu_2^2 \approx 0)\), corresponding to similar amplitude contributions from two virtual paths that destructively interfere in \(\mu_1\), the relative intensity of the \(O\) and \(S\) series to that of the \(Q\) series will be large. (ii) Second, if the excitation is via two parallel transitions only \((\mu_1, \mu_1 = 0), \mu_1^2/\mu_2^2 = 0.25\) and relative intensity of the \(O\) and \(S\) series to that of the \(Q\) series will be smaller than in (i) but still significantly large. (iii) Third, if the excitation is via two perpendicular transitions only \((\mu_2, \mu_2 = 0), \mu_1^2/\mu_2^2 = 1\) and \(I(O,S)/I(Q)\) is rather

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**TABLE IV. Two-photon transition strengths for diatomic molecular transitions of the type \(\Omega = 0 - \Omega = 0\), for linear polarization.**

<table>
<thead>
<tr>
<th>Line series</th>
<th>Transition strengths for linear polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O) branch</td>
<td>((2J = 0)(2J = 1)) (\frac{1}{20})</td>
</tr>
<tr>
<td>(Q) branch</td>
<td>((2J = 1)(2J = 2)) (\frac{1}{9})</td>
</tr>
<tr>
<td>(S) branch</td>
<td>((2J = 2)(2J = 3)) (\frac{1}{45})</td>
</tr>
</tbody>
</table>

*References 35.*
small. (iv) Fourth, if $\mu_2^2$ is very small near zero (corresponding to similar amplitude contributions from two virtual paths that destructively interfere in $\mu_2$) and the $O$ and $S$ series will not be observed. In summary $[I(O,S)/I(Q)]$, will change as $I(iii)\gg I(ii)>I(iv)$.

Most $v'$ spectra of HCl for the $E$ and the $V$ states could be simulated by using $\mu_1^2/\mu_2^2 \approx -0.25$, which could be explained by case (ii) above (although not definitely determined), i.e., minimizing two parallel transition's excitation mechanism. This could be symbolized by

$$E([\sigma^2 \pi^3]3p \pi) \rightarrow X([\sigma^2 \pi^3])$$

where $[[\sigma^2 \pi^3]3p \pi]$ is representative of all virtual Rydberg states with Rydberg electron configurations $np \pi$ and $nd \pi$.

The first step is very nonresonant, but it could to some extent be compensated by the strong nature of two parallel transitions.

The $E$ state, $v'$ bands of HBr could be simulated by using $\mu_1^2/\mu_2^2 \approx 0.15$ for $v' = 0$, $\mu_1^2/\mu_2^2 \approx 0.85$ for $v' = 1$ and $\mu_1^2/\mu_2^2 \approx 0.85$ for $v' = 2$. Judging from the above arguments, this could be due to a gradual increase in perpendicular transitions/dissociation in parallel transition paths. The most likely virtual states to contribute significantly to the double perpendicular transition step would be the repulsive II states $A^1\Pi$ and $a^3\Pi$, in which case the path could be represented by

$$E([\sigma^2 \pi^3]3p \pi) \rightarrow X([\sigma^2 \pi^3])$$

CONCLUSIONS

Room temperature (2 + 1) REMPI spectra of HX (X = Cl, Br and I) have proved to facilitate the derivation of rotational parameters beyond that possible from jet cooled spectra. A large number of (2 + 1) REMPI vibrational bands of $\Omega = 0$ states, recorded at room temperature for HCl, HBr and HI, have been analyzed by simulation calculations in order to determine rotational constants and band origin values. Among those were several new bands to the $E$ and the $V$ states of HBr and HI. Some new $\Omega = 0$ state bands were also observed and analyzed for HBr. Somewhat analogous patterns are observed in terms of vibrational band spacings and rotational constants vs energy for the $V$ and the $E$ states for HBr and HI, as have been observed for HCl. Observed vibrational and rotational perturbations are described as being largely due to a medium strong, homogeneous interaction between these two states. The perturbation interaction is repulsive in nature, causing shifts in energies of rovibrational levels. An overall compression of energy levels in the Rydberg state $[E^1(1S^+)]$ and expansion of levels in the ion-pair state $V^1(1S^+)$ is occurring. This is what is to be expected for interactions between states with a large difference in average internuclear distances, hence different rotational constants (see Fig. 4). Interactions between the $V$ states and other $\Omega = 0$ states are also suggested, the effect of which increases as HCl > HBr > HI.

Variations observed in the intensity ratio of $O$ and $S$ line series to $Q$ line series in vibrational bands of the $E$ and $V$ states for HCl and HBr are interpreted in terms of the effect of intermediate states on the two-photon excitation mechanism. The observations are consistent with dominating parallel transitions via nonresonant intermediate states in HCl but with gradually increasing importance of perpendicular to parallel transitions with increasing energy in HBr.

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