Two-dimensional \((2 + n)\) REMPI of HCl: Observation and characterisation of a new Rydberg state

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**Article info**

**Abstract**

Two-dimensional REMPI data, obtained by recording ion mass spectra for HCl as a function of two-photon wavenumber, revealed a previously unobserved \((2 + n)\) REMPI spectra for \(H_{35}Cl\) and \(H_{37}Cl\) with band origin for \(H_{35}Cl\) at 82 521.2 cm\(^{-1}\). Analysis of the data, involving simulation calculations, relative ion-yield determinations laser-power-dependence measurements and comparison with earlier experimental and theoretical work allowed the upper state to be assigned as the \(g^3\Sigma^+(1), \nu = 0\) Rydberg state with \(B_0 = 10.26\) cm\(^{-1}\) for \(H_{35}Cl\).

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**1. Introduction**

Hydrogen chloride is one of the most studied molecules in the fields of spectroscopy, for a number of reasons. Quantitative data on molecule-photon interactions are of interest in understanding stratospheric photochemistry as well as being relevant to the photochemistry of planetary atmospheres and the interstellar medium [1]. Furthermore, relatively intense single- and multi-photon absorption in conjunction with electron excitations, as well as rich band-structured spectra, make the molecule ideal for fundamental studies in these fields.

Green et al. reported a comprehensive \((2 + 1)\) REMPI study of the HCl molecule [2–5]. In their papers more than 50 new states are reported and combined with previous work by others. Furthermore, Tilford et al. reported \(3\Pi\) states [6] and Ginter and Ginter have reported a \(1\Sigma^+\) state [7] using single photon excitations. More recently our group reported observations of \(\Phi\) states using \((3 + 1)\) REMPI [8,9].

Despite numerous experimental studies on the photochemistry and photophysics of the electronically excited states of HCl, only a limited number of theoretical studies have been performed on the excited states [10–16]. Of particular interest to our work presented in this paper are \(\text{ab initio}\) CI (configuration interaction) calculations carried out by Li et al. [14] and semi-empirical studies performed by Liyanage et al. [15] concerning energy levels of \(\Sigma^+\) states of HCl. Additionally, Greening has calculated the energy difference for \(\Sigma^+\) and \(\Sigma^+\) states, using Recknagel parameters [16].

No \(\Sigma^+\) states have been detected experimentally, despite being theoretically predicted (10–11). In this paper we present a previously unreported spectrum which we believe to be due to transitions to a \(\Sigma^+(1)\) state of HCl.

**2. Experimental and method of analysis**

Resonance enhanced multi-photon ionisation (REMPI) of jet-cooled HCl gas was performed. Ions were directed into a time-of-flight tube and detected by a MCP detector to record the ion-yield as a function of mass and laser radiation wavenumber, i.e. to obtain two-dimensional REMPI data.

The apparatus used is similar to that described elsewhere [8,13,17,18]. Tunable excitation radiation was generated by an Excimer laser-pumped dye laser system, using a Lambda Physik COMPex 205 Excimer laser with a Coherent ScanMatePro dye laser. The C-480 dye was used and frequency doubling was performed with a BBO-2 crystal. The repetition rate was typically 10 Hz. The bandwidth of the dye laser beam was about 0.095 cm\(^{-1}\). Typical laser intensity used was about 0.1–0.3 mJ/pulse. The radiation was focused into an ionisation chamber between a repeller and an extractor plate. Undiluted pure HCl gas sample (Merck–Schuchardt OHG; purity >99.5%) was pumped through a 500 µm pulsed nozzle from a typical total backing pressure of about 1.0–1.5 bars into the ionisation chamber. The pressure in the ionisation chamber was lower than 10\(^{-6}\) mbar during experiments. The nozzle was kept open for about 200 µs and the laser beam was typically fired...
500 μs after opening the nozzle. Ions were extracted into a time-of-flight tube and focused onto a MCP detector, of which the signal was fed into a LeCroy 9310A, 400 MHz storage oscilloscope as a function of flight time. Average signal levels were evaluated and recorded for a fixed number of laser pulses to obtain the mass spectra. Mass spectra were typically recorded in 0.05 or 0.1 cm⁻¹/laser wavenumber steps. Spectral points were generally obtained by averaging over 100 pulses. The power dependence of the ion signal was determined by integrating the mass signals repeatedly and averaging over a large number of pulses. Laser calibration was performed by recording an optogalvanic spectrum, obtained from a built-in Neon cell, simultaneously with the recording of the REMPI spectra. Line positions were also compared with hydrogen chloride rotational lines reported by Green et al. [2–4]. Care was taken to prevent saturation effects as well as power broadening by minimising laser power.

![Figure 1](image1.png)

**Fig. 1.** (a) (2 + n) REMPI spectrum of HCl derived by recording H35Cl+. Overall simulation of the new band (see b) is shown at bottom, obtained for two-photon resonance transitions from the ground state (X1Σ⁺(v' = 0)) to a Λ = 0 upper state. The calculated spectrum shows relatively strong Q-branch lines, whereas S- and O-branch lines are weak and not detectable in the experimental spectrum. Peaks due to transitions to the Rydberg states f3D1 and D1P1 have been assigned [2]. Peaks marked with asterisks are due to transitions to the V1R+, v'0 = 9 ion-pair state [2]. (b) (2 + 1) REMPI spectra of the new system derived by recording the H35Cl+ and H37Cl+ ions.

### Table 1

<table>
<thead>
<tr>
<th>J'</th>
<th>H35Cl</th>
<th>H37Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>82 520.8 ± 0.5</td>
<td>82 520.6 ± 0.5</td>
</tr>
<tr>
<td>2</td>
<td>82 519.7 ± 0.5</td>
<td>82 519.6 ± 0.5</td>
</tr>
<tr>
<td>3</td>
<td>82 518.5 ± 0.5</td>
<td>82 518.4 ± 0.5</td>
</tr>
<tr>
<td>4</td>
<td>82 517.2 ± 0.5</td>
<td>82 517.2 ± 0.5</td>
</tr>
<tr>
<td>5</td>
<td>82 515.3 ± 0.5</td>
<td>82 515.2 ± 0.5</td>
</tr>
<tr>
<td>6</td>
<td>82 512.8 ± 0.5</td>
<td>82 512.8 ± 0.5</td>
</tr>
<tr>
<td>7</td>
<td>82 509.4 ± 0.5</td>
<td>82 509.8 ± 0.5</td>
</tr>
<tr>
<td>8</td>
<td>82 504.4 ± 0.8</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 2](image2.png)

**Fig. 2.** Simulation of the H37Cl spectrum in Fig. 1b obtained by assuming two-photon resonance transitions from the ground state (X1Σ⁺(v' = 0)) to a Λ = 0 upper state (Hunds case (b)), Q-branch lines. J' = J' numbers are indicated.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>E' [cm⁻¹]</th>
<th>Δ' [cm⁻¹]</th>
<th>v'0 [cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H35Cl</td>
<td>10.26 ± 0.02</td>
<td>0.0010 ± 0.0003</td>
<td>82 521.2 ± 0.5</td>
</tr>
<tr>
<td>H37Cl</td>
<td>10.27 ± 0.02</td>
<td>0.0009 ± 0.0003</td>
<td>82 521.0 ± 0.5</td>
</tr>
</tbody>
</table>

![Figure 3](image3.png)

**Fig. 3.** Mass spectra for Q lines in the new spectral system (excitation region 82 508–82 522 cm⁻¹). (a) For rotational lines corresponding to J' = J' = 1–8. (b) For rotational line corresponding to f' = f' = 6.
3. Results and analysis

Fig. 1a shows a \((2 + n)\) REMPI spectrum in the region of 82 370–82 710 cm\(^{-1}\) obtained by recording H\(^{35}\)Cl\(^+\) ions as a function of excitation wavenumber. Rotational peaks due to two-photon resonance transitions to the \(V^1\Sigma^+\) \((\nu = 9)\), \(D^1\Pi\) \((\nu = 0)\) and \(C^3\Delta_1\) \((\nu = 0)\) states were identified, whereas a rotationally-structured spectrum, not previously reported, was observed in the spectral region of 82 508–82 522 cm\(^{-1}\) (Fig. 1a and b). Peak positions are listed in Table 1.

The new structure could be simulated by assuming two-photon resonance absorption for \(Q\)-branch transitions to a \(\Lambda = 0\) state in Hunds case (b) approximation (see Fig. 2). Two-photon transitions to \(\Lambda = 1\) or 2 states (or to \(\Omega = 1\) or \(\Omega = 2\) states in Hunds case (c)) could be ruled out due to structural differences in the \(Q\)-branch, and to nonobservable \(P\)- and \(R\)-branch lines. Spectroscopic constants derived from simulations of the H\(^{35}\)Cl and H\(^{37}\)Cl spectra are listed in Table 2. The rotational constants \(B\), being close to those for the ground states of the neutral and ion species, \(\langle B_r^{-}\rangle\) \((\text{H}^{35}\text{Cl},\space X^1\Sigma^+) = 10.439826\space \text{cm}^{-1}\) and \(\langle B_{r-}\rangle\) \((\text{H}^{35}\text{Cl},\space X^1\Pi) = 9.79303\space \text{cm}^{-1}\) [23]), are typical values observed for unperturbed or only slightly perturbed Rydberg states [2]. The small isotope shift observed for the two isotopomers suggests that the spectra correspond to transitions to \(v' = 0\).

Fig. 3 shows mass spectra derived from the excitations via the \(J' = 0\)–8 levels in the new system. Strong signals are found for HCl\(^+\), whereas weak H\(^+\) signals are observed. Expansion of the mass spectra in the region of the chlorine containing ions revealed very weak \(^{35}\text{Cl}^+\) ion signals for the maximum at \(J' = 6\) (see Fig. 3b). A plot of \(^{35}\text{Cl}^+\) ion signals over H\(^{35}\text{Cl}\) ion signals (i.e. “normalised \(^{35}\text{Cl}^+\) ion signals” [13]) as a function of \(J\) shows a ratio for \(J' = 6\) which contrasts sharply with those observed for \(J' = 1\)–5, 7–8 (Fig. 4). This observation is typical for a transition to a Rydberg state which only couples very weakly to the \(V^1\Sigma^+\) \((\Omega = 0)\) ion-pair state such as to \(\Delta \Omega > 0\) singlet states [13] or to triplet states [24,25] showing enhanced Cl\(^+\) ion signal for near-resonance interactions between a Rydberg state level and an ion-pair level [13]. This is consistent with the energies derived for \(J\) levels for the new state and the \(V^1\Sigma^+\) \((\nu = 9)\) where the energy-gap is found to be smallest for \(J' = 6\), \(\Delta \Omega = 0\) (see Fig. 5 and Table 3). Furthermore, power-dependence measurements for the H\(^{35}\)Cl\(^+\) and H\(^+\) ion signals revealed these to behave proportionally with laser power cubed and laser intensity.
power to the fourth, respectively, as expected for a near-diabatic Rydberg state [13]. These observations further support the energetics for the new state and rule out an $\Omega = 0$ assignment. Therefore the new, $\Lambda = 0$, state must be a triplet state, i.e. a $^3\Sigma$ state.

Four low-lying $^3\Sigma$ Rydberg states, with the configuration $\sigma^2\pi^4(3\Pi)4p\pi$, are expected to be found in this energy region, the $g^3\Sigma^+(0^+)$, $g^3\Sigma^-(1)$, $g^3\Sigma^+(0^-)$ and $g^3\Sigma^+(1)$ states, assuming these to belong to Hunds cases intermediate between (b) and (c) [26]. Whereas the $g^3\Sigma^+(0^+)$ and $g^3\Sigma^-(1)$ states have been observed ($v_0 = 83 087.7$ cm$^{-1}$ and $v_0 = 83 263.6$ cm$^{-1}$, respectively) both in absorption [7] and in $(2+1)$ REMPI [23], the $g^3\Sigma^+(0^-)$ and $g^3\Sigma^+(1)$ have not. Fig. 6a and b shows schematic energy level structures for the $^3\Sigma^+$ (Fig. 6a) and $^3\Sigma^+$ (Fig. 6b) states in the Hunds cases (b) and (c) representations and energy levels for the ground state ($X^1\Sigma^+$). Parities of levels are indicated as + and −. Strong signals are observed in $(2+n)$ REMPI for the $g^3\Sigma^+(0^-)$ --- $X^1\Sigma^+$ transitions whereas weaker (or) signals are observed for the $g^3\Sigma^-(1)$ --- $X^1\Sigma^+$ transitions corresponding to $\Delta J = -1$ (0 lines), $\Delta J = 0$ (Q) and $\Delta J = +1$ (R) only. This is indicated by broad and narrow double arrows for transitions from one selected ground state level ($J^* = 3$) in Fig. 6a. Due to the two-photon excitation selection rules in terms of the parities

$+\leftrightarrow +$ or $-\leftrightarrow -$

and in terms of $J$

$\Delta J = 0, \pm 2$

no transitions are to be expected for $g^3\Sigma^-(0^-)$ --- $X^1\Sigma^+$. The latter is indicated in Fig. 6b by dashed arrows. Hence we believe that the new excited state of concern is the $^3\Sigma^+(1)$ state, which by comparison with the $g^3\Sigma^-(1) --- X^1\Sigma^+$ REMPI spectrum and by assuming Hunds case (b) dominance will show negligible or no P and R lines.

Based on united-atom guideline-calculations made by Greening in 1975 [16], where HCl was replaced by the argon atom, the two $g^3\Sigma^-$ states were predicted to be close in energy and lower than the $g^3\Sigma^+(0^-)$ state by about 2000 cm$^{-1}$ (i.e. $v_0 \approx 81 000$ cm$^{-1}$). Ab initio multireference single- and double-excitation configuration interaction (MRD-CI) calculations, which, based on calculations for known states, could be in error by several hundreds of wavenumbers [11,14], predict the $g^3\Sigma^-$ states to be located at about 81 300 cm$^{-1}$ relative to the ground state [14]. The semi-empirical effective Hamiltonian method, which allowed deperturbation of several Rydberg states as well as the $V^3\Sigma^+$ ion-pair state of HCl, predicts the origin of the $^3\Sigma^-$ state to lie near the origin of the zero-order d$^3$II state ($v_0 = 81 932.5$ cm$^{-1}$), i.e. at an energy of about 81 860 cm$^{-1}$ [15]. Taking into account the expected uncertainties and the discrepancies in the theoretically-based predictions (see Table 4), as well as allowing for possible deviation of the energies of the $g^3\Sigma^-(1)$ and $g^3\Sigma^+(0^-)$ states from zero-order $^3\Sigma^-$ state due to interactions and perturbations, we feel that $v_0 = 82 521.2$ cm$^{-1}$ for the $^3\Sigma^-(1)$ state is a truthful value.

- Table 4

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Greening [16]</th>
<th>Li et al. [14]</th>
<th>Liyanage et al. [15]</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E(g^3\Sigma^-(1))$</td>
<td>$\approx 81 000$</td>
<td>$81 305$</td>
<td>$81 860 \pm 50$</td>
<td>$82 521.2 \pm 0.5$</td>
</tr>
</tbody>
</table>
Ab initio MRD-CI calculations [11,14] predict pronounced Rydberg-valence mixing in the $3\Sigma^+$ manifolds. Therefore large predissociation linewidths have been predicted for the $v' = 0$ and 1 vibrational levels of the lowest bound $3\Sigma^+$ state, whereas these are expected to decrease as $v'$ increases. This has been taken to be consistent with the fact that the corresponding state has not been identified by spectroscopic means. Our simulation calculations (Fig. 2), on the other hand, reveal rather sharp lines which are expected to decrease as vibrational levels of the lowest bound $X_1^0$ (H$^{35}$Cl) = 82 521.2 cm$^{-1}$ for H$^{35}$Cl [2]).

4. Conclusions

A previously unobserved $(2 + n)$ REMPI spectrum of HCl in the two-photon resonance excitation region 82 508–82 522 cm$^{-1}$ was recorded and analysed. Spectra simulations allowed peak assignments and determinations of band origins $(\nu_0(\text{H}^{35}\text{Cl}) = 82 521.2 \text{ cm}^{-1})$, as well as rotational constants for the upper state. The simulation calculations, along with ion-yield analysis of mass resolved spectra, and laser-power-dependence measurements for ion signals, revealed this spectral structure to be due to a two-photon resonance excitation from the ground state ($X^1\Sigma^+(v' = 0)$) to a $3\Sigma^+(v' = 0)$ Rydberg state. Based on previous experimental observations of spectra due to resonance transitions to the $g^3\Sigma^-$ $^0$ and $g^3\Sigma^-$ $^1$ states, theoretical predictions of energies of $g^3\Sigma^-$ states ($g^3\Sigma^-(0')$ and $g^3\Sigma^-(1')$) and two-photon excitation selection rules, the new excited state is assigned as the lowest energy $g^3\Sigma^-(1')$, $\sigma^2\pi^2[3\Pi]4\pi$, $v' = 0$ Rydberg state.

Acknowledgments

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References