Laser Magnetic Resonance Rotational Spectroscopy of the Hydrogen Halide Molecular Ions: $^{35}\text{Cl}^+$ and $^{37}\text{Cl}^+$

KAREN G. LUBIC, DOUGLAS RAY, DAVID C. HOVDE, LEIF VESETH, AND RICHARD J. SAYKALLY

Department of Chemistry, University of California, Berkeley, California 94720

Pure rotational spectra of the $X^2\Pi$ vibronic ground states of $^{35}\text{Cl}^+$ and $^{37}\text{Cl}^+$ molecular ions have been measured by far-infrared laser magnetic resonance (LMR). The spectrometer, which contains an intracavity transverse dc discharge, is described in some detail. The theoretical formalism used to analyze the LMR spectra of HF$^+$, HCl$^+$, and HBr$^+$ is presented. The constants $B, q, h, eQq_0, eQq_2, g_0$, and $g_\perp$ were determined from a least-squares regression analysis of the $J = \frac{3}{2} \leftarrow \frac{1}{2}$ and $J = \frac{5}{2} \leftarrow \frac{3}{2}$ transitions in $^{35}\text{Cl}^+$ and $^{37}\text{Cl}^+$. Values obtained for the molecular parameters support a model of HCl$^+$ with the electron density strongly localized on chlorine and with hydrogen exhibiting a substantial positive charge.

INTRODUCTION

While rotational spectroscopy has produced the largest share of data leading to the present state of our knowledge regarding structure and bonding in simple molecules, only within the last decade has it become possible to measure rotational spectra of molecules having a net charge. The first such experiments were carried out in the millimeter region of the spectrum by Woods and co-workers (1, 2) on CO$^+$, HCO$^+$, and HNN$^+$; since that time, swept frequency techniques in the millimeter, far-infrared, and infrared regions have produced rotational and rovibrational spectra of a sizable number of ions, including the hydroxide anion (3).

In 1979 Saykally and Evenson (4) employed the technique of far-infrared laser magnetic resonance to study the rotational spectrum of HBr$^+$. Some time later Ray et al. (5) and Hovde et al. (6) reported the detection of rotational spectra of the isovalent ions $^{35}\text{Cl}^+$ and HF$^+$, respectively, with a laser magnetic resonance spectrometer capable of more general application to studies of charged molecules than the system used for the original detection of HBr$^+$. In this paper we present a more detailed description of this laser magnetic resonance system and its utilization to measure over 80 LMR transitions in $^{35}\text{Cl}^+$ and $^{37}\text{Cl}^+$. We describe the analysis of these spectra in terms of the theoretical formalism developed by Veseth (7) and discuss the interpretation of the resulting molecular parameters to provide a characterization of the electronic structure of the ground states of these simple ions. In an accompanying

1 Present address: Intel Corporation, 2250 Mission College Blvd., Santa Clara, CA 95025-8125.
2 Present address: Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, CO 80309-0440.
3 Present address: Institute of Physics, Universitetet i Oslo, P.O. Box 1048, Blindern, 0316 Oslo 3, Norway.

0022-2852/89 $3.00
Copyright © 1989 by Academic Press, Inc.
All rights of reproduction in any form reserved.
paper (8), we report the detection and analysis of about 130 new transitions in H\textsuperscript{79}Br\textsuperscript{+} and H\textsuperscript{81}Br\textsuperscript{+}.

The hydrogen halide ions are of practical importance with regard to possible roles in the chemistry of the upper atmosphere. Similarly, the cosmic abundance of chlorine (9) ($\sim 10^{-6}$ of hydrogen) is high enough to warrant serious consideration of the role of chlorine chemistry in the dynamics of interstellar gas clouds, and neutral HCl has been detected in the interstellar medium by Blake et al. (10). The accurate spectroscopic data obtained in the present experiments create new possibilities for detection and study of the HCl\textsuperscript{+} molecular ion in these contexts.

Brice and Jenkins (11) first observed the electronic emission spectrum of HCl\textsuperscript{+} in 1929. Since then the $A^2\Sigma^+ - X^2\Pi$ transitions have been studied extensively in emission from hollow cathode (12), Geissler (13), Schuler (14), and microwave discharges (15), as well as from electron impact (16) and ion beam excitation (17). Each study has provided information about new vibronic bands. The most recent emission work by Sheasley and Mathews (15) extended the upper state progression to include the 6--0 band and the lower state progression to $v^\prime = 2$. Their analysis showed a discrepancy between the observed and the predicted isotope shift for the centrifugal distortion correction to the spin–orbit constant, $A_D$. In order to resolve this, Saenger et al. (18) reanalyzed the emission data using the diatomic Hamiltonian and “direct approach” of Zare et al. (19). Later Brown and co-workers (20, 21) also reanalyzed the Sheasley and Mathews data using an effective Hamiltonian approach. They reconciled the two different theoretical models and discussed the relationship between $A_D$ and $\gamma$ in the pure precession limit. The most recent optical study of HCl\textsuperscript{+} is that of Martner et al. (22), who observed the $A-X$ system by laser-induced fluorescence of HCl\textsuperscript{+} ions confined in an RF-quadrupole ion trap. Rotational state resolved radiative lifetimes of the $A^2\Sigma^+$ state were determined in that work ($\tau = 3.4 \pm 0.4$ µsec).

In an attempt to understand the photoelectron spectrum of HCl\textsuperscript{+}, Raftery and Richards (23) calculated SCF potential energy curves for $X^2\Pi$, $A^2\Sigma$, and $^4\Pi$ states. They found that the $^4\Pi$ state causes a predissociation in the $A^2\Sigma$ state above $v = 7$, explaining the lack of higher vibrational levels in the photoelectron spectrum.

Because of the possible role of HCl\textsuperscript{+} in radiative cooling of interstellar gas clouds (24), Fehsenfeld and Ferguson (25) investigated the production of HCl\textsuperscript{+} via Cl\textsuperscript{+} and H\textsubscript{2} and its destruction by reactions with H\textsubscript{2} and HCl using the flowing afterglow technique. Gold et al. (26) proposed that HCl\textsuperscript{+} might actually be a possible interstellar maser and estimated the appropriate $\Lambda$-doubling transitions from optical data.

Ray et al. (5) reported the detection and analysis of the rotational spectrum of H\textsuperscript{35}Cl\textsuperscript{+}, in which the constants $B$, $h$, $g$, $eQq_0$, and $eQq_2$ were determined from a fit of 24 LMR transitions in $v = 0$ of the $^2\Pi$ ground state. More recently, Davies and co-workers (27) have measured portions of the vibration–rotation spectrum of HCl\textsuperscript{+} by velocity modulation spectroscopy with a diode laser, and Urban and his colleagues (28) have studied vibration–rotation spectra of DCl\textsuperscript{+} with the new Faraday laser magnetic resonance technique. In the latter work, infrared transitions among the lowest seven vibrational states were measured; hyperfine splittings were not resolved in either case.

In the present study, 82 hyperfine and magnetic sublevels of the $J = \frac{3}{2} \leftarrow \frac{3}{2}$ and $J = \frac{9}{2} \leftarrow \frac{7}{2}$ rotational transitions in the $\Omega = \frac{3}{2}$ spin level of the vibronic ground state were
measured for both H$^{35}$Cl$^+$ and H$^{37}$Cl$^+$. For each isotopic species, nonlinear least-squares fits of the LMR data gave well-determined values for the rotational constant $B$, $\Lambda$-doubling constant $q$, magnetic hyperfine constants $h$ and $b$, nuclear electric quadrupole constants $eQq_0$ and $eQq_2$, and the $g$ factors $g_l$ and $g_R$. These parameters are subsequently interpreted in terms of the electronic structure of HCl$^+$.

EXPERIMENTAL DETAILS

A. The LMR Spectrometer System

A diagram of the far-infrared laser magnetic resonance spectrometer is given in Fig. 1. The far-infrared laser cavity, defined by a mirror fixed to a piezoelectric translator (PZT) and a movable mirror mounted on a micrometer drive, is a nearly confocal Fabry–Perot resonator about 1 m in length. The laser cavity is divided into a gain cell and a sample region by a rotatable polypropylene Brewster window (12 µm thick). The gain cell typically contains 0.01 to 0.5 Torr of a vapor such as methanol or formic acid which strongly absorbs a CO$_2$ laser frequency. The CO$_2$ pump laser then creates a population inversion between rotational levels of the ground or an excited vibrational state, and lasing action between selected rotational levels occurs. Currently about 2300 cw lines in about 60 different gases have been made to oscillate between 40 and 2000 µm (29), although many of these will not lase in this LMR spectrometer.

The gain cell is pumped transversely by a CO$_2$ laser using plane parallel mirrors in a multiple reflection configuration. This geometry allows the resonator to accept the full pump power without destroying the beamsplitter. The spacing between the pump-
ing mirrors is adjustable and can be optimized for each laser line. The 3-m CO\textsubscript{2} pump laser operates cw with up to 80 W on the strongest line ($\text{10P20}$) and is tuned by grating and piezoelectric drives. The near-confocal FIR resonator selects lasing on a single longitudinal mode, since the mode spacing is $\sim 165$ MHz and the far-infrared gain bandwidth is only a few megahertz. High-order transverse modes are eliminated with an iris. The rotatable Brewster window allows perpendicular or parallel polarization of the far-infrared laser radiation (relative to the dc magnetic field) to be selected, because only the $P$ polarization (relative to the beamsplitter) has low loss. Power is coupled out of the far-infrared cavity via a cylindrical copper mirror at 45° to the laser axis, which can be inserted into the laser mode pattern any desired distance.

A liquid-helium-cooled, gallium-doped germanium bolometer (Infrared Laboratories, Inc. Bolometer No. 494, Dewar Model HD-3) is used as a detector. The bolometer is continually pumped to maintain a temperature near 1.5 K, with baffles to reduce background radiation. The cooled filters were removed to increase the laser throughput, with a consequent decrease in the hold time of the 1.5-liter Dewar from 36 to about 32 hr. The bolometer system has a measured NEP of $2.4 \times 10^{-13}$ W/Hz$^{1/2}$ and a 3-dB point of 2300 Hz. A Teflon lens (5-cm focal length) is mounted over the Teflon window of the detector to focus the far-infrared beam onto the detector element.

The intracavity sample cell is placed between the ring-shimmed pole pieces of a 38-cm electromagnet (Varian Model No. V-3800), which can produce fields up to 20 kG (2 T) with high homogeneity over much of the 7-cm air gap. Helmholtz coils are mounted on the pole pieces of the magnet. Each coil consists of 150 turns of 18-gauge varnished copper wire with a resistance of 0.8 ohm. The coils are driven by the internal reference oscillator of a lock-in amplifier (PAR No. HR-8) whose output is then fed to a 300-W audio amplifier (Bogen MT250). This provides a 2.5-kHz sinusoidal modulation field with a peak-to-peak amplitude of about 30 G. The modulated signal from the detector is processed by the lock-in amplifier. The spectra are recorded on an $X$-$Y$ recorder (HP-7044B) and appear as the first derivative of the intracavity laser power vs magnetic field. Magnetic flux density measurements are made with a nuclear magnetic resonance digital gaussmeter (Cyclotron Corp. Model 5300). The center of the absorption signal is determined by recording the signal at several modulation amplitudes, with the flux reading taken with the modulation coils turned off and the probe rf drive and field modulation drive as low as possible.

To generate the molecular ions HCl$^+$ and HBr$^+$, a glow discharge is maintained in the intracavity sample cell through 1–1.5 Torr He flowing past the end mirror and a few milliTorr of hydrogen halide gas added at the center of the discharge by means of a flow tube. The flow tube consists of two concentric glass tubes, each with isolated gas inlet ports. A pair of brass shimstock discharge electrodes ($150 \times 40 \times 0.36$ mm) is held by four screws to the inside of a 15-cm-long, 50-mm-i.d. piece of Teflon tubing. The Teflon tubing is 4 mm thick and has machined holes to allow for gas flow. The tubing slides into the tee, and electrical connections are made by means of electrical feedthroughs located in the tee. The discharge is driven by a 3-kV, 150-mA, voltage-regulated power supply (Alfred Electronics No. 231A) through a 3.5-kΩ ballast resistor. The discharge noise voltage is monitored on an oscilloscope through a blocking capacitor. The pressure of each gas and the discharge current are adjusted to minimize
discharge noise while maintaining good $S/N$. Typically, currents of $\sim 20$ mA were used in all of the work described in this series.

**B. Spectra of HCl$^+$**

An energy level diagram for the $X^2\Pi, v = 0$ state of HCl$^+$ is given in Fig. 2. The far-infrared rotational transitions were predicted using Brown’s (20, 21) analysis of Sheasley and Mathews’ (15) optical data and a simplified $^2\Pi$ Hamiltonian. Table I lists the observed transitions and the far-infrared laser lines used to detect them. The frequencies of the laser lines are taken from Knight’s (29) tables and are considered accurate to $\pm 0.5$ MHz (30).

Figures 3 and 4 are samples of the observed spectra of HCl$^+$ for both isotopes. All of these spectra were optimized in a discharge through $\sim 1.5$ Torr of He containing a few milliTorr of HCl at currents of 10–20 mA. The spectra could not be observed at lower or higher pressures, due to the very specific conditions required for a stable discharge. The quartet splitting in all the spectra is due to the magnetic hyperfine interactions of the Cl nucleus ($I = \frac{3}{2}$) while the larger doublet splitting arises from $\Lambda$-doubling (Figs. 3 and 4 each show only one $\Lambda$-doubling component). The proton hyperfine structure could not be resolved for HCl$^+$, although it was clearly observed in the case of HF$^+$. In all, 32 transitions were measured for H$^{35}$Cl$^+$ and 50 for H$^{37}$Cl$^+$.

---

**Fig. 2.** Energy level diagram for HCl$^+$. For clarity, the $\Lambda$-doubling of the $\Omega = \frac{3}{2}$ substate has been exaggerated. LMR transitions were observed using lasers near 148.4 and 115.5 $\mu$m.
### TABLE I

Observed LMR Transitions and FIR Laser Lines Used

<table>
<thead>
<tr>
<th>Transition</th>
<th>Laser Medium</th>
<th>Laser $\lambda$ (\textmu m)</th>
<th>Laser $\nu$ (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{35}\text{Cl}^+$, $J=7/2-5/2$, $a=3/2$</td>
<td>CH$_3$NH$_2$</td>
<td>147.9</td>
<td>2027.7526</td>
</tr>
<tr>
<td>$^{35}\text{Cl}^+$, $J=7/2-5/2$, $a=3/2$</td>
<td>$^{13}$CH$_3$OH</td>
<td>149.3</td>
<td>2008.3600</td>
</tr>
<tr>
<td>$^{37}\text{Cl}^+$, $J=7/2-5/2$, $a=3/2$</td>
<td>$^{13}$CH$_3$OH</td>
<td>149.3</td>
<td>2008.3600</td>
</tr>
<tr>
<td>$^{35}\text{Cl}^+$, $J=9/2-7/2$, $a=3/2$</td>
<td>$^{13}$CH$_3$OH</td>
<td>115.8</td>
<td>2588.3630</td>
</tr>
<tr>
<td>$^{37}\text{Cl}^+$, $J=9/2-7/2$, $a=3/2$</td>
<td>$^{13}$CH$_3$OH</td>
<td>115.8</td>
<td>2588.3630</td>
</tr>
</tbody>
</table>

*a) Laser frequencies taken from (29).*

The average precision of a flux density measurement was equivalent to a frequency of $\sim 2$ MHz, but the signal-to-noise varied substantially among various transitions, causing some measurements to be less precise.

The signs of the magnetic tunabilities ($\partial H/\partial \nu$) of the transitions were determined by red or blue shifting the far-infrared laser frequency and observing the corresponding change in the magnetic flux density. For molecules with a linear Zeeman effect, the sign of the tunability determines whether the laser frequency is above or below the zero field transition frequency. Disappearance of the spectra when HCl was replaced by DCI supported the assignment of the spectra to HCl$^+$. Both the addition of H$_2$ and raising the concentration of HCl similarly caused the spectra to disappear, which is

![Figure 3](image-url)

**FIG. 3.** (a) One A-doubling component of the $J = \frac{7}{2} \rightarrow \frac{5}{2}$ transition in $^{35}$Cl$^+$ observed in a 15 mA dc discharge through 1.5 Torr He and 5 mTorr HCl. (b) As in (a), but with the modulation amplitude tripled. (c) As in (a), but with 20 mTorr O$_2$ added.
ROTATIONAL SPECTRUM OF $\text{HCl}^+$

$^{37}\text{Cl}^+$ $^2\Pi$ $\Omega = 3/2$ $v = 0$

$J = 9/2 \leftrightarrow 7/2$

$116 \mu$m $^{13}\text{CH}_2\text{OH}$

Fig. 4. One $\Delta$-doubling component of two different Zeeman sublevels of the $J = 9/2 \leftrightarrow 7/2$ transition of $^{37}\text{Cl}^+$ observed with the same conditions as Fig. 3a.

consistent with known rapid reactions of $\text{HCl}^+$ with $\text{H}_2$ or $\text{HCl}$ to form $\text{H}_2\text{Cl}^+$ (25). Addition of $\text{O}_2$ to the discharge also resulted in disappearance of the $\text{HCl}^+$ spectra. No $\text{HCl}^+$ spectra were observed when argon was substituted for the helium buffer.

The presence of $\text{N}_2$ impurities in the reactant gases resulted in hyperfine triplets and sextets appearing in the spectra, as seen in Fig. 3. Upon increasing the modulation amplitude, as in Fig. 3b, the sextet condensed into a doublet while the $\text{HCl}^+$ quartet was unchanged. Addition of $\text{O}_2$ to the discharge caused the quartet to disappear, but the sextet was unperturbed (Fig. 3c). Clearly the quartet and sextet are not due to the same chemical species. Using the far-infrared LMR data of Radford and Litvak (31), the sextets in the 147.9- and 149.3-Å spectra were assigned to $X^3\Sigma^+ \text{NH}_2, \left(\Omega = 0, N = 2 \leftrightarrow 1 \right)$, $\left(\Omega = 2, J = 2 \leftrightarrow 2, J = 3 \leftrightarrow 2 \right)$. The triplets in the 115.8-Å spectrum could not be definitively assigned, but their structures and chemistry, and the reported observation of $\text{NH}_2$ spectra with the 118.6-Å $\text{H}_2\text{O}$ laser (32), indicate $\text{NH}_2$ as the probable carrier of these triplet features. Oxygen-containing impurities in the discharge resulted in the appearance of broad lines due to high-$J$ $\text{ClO}$ transitions (33–37) at high magnetic fields in the 115.8- and 149.3-Å spectra.

THEORY AND ANALYSIS

A. Fine Structure

The theory of $^2\Pi$ states of diatomic molecules needed to interpret EPR and LMR spectra has been the subject of several recent investigations (7, 38). For the convenience of the reader, a brief review of the theoretical approach developed by Veseth is given here. The general form of the Hamiltonian of a diatomic molecule in an external magnetic field is

$$H = H_{\text{ev}} + H_{\text{rot}} + H_{\text{hf}} + H_z,$$

where $H_{\text{ev}}$ denotes the electronic and vibrational Hamiltonian, $H_{\text{rot}}$ represents the rotational energy, $H_{\text{hf}}$ refers to the hyperfine interaction, and $H_z$ represents the interaction of the molecule with an external magnetic field. Note that $H_{\text{ev}}$ also includes spin-dependent and other relativistic interactions, such as the spin–orbit coupling. In
previous investigations (7) the Schrodinger equation associated with Eq. (1) was solved in terms of a fully coupled (in both molecule and space-fixed axis systems) basis set of the type \( |q\Omega_l I FM_F\rangle \), where \( F \) is the total angular momentum (including the nuclear spin \( I \)), and \( \Omega_l \) and \( \Omega \) represent the molecule-fixed components of \( I \) and \( L + S \), respectively. The label \( q \) is needed to identify different states with the same value of \( \Omega \). The fully coupled basis set is chosen for computational conveniences. It yields simple matrix elements for the Hamiltonian of Eq. (1), and the important spin–orbit interaction is easily included to high orders.

The matrix elements of the electronic, vibrational, and rotational parts of the Hamiltonian,

\[
H_{ev} + H_{rot} = H_{ev} + B(F - L - S - I)^2,
\]

are considered first. In terms of the parity eigenstates

\[
|\pm q\Omega_l I FM_F\rangle = \frac{1}{\sqrt{2}} (|q\Omega_l I FM_F\rangle \pm (-1)^{F+S+I} |q - \Omega - \Omega_l I FM_F\rangle)
\]

the general result is (7)

\[
\langle \pm q\Omega_l I FM_F | H_{ev} + H_{rot} | \pm q'\Omega'\Omega'_l I FM_F\rangle
= [E_n + B_n(F(F + 1) + 2\Omega_l - 2(\Omega + \Omega_l)^2)]\delta_{qq'}\delta_{\Omega\Omega'}\delta_{\Omega_l\Omega_l'}
\]

\[
- B_n[(I + \Omega_l)(I - \Omega_l + 1)(F + \Omega + \Omega_l)(F - \Omega - \Omega_l + 1)]^{1/2}
\]

\[
\times (\delta_{\Omega_l-1,\Omega_l'} \pm \delta_{\Omega_l}\delta_{\Omega_l-1,\Omega_l'} \delta_{qq'}\delta_{\Omega\Omega'}) + \langle q\Omega | BJ_{q+1} | q'\Omega - 1 \rangle [(I + \Omega_l + 1)(I - \Omega_l)]^{1/2}
\]

\[
\times (\delta_{\Omega_l-1,\Omega_l'} \delta_{\Omega_l+1,\Omega_l'} \pm (-1)^{F+S+I} \delta_{\Omega_l-1,\Omega_l'} \delta_{\Omega_l+1,\Omega_l'}) - \langle q\Omega | BJ_{q+1} | q'\Omega - 1 \rangle
\]

\[
\times [(F + \Omega + \Omega_l)(F - \Omega - \Omega_l + 1)]^{1/2}(\delta_{\Omega_l-1,\Omega_l'} \delta_{qq'}\delta_{\Omega\Omega'}) \pm (-1)^{F+S+I} \delta_{\Omega_l-1,\Omega_l'} \delta_{\Omega_l+1,\Omega_l'}).
\]

The reader is referred to previous publications (7) for further details on the derivation of Eq. (4). The phase factor \( S_{qq'} \) of Eqs. (3)–(4) equals \(- (S + I)\), where \( S \) is the electronic spin, except for \( \Sigma^- \) states where \( S_{qq'} = -(S + I) + 1 \). For molecules with only one nuclear spin, there are no matrix elements off diagonal in \( I \).

Equation (4) contains several “nonstandard” parameters because the spin–orbit interaction is not included explicitly, but rather included in the electronic Hamiltonian. For a \( ^2\Pi \) state there are two substates, corresponding to \( \Omega = \frac{3}{2} \) and \( \Omega = \frac{1}{2} \). Explicit consideration of the spin–orbit interaction yields the relations

\[
E_{\Omega=3/2} - E_{\Omega=1/2} = A + 2B
\]

\[
B_{\Omega=3/2} = B + 1/2A_D
\]

\[
B_{\Omega=1/2} = B - 1/2A_D,
\]

where \( A \) and \( B \) are the standard spin–orbit and rotational constants, respectively, and \( A_D \) represents the centrifugal distortion in the spin–orbit coupling. Expanding the present fully coupled basis states in terms of Hund’s coupling case (a) states to second order, one obtains
\begin{equation}
\langle q\Omega = \frac{1}{2} | BJ_{a^+} | q\Omega = -\frac{1}{2} \rangle
\end{equation}
\begin{equation}
= \sum_{\Sigma, \Sigma'} (-1)^{s} \frac{\langle 2 \Pi v | BL_{+} | 2 \Sigma v' \rangle \langle 2 \Pi v | (A + 2B) L_{+} | 2 \Sigma v' \rangle}{E_{1v} - E_{2v'}}
\end{equation}
\begin{equation}
= 1/2 p + q,
\end{equation}
where \( p \) and \( q \) denote the standard \( \Delta \)-doubling constants of a \( ^2 \Pi \) state. The off-diagonal parameter \( \langle q\Omega = \frac{1}{2} | BJ_{a^+} | q\Omega = \frac{1}{2} \rangle \) is evaluated in a similar way and is found to be
\begin{equation}
\langle q\Omega = \frac{1}{2} | BJ_{a^+} | q\Omega = \frac{1}{2} \rangle
= B + \frac{1}{2} \sum_{\Sigma, \Sigma'} \frac{\langle 2 \Pi v | AL_{+} | 2 \Sigma v' \rangle \langle 2 \Pi v | BL_{+} | 2 \Sigma v' \rangle}{E_{1v} - E_{2v'}}
\end{equation}
\begin{equation}
+ \frac{1}{2} \sum_{\Delta, \Delta'} \frac{\langle 2 \Sigma v' | AL_{+} | 2 \Pi v \rangle \langle 2 \Delta v' | BL_{+} | 2 \Pi v \rangle}{E_{1v} - E_{\Delta v'}}
\end{equation}
\begin{equation}
= B - \frac{1}{2} \gamma^{(2)}.
\end{equation}
The spin–rotation coupling is included by the effective Hamiltonian
\begin{equation}
H_{SR} = \gamma N \cdot S,
\end{equation}
where the coupling constant \( \gamma \) has a first-order contribution \( \gamma^{(1)} \) which is usually totally dominated by the second order contribution \( \gamma^{(2)} \) defined by Eq. (7) (i.e., \( \gamma = \gamma^{(1)} + \gamma^{(2)} \)).

The general parameters of Eq. (4) include the spin–orbit interaction to all orders; it is interesting to note that the number of parameters has not been reduced by invoking the second-order case (a) approximation. Hence, it is clear that no new adjustable parameters will be obtained by including higher-order spin–orbit terms with a case (a) basis.

The \( ^2 \Pi \) secular matrix considered so far would be incomplete unless the interaction with other electronic states is included. The coupling to other electronic states arises from the Coriolis terms of the rotational Hamiltonian. A Van Vleck transformation to second order includes the Coriolis interaction in the effective \( ^2 \Pi \) matrix, and the only important contribution is a correction to the \( ^2 \Pi_{1/2} - ^2 \Pi_{3/2} \) off-diagonal elements which is given by Eq. (7):
\begin{equation}
\langle q\Omega = \frac{1}{2} | \Omega_{i} IF | H^{(2)} | q\Omega = \frac{1}{2} \Omega_{j} IF \rangle
= \pm \frac{1}{2} q \{ [ (F + \frac{1}{2} + \Omega_{i})(F + \frac{1}{2} - \Omega_{j})(F + \frac{1}{2} + \Omega_{j})(F + \frac{1}{2} + \Omega_{i})]^{1/2} \delta_{\Omega_{i} - \Omega_{j}}
- 2[(I + \Omega_{i} + 1)(I - \Omega_{i})(F + \frac{1}{2} - \Omega_{j})(F + \frac{1}{2} + \Omega_{j})]^{1/2} \delta_{\Omega_{i} + 1, -\Omega_{j}}
+ [(I + \Omega_{i} + 1)(I - \Omega_{i})(I - \Omega_{i} - 1)(I + \Omega_{i} + 2)]^{1/2} \delta_{\Omega_{i} + 2, -\Omega_{j}} \}.
\end{equation}
On the RHS of Eq. (9) above, \( q \) is the standard \( ^2 \Pi \) \( \Delta \)-doubling parameter defined by Eq. (6).

Finally, the centrifugal distortion effects need to be considered. These are handled in the computationally most efficient manner by squaring the rotational part of the secular matrix (with the rotational constant removed), and multiplying the squared
matrix by the negative of the centrifugal distortion constant $D_c$. The matrix proportional to $-D_c$ may then be multiplied by the rotational matrix to produce higher-
order corrections proportional to $H_c$. Centrifugal distortion in the $\Lambda$-doubling parameters $p$ and $q$ is included in a similar way. In this case the rotational matrix is multiplied by the part of the Hamiltonian matrix which contains the relevant $\Lambda$-doubling parameter, and the resulting matrix is multiplied by either the constant $p_D$ or the constant $q_D$.

B. Hyperfine Structure

Matrix elements of the hyperfine Hamiltonian are also easily obtained in the present coupled basis set. General results, including second-order spin–orbit corrections, have already been derived in Ref. (7). For doublet states the second-order corrections were found to be completely absorbed by the standard Frosch and Foley magnetic hyperfine parameters $a$, $b$, $c$, and $d$. Hence, it is sufficient to give the matrix elements of the hyperfine Hamiltonian in the case (a) basis. For a $^2\Pi$ state the result is

\[
\langle \pm q\Omega_f IF | H_{hf} | \pm q\Omega_i IF \rangle = \left\{ [a\Lambda + (b + c)\Sigma] \Omega_f + \frac{3e\Omega q_0}{4I(2I-1)} \Omega_f^2 \right\} \delta_{\Omega,\Omega_f} \delta_{\Lambda,\Lambda_f} \\
+ \frac{1}{2} b [(\Sigma + \frac{1}{2})(\frac{1}{2} - \Sigma)(I + \Omega_f + 1)(I - \Omega_f)]^{1/2} \delta_{\Omega-1,\Omega_f} \delta_{\Omega_f+1,\Omega_i} \mp (-1)^{F-1/2} \\
\times \frac{1}{2} d [(\Sigma + \frac{1}{2})(\frac{1}{2} - \Sigma)(I - \Omega_f)(I + \Omega_f + 1)]^{1/2} \delta_{\Omega-1,\Omega_f} \delta_{\Omega_f+1,\Omega_f} \\
\mp (-1)^{F-1/2} \frac{3e\Omega q_2}{8I(2I-1)} [(I + \Omega_f + 1)(I - \Omega_f)(I + \Omega_f + 2)(I - \Omega_f - 1)]^{1/2} \\
\times \delta_{\Omega-2,\Omega_f} \delta_{\Omega_f+2,\Omega_f}. \tag{10}
\]

Here, of course, $\Omega = \Lambda + \Sigma$, with $\Sigma = \pm \frac{1}{2}$. Only positive values of $\Lambda$ and $\Omega$ need be considered in the parity conserving basis. In Eq. (10) $a$, $b$, $c$, and $d$ denote the standard magnetic hyperfine parameters (39), and $e\Omega q_0$ and $e\Omega q_2$ are the standard quadrupole coupling constants (7, 40). In a decoupled (case (a) or (b)) basis rather complex hyperfine matrix elements with $\Delta J \neq 0$ would have to be considered. These interactions are automatically included by Eq. (10).

C. Zeeman Effect

The interaction between an external magnetic field and a diatomic molecule is described by the Hamiltonian

\[
H_z = \mu_B (g_L L + g_S S - g_I I + g_K^N R) \cdot B \\
= \mu_B [(g_L - g_K^N) L + (g_S - g_K^N) S - (g_I + g_K^N) I + g_K^N F] \cdot B. \tag{11}
\]

Here $g_L$, $g_S$, and $g_I$ are the electronic orbital, electronic spin, and nuclear spin $g$ factors, respectively. $g_K^N$ denotes the nuclear rotational $g$ factor which is given in Ref. (7)

\[
g_K^N = -\frac{m}{M_a + M_b} \frac{Z_b M_a^2 + Z_a M_b^2}{M_a \cdot M_b}. \tag{12}
\]

The matrix elements of the Zeeman Hamiltonian in the present coupled basis have been derived earlier and are given in a more compact form:
\[ \langle q\Omega_l | IFM_F | H \rangle = \sum_{q} \langle q\Omega_l | L \rangle \langle L | q'\Omega' \rangle | IF' \rangle M_F = \mu_B B g_k^N M_F \delta_{q'q} \delta_{\Omega'\Omega} \delta_{F,F'} \]

\[ + (-1)^{M_F - \Omega - \Omega'} \mu_B B \sum_{\mu} (-1)^{\mu} \langle g_l - g_k^N | q\Omega_l | L \rangle | q'\Omega' \rangle \]

\[ + (g_l - g_k^N) \langle q\Omega_l | S \rangle | q'\Omega' \rangle - (g_l + g_k^N) \langle \Omega_l | I \rangle | q'\Omega' \rangle \]

\[ \times [(2F + 1)(2F' + 1)]^{1/2} \left( \begin{array}{ccc}
F & 1 & F' \\
\Omega & -\mu & -\Omega' - \Omega_f
\end{array} \right) \left( \begin{array}{ccc}
F & 1 & F' \\
M_F & 0 & -M_F
\end{array} \right). \] (13)

Here \( L, S, \) and \( I \) denote the molecule-fixed spherical components of \( L, S, \) and \( I, \) respectively. Matrix elements for the parity eigenstates of Eq. (3) are now easily worked out by use of Eq. (13). The matrix elements of \( L, S, \) and \( I \) contained in Eq. (13) are best evaluated in terms of the coupling case (a) basis (7). By using the second-order expansion

\[ |q\Omega_l\rangle = |q\Lambda \Sigma \Omega_l\rangle + \sum_{q',\Delta',\Sigma', \delta} \langle q\Lambda \Sigma |(A + 2B)L \cdot S| q'\Delta' \Sigma' \rangle \]

\[ \frac{E_q - E_{q'}}{|q'\Delta' \Sigma' \Omega_l\rangle}, \] (14)

it is found that for a \( ^2\Pi \) state there will be no second-order corrections to the matrix elements of \( S_\mu \) and \( I_\mu. \) For the matrix elements of \( L_\mu \) three different important second-order corrections are encountered. They are (7)

\[ (g_l - g_k^N) \langle q\Omega = \frac{1}{2}\rangle | L_\mu | q\Omega = -\frac{1}{2}\rangle \]

\[ = g_k^* = (g_l - g_k^N) \sum_{2\Sigma, \nu} (-1)^s \frac{\langle ^2\Pi \nu | L_\mu | ^2\Sigma \nu' \rangle \langle ^2\Pi \nu | (A + 2B)L_\mu | ^2\Sigma \nu' \rangle}{E_{\Pi\nu} - E_{2\Sigma\nu}}, \] (15)

and

\[ (g_l - g_k^N) \langle q\Omega = \frac{3}{2}\rangle | L_\mu | q\Omega = \frac{1}{2}\rangle = \Delta g_S + g_k^*, \]

with

\[ \Delta g_S = \frac{1}{2} (g_l - g_k^N) \left[ \sum_{2\Delta, \nu} \frac{\langle ^2\Delta \nu' | L_\mu | ^2\Pi \nu \rangle \langle ^2\Delta \nu' | AL_\mu | ^2\Pi \nu \rangle}{E_{\Pi\nu} - E_{\Delta\nu}} \right] \]

\[ + \sum_{2\Sigma, \nu} \frac{\langle ^2\Pi \nu | L_\mu | ^2\Sigma \nu' \rangle \langle ^2\Pi \nu | AL_\mu | ^2\Sigma \nu' \rangle}{E_{\Pi\nu} - E_{2\Sigma\nu}} \]

\[ g_k^* = (g_l - g_k^N) \left[ \sum_{2\Delta, \nu} \frac{\langle ^2\Delta \nu' | L_\mu | ^2\Pi \nu \rangle \langle ^2\Delta \nu' | BL_\mu | ^2\Pi \nu \rangle}{E_{\Pi\nu} - E_{\Delta\nu}} \right] \]

\[ + \sum_{2\Sigma, \nu} \frac{\langle ^2\Pi \nu | L_\mu | ^2\Sigma \nu' \rangle \langle ^2\Pi \nu | BL_\mu | ^2\Sigma \nu' \rangle}{E_{\Pi\nu} - E_{2\Sigma\nu}} \]. \] (16)

In Eqs. (6) and (15), the phase factor \((-1)^s\) equals 1 for \(^2\Sigma^+\) states and \(-1\) for \(^2\Sigma^-\) states.
Finally, second-order cross terms between the rotational Hamiltonian and the electronic orbital part of the Zeeman Hamiltonian must be included. Their effect is to introduce another second-order g factor $g^L_R$ defined in Ref. (7)

$$g^L_R = (g_l - g^N_R) \sum_{\Sigma, \nu'} (-1)^{\nu'} \frac{\langle 2 \Pi_\nu | L_+ | 2 \Sigma \nu' \rangle \langle 2 \Pi_\nu | B L_+ | 2 \Sigma \nu' \rangle}{E_{\Pi \nu} - E_{\Sigma \nu'}}$$  \hspace{1cm} (17)

and a correction term to the electronic orbital g factor, such that the effective $g_l$ factor is given by

$$g_{\text{eff}} = g_l + (g_l - g^N_R) \left[ \sum_{\Sigma, \nu'} \frac{\langle 2 \Delta \nu' | L_+ | 2 \Pi_\nu \rangle \langle 2 \Delta \nu' | B L_+ | 2 \Pi_\nu \rangle}{E_{\Pi \nu} - E_{\Delta \nu'}} \right. \right.$$

$$\left. - \sum_{\Sigma, \nu'} \frac{\langle 2 \Pi_\nu | L_+ | 2 \Sigma \nu' \rangle \langle 2 \Pi_\nu | B L_+ | 2 \Sigma \nu' \rangle}{E_{\Pi \nu} - E_{\Sigma \nu'}} \right].$$  \hspace{1cm} (18)

In addition new terms proportional to the g factor $g^N_R$ of Eq. (16) are introduced, and the effect of all terms proportional to $g^N_R$ is to define a new total molecular rotational g factor which becomes

$$g_R = g^N_R - g^T.$$  \hspace{1cm} (19)

The second-order g factors discussed above are equivalent to those introduced by Brown et al. (38) from a partially decoupled basis set (case (a$\Delta$)).

In practice it will be difficult to obtain fitted values for all the g factors introduced above for a given set of spectroscopic data of a $^2\Pi$ state. In addition there is the problem of high correlations between some of the zero-field parameters, in particular between the centrifugal distortion $A_D$ in the spin–orbit coupling constant and the spin–rotation coupling constant $\gamma$. In a previous investigation (7) this problem was handled by a basis transformation, merging the parameters $A_D$, $\gamma$, and $\Delta g_S$, and yielding a new set of effective parameters

$$A_D' = A_D - \frac{2 \gamma B}{A - 2 B},$$

$$g^I = g_{\text{eff}} + g_T$$

$$g_R(2 \Pi_{1/2}) = g_R - g_T$$

$$g_R(2 \Pi_{3/2}) = g_R + g_T,$$  \hspace{1cm} (20)

and the new g factor $g_T$, which replaces $\Delta g_S$:

$$g_T = [\frac{1}{2} \gamma (g_s - g^N_R) - \Delta g_S B] (A - 2 B).$$  \hspace{1cm} (21)

Separate rotational g factors are thereby introduced for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ diagonal matrix elements. Since the off-diagonal $^2\Pi_{1/2}$-$^2\Pi_{3/2}$ elements of the Zeeman Hamiltonian also contain the rotational g factor $g_R$, it is, however, best to consider $g_T$ as a new adjustable g factor. For a $^2\Pi$ state approximately described by case (a), the off-diagonal terms proportional to $g_R$ will be negligible, and it may be more convenient to fit the effective rotational g factors of Eq. (20).
Molecular parameters were obtained from a weighted nonlinear least-squares fit of the observed lines to the Hamiltonian described earlier. The fitted parameters and their correlation matrices are presented in Tables II and IV for H$^{35}$Cl$^+$ and H$^{37}$Cl$^+$, respectively. Most of the LMR transitions were fit to within the experimental uncertainty (2 MHz), as shown in Tables III and V. In the analysis of the spectra of HBr$^+$ (8), combination differences for the $X^2Π$ state were formed from the $A^2Σ^+−X^2Π$ electronic spectrum and included in the fit simultaneously with the LMR transitions. In this way, no significant zero-field parameter had to be given a fixed value in the fit to the HBr$^+$ data. For HCl$^+$ there already exists an extensive fit of the optical data, and it was decided not to repeat the laborious process of refitting all of the combination differences in this case. This decision was also based on the fact that the model used by Saenger et al. (18) in their analysis of the HCl$^+$ optical data is identical to the present one with regard to the rotational and fine structure parameters. Hence, only the rotational constant $B$, the Λ-doubling parameter $q$, and the hyperfine parameters $h = a + 1/2(b + c)$, $b$, $eQq_0$, and $eQq_2$, and two of the six $g$ factors were allowed to vary in the fit for HCl$^+$, and the remaining parameters were fixed at the value of Saenger et al. (18). A consequence of fixing parameters in the fit is that the uncertainties obtained for some of the adjusted parameters may be too low, perhaps by an order of magnitude. For HCl$^+$ this conclusion applies in particular to the rotational constant $B$, which would show a considerable correlation to other zero-field parameters in a simultaneous fit to optical and LMR data.

The spin–rotation coupling constant $γ$ was constrained in the fit to the unique perturber value of its dominant second-order contribution, $γ_{up} = -1/2p$, assuming contributions from only one $2Σ^+$ state (cf. Eqs. (6)–(7)). In this way, the definition of the effective parameter $A_D'$ is

$$A_D' = A_D - 2(γ(\text{true}) - γ_{up})B/(A - 2B),$$

where $γ(\text{true})$ is the true (unknown) value of $γ$.

By examining the parameter uncertainties and their isotope ratios, we can see that $B$, $q$, and $h$ are very well determined; the fitted values of the $b$ hyperfine term and both $g$ factors are considerably less satisfactory, and the quadrupole hyperfine terms are quite poorly determined, even establishing an isotope dependence in the wrong direction. Moreover, because the eigenstates sampled in these experiments are essentially pure $Ω = 3/2$ states, the $a$, $c$, and $d$ hyperfine parameters cannot be separately determined, nor can the respective $g$ factors. Hence, a complete interpretation of the unpaired electron distribution and the field gradient in HCl$^+$ is not possible at this time.

The fitted values of $B$ and $q$ are seen to be in good agreement with the previous values of Saenger et al. (18) but are, of course, considerably more precise. Gold et al. (26) calculated values of the Λ-doubling constants $p$ and $q$ in HCl$^+$, assuming that the $A^2Σ^+$ state was the only state contributing to the Λ-doubling perturbation, also assuming separation of the vibrational and electronic parts of the wavefunction, and neglecting configuration interaction. Our value of $q$ actually agrees with their value of $q = -372$ MHz to within 10%. An examination of the relevant $g$ factors indicates,
TABLE II
Molecular Parameters for the $X^2II, v = 0$ State of H$_{35}$Cl (in MHz; $1\sigma$ Uncertainties
Given in Units of the Last Digit Quoted)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This Work$^a$</th>
<th>Saenger et al. (18)</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>293441.830(61)</td>
<td>293440.1(24)</td>
<td></td>
</tr>
<tr>
<td>$D$</td>
<td>F</td>
<td>16.429(13)</td>
<td></td>
</tr>
<tr>
<td>$H$</td>
<td>F</td>
<td>0.000457(23)</td>
<td></td>
</tr>
<tr>
<td>$A_x$</td>
<td>F</td>
<td>-1.9279390(93) x 10$^7$</td>
<td></td>
</tr>
<tr>
<td>$A_y$</td>
<td>F</td>
<td>62.60(48)$^{b)}$</td>
<td></td>
</tr>
<tr>
<td>$P$</td>
<td>F</td>
<td>18259(12)</td>
<td>19900$^{c)}$</td>
</tr>
<tr>
<td>$q$</td>
<td>-334.55(53)</td>
<td>-335.1(18)</td>
<td>-372$^{c)}$</td>
</tr>
<tr>
<td>$p_0$</td>
<td>F</td>
<td>-0.981(57)</td>
<td></td>
</tr>
<tr>
<td>$q_0$</td>
<td>F</td>
<td>0.0471(60)</td>
<td></td>
</tr>
<tr>
<td>$h$</td>
<td>359.8(24)</td>
<td>348.5$^{d)}$</td>
<td></td>
</tr>
<tr>
<td>$b$</td>
<td>132(46)</td>
<td>116.3$^{d)}$</td>
<td></td>
</tr>
<tr>
<td>$eQq_0$</td>
<td>-7.8(83)</td>
<td></td>
<td>-12$^{e)}$</td>
</tr>
<tr>
<td>$eQq_2$</td>
<td>-143(25)</td>
<td></td>
<td>-33$^{e)}$</td>
</tr>
<tr>
<td>$g_1$</td>
<td>0.99945(17)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$g_{(12,3/2)}$</td>
<td>0.532(57)x 10$^{-3}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Correlation Matrix$^f$

<table>
<thead>
<tr>
<th></th>
<th>$B$</th>
<th>$q$</th>
<th>$h$</th>
<th>$b$</th>
<th>$eQq_0$</th>
<th>$eQq_2$</th>
<th>$g_1$</th>
<th>$g_{(12,3/2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q$</td>
<td>0.008</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$h$</td>
<td>-0.017</td>
<td>0.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b$</td>
<td>0.012</td>
<td>0.001</td>
<td>-0.810</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$eQq_0$</td>
<td>-0.001</td>
<td>0.000</td>
<td>-0.008</td>
<td>0.005</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$eQq_2$</td>
<td>0.000</td>
<td>-0.001</td>
<td>-0.001</td>
<td>0.002</td>
<td>-0.008</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$g_1$</td>
<td>-0.647</td>
<td>-0.025</td>
<td>0.005</td>
<td>-0.004</td>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>$g_{(12,3/2)}$</td>
<td>0.584</td>
<td>-0.002</td>
<td>-0.004</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.784</td>
</tr>
</tbody>
</table>

a) $F$ implies fixed at the value of Saenger et al. (18).
b) $Y$ constrained to the unique perturber value $\gamma_{up} = -1/2p$ (cf. Eqs. (6-7)).

The value of $Y$ to be inserted in the expressions for $A_y$ and $g_{(12,3/2)}$ (cf. Eqs. (20-21)) is then $Y_{\text{true}} = \gamma_{up}$.
c) Ref. (26).
d) Kristiansen and Veseth (unpublished).
e) SCF results from Dr. S. Green (unpublished).
f) Constants used in this work:

- Speed of light: 2.99792458 x 10$^8$ m/s
- Bohr Magneton: 1.3996106 MHz/G
- Nuclear g-factors: 2.481 x 10$^{-8}$ ($^{37}$Cl)
  2.9806 x 10$^{-8}$ ($^{35}$Cl)


ROTATIONAL SPECTRUM OF HCl+

TABLE III
Frequencies and Flux Densities for H\textsuperscript{32}Cl\textsuperscript{+}, \textit{X}\textsubscript{2}Π, \(v = 0\)

<table>
<thead>
<tr>
<th>J\textsuperscript{'+}</th>
<th>J\textsuperscript{''}</th>
<th>H\textsubscript{32}Cl\textsuperscript{+}</th>
<th>Parity of Lower State</th>
<th>Flux Density(G)</th>
<th>(v_{\text{obs}}\text{(MHz)})</th>
<th>(v_{\text{calc}}\text{(MHz)})</th>
<th>(v_{\text{obs}} - v_{\text{calc}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/2</td>
<td>5/2</td>
<td>-3/2</td>
<td>-5/2</td>
<td>3/2</td>
<td>3/2</td>
<td>-7790.0 2027 752.6</td>
<td>2027 748.6 4.0</td>
</tr>
<tr>
<td>-3/2</td>
<td>-5/2</td>
<td>1/2</td>
<td>-1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-7916.3 194.7 3.2</td>
<td></td>
</tr>
<tr>
<td>-3/2</td>
<td>-5/2</td>
<td>1/2</td>
<td>1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>8039.0 750.0 2.6</td>
<td></td>
</tr>
<tr>
<td>-3/2</td>
<td>-5/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>8159.1 750.6 2.0</td>
<td></td>
</tr>
<tr>
<td>-3/2</td>
<td>-5/2</td>
<td>1/2</td>
<td>1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>8386.8 749.6 3.0</td>
<td></td>
</tr>
<tr>
<td>-3/2</td>
<td>-5/2</td>
<td>-1/2</td>
<td>-1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>8505.4 752.9 -0.3</td>
<td></td>
</tr>
<tr>
<td>-3/2</td>
<td>-5/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>8628.1 753.4 0.8</td>
<td></td>
</tr>
<tr>
<td>-3/2</td>
<td>-5/2</td>
<td>3/2</td>
<td>3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>8756.0 751.6 1.0</td>
<td></td>
</tr>
<tr>
<td>-1/2</td>
<td>-3/2</td>
<td>3/2</td>
<td>3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>10 518.2 754.9 -2.3</td>
<td></td>
</tr>
<tr>
<td>-1/2</td>
<td>-3/2</td>
<td>1/2</td>
<td>1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>10 642.4 755.0 -2.4</td>
<td></td>
</tr>
<tr>
<td>-1/2</td>
<td>-3/2</td>
<td>-1/2</td>
<td>-1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>10 765.0 755.1 -2.5</td>
<td></td>
</tr>
<tr>
<td>-1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>10 885.0 754.7 -2.1</td>
<td></td>
</tr>
<tr>
<td>-1/2</td>
<td>-3/2</td>
<td>1/2</td>
<td>1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>11 308.3 752.5 0.1</td>
<td></td>
</tr>
<tr>
<td>-1/2</td>
<td>-3/2</td>
<td>-1/2</td>
<td>-1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>11 425.8 753.2 -0.6</td>
<td></td>
</tr>
<tr>
<td>-1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>11 548.3 753.3 -0.7</td>
<td></td>
</tr>
<tr>
<td>-5/2</td>
<td>-5/2</td>
<td>3/2</td>
<td>3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>12 358.8 752.7 -0.1</td>
<td></td>
</tr>
<tr>
<td>-5/2</td>
<td>-5/2</td>
<td>1/2</td>
<td>1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>12 489.4 753.1 -0.5</td>
<td></td>
</tr>
<tr>
<td>-5/2</td>
<td>-5/2</td>
<td>-1/2</td>
<td>-1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>12 615.8 752.4 0.2</td>
<td></td>
</tr>
<tr>
<td>-5/2</td>
<td>-5/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>12 740.4 752.1 0.5</td>
<td></td>
</tr>
<tr>
<td>-5/2</td>
<td>-5/2</td>
<td>3/2</td>
<td>3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>13 296.4 753.8 -1.2</td>
<td></td>
</tr>
<tr>
<td>-5/2</td>
<td>-5/2</td>
<td>1/2</td>
<td>1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>13 419.9 754.4 -1.8</td>
<td></td>
</tr>
<tr>
<td>-5/2</td>
<td>-5/2</td>
<td>-1/2</td>
<td>-1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>13 546.9 754.1 -1.5</td>
<td></td>
</tr>
<tr>
<td>-5/2</td>
<td>-5/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>13 675.3 751.6 1.0</td>
<td></td>
</tr>
<tr>
<td>7/2</td>
<td>9/2</td>
<td>5/2</td>
<td>7/2</td>
<td>3/2</td>
<td>3/2</td>
<td>13 271.1 2588 363.0 2588 363.3 -0.3</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>7/2</td>
<td>1/2</td>
<td>1/2</td>
<td>-1/2</td>
<td>-1/2</td>
<td>13 409.5 361.9 1.1</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>7/2</td>
<td>-1/2</td>
<td>-1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>13 536.1 361.2 1.8</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>7/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>13 664.6 364.4 1.4</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>7/2</td>
<td>3/2</td>
<td>3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>14 812.1 362.1 0.9</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>7/2</td>
<td>1/2</td>
<td>1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>14 927.6 362.3 0.7</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>7/2</td>
<td>-1/2</td>
<td>-1/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>15 048.1 364.5 -1.5</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>7/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
<td>15 181.8 364.4 -1.4</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Average precision of measurement is \(-2\) MHz. Standard deviation of fit is \(2.1\) MHz.

however, that there is considerable interaction between the \(2\)Π ground state and the excited \(^2\Delta\) states.

Since external field data are presently available only for the \(2\)Π\textsubscript{3/2} substate of HCl\textsuperscript{+}, significant fitted values were obtained only for the two g factors \(g\textsubscript{r}(2\Pi\textsubscript{3/2})\) defined by Eqs. (18)–(21). The electronic spin g factor was constrained to the free electron value \(g\textsubscript{e} = 2.002319\), and the nuclear spin g factors \((g\textsubscript{N})\) were fixed at the values of the relevant halogen isotopes. An unsuccessful attempt was made to fit the parity-dependent g factor, \(g\textsubscript{\#},\) defined by Eq. (17).

The fitted results for HCl\textsuperscript{+} are presented in Table VI, where they are compared to results for the isoelectronic species SH, obtained by fitting the existing high-resolution data. (41–44). The number of fitted g factors is seen to be more comprehensive for SH due to the fact that more external field data are available.

From Eq. (20) one obtains

\[ g\textsubscript{r} - g\textsubscript{R}(2\Pi\textsubscript{3/2}) = g\textsubscript{R}(2\Pi\textsubscript{3/2}) = \delta L_{ee} - \delta K, \]

and from Eqs. (16), (18), and (19)

\[ g\textsubscript{r} - g\textsubscript{R}(2\Pi\textsubscript{3/2}) = g\textsubscript{R}(2\Pi\textsubscript{3/2}) = g\textsubscript{R} + 2\Delta g\Delta, \]
TABLE IV
Molecular Parameters for the $X^2\Pi, v = 0$ State of $\text{H}^3\text{Cl}^+$ (in MHz; 1σ Uncertainties Given in Units of the Last Digit Quoted)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This Work$^a$</th>
<th>Saenger et al. (18)</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>292999.489(65)</td>
<td>292993.7(39)</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>F</td>
<td>16.331(30)</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>F</td>
<td>0.000810(66)</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>F</td>
<td>-1.927936(14)x10^7</td>
<td></td>
</tr>
<tr>
<td>$A'D$</td>
<td>F</td>
<td>63.74(18)$^b$</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>F</td>
<td>18229(18)</td>
<td></td>
</tr>
<tr>
<td>q</td>
<td>-332.68(32)</td>
<td>-327.5(36)</td>
<td></td>
</tr>
<tr>
<td>$P_D$</td>
<td>F</td>
<td>-0.94(11)</td>
<td></td>
</tr>
<tr>
<td>$Q_D$</td>
<td>F</td>
<td>0.021(15)</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>299.1(27)</td>
<td>290.2$^{c}$</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>99(35)</td>
<td>96.8$^c$</td>
<td></td>
</tr>
<tr>
<td>$eQ_{q0}$</td>
<td>-8.8(69)</td>
<td>-9.6$^d$</td>
<td></td>
</tr>
<tr>
<td>$eQ_{q2}$</td>
<td>-90(22)</td>
<td>-260$^d$</td>
<td></td>
</tr>
<tr>
<td>$g_4$</td>
<td>0.99927(20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$g_R^{(2\pi/3)/2}$</td>
<td>0.471(41)x10$^{-3}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Correlation Matrix

<table>
<thead>
<tr>
<th>B</th>
<th>q</th>
<th>h</th>
<th>b</th>
<th>$eQ_{q0}$</th>
<th>$eQ_{q2}$</th>
<th>$g_4$</th>
<th>$g_R^{(2\pi/3)/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>0.008</td>
<td>-0.017</td>
<td>0.012</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.584</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>1.000</td>
<td>0.000</td>
<td>-0.810</td>
<td>0.006</td>
<td>-0.008</td>
<td>-0.002</td>
<td>-0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.000</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.000</td>
<td>0.002</td>
<td>-0.008</td>
<td>0.002</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

$^a$ F indicates fixed at the value of Saenger et al. (18).

$^b$ $\gamma$ constrained to the unique perturber value $\gamma_{up} = -1/2p$ (cf. Eqs. (6-7)).

The value of $\gamma$ to be inserted in the expressions for $A'D$ and $g_R$ (cf. Eqs. (20-21)) is then $\gamma(true) = \gamma_{up} (2)$.

$^c$ Kristiansen and Weseth (unpublished).

$^d$ SCF results from Dr. S. Green (unpublished).
with $\Delta g_\Delta$ defined by

$$\Delta g_\Delta = (g_l - g_R^N) \sum_{_\Delta v'} \langle{}^2\Delta v'|L_l|{^2\Pi}_v\rangle \langle{}^2\Delta v'|B{^2\Pi}_l|{^2\Pi}_v\rangle \frac{E{^2\Pi}_v - E_{\Delta v'}}{E{^2\Pi}_v - E_{\Delta v'}},$$

(25)

Since $g_R^N$ is precisely known from Eq. (12), the above relations show that knowledge of $g_l$ allows the parameter $\Delta g_\Delta$ to be determined from the fitted values of $g_l$ and
TABLE VI

\begin{tabular}{|c|c|c|}
\hline
Quantity & $^3\text{Cl}^+$ & $^7\text{Cl}^+$ & SH  \\
\hline
$g_1$ & 0.99995(17) & 0.99972(20) & 1.000427(11)  \\
$g_6(2)^{1/2}(b)$ & 0.532(57)x10^{-3} & 0.471(41)x10^{-3} & 0.5430(37)x10^{-3}  \\
$g_4$ & 0.000a) & 0.000a) & 0.5941(30)x10^{-3}  \\
$g_5$ & 2.002319a) & 2.002319a) & 2.002319a)  \\
$g_I$ & 2.9806x10^{-4}a) & 2.4810x10^{-4} a) & 3.042x10^{-3} a)  \\
$\langle T \rangle / mc^2$ & 1.25x10^{-4} & 1.25x10^{-4} & -0.94x10^{-4}  \\
$\Delta g_6$ & -0.69(10)x10^{-3} & -0.75(10)x10^{-3} & -2.32(10)x10^{-4}  \\
\hline
\end{tabular}

a) Fixed value  
b) The derived value of the parameter $\Delta g_6$ (cf. Eq. (24)) is also included.  
c) From fit of data given (41-44).


$g_R(2^{3/2})$. In this way information can be obtained regarding the contamination of the $^2\Pi$ state by $^2\Delta$ states. $g_1$ deviates slightly from unity due to some small relativistic corrections which may be computed ab initio (7). Since $g_s$ was constrained to the free electron value by the fit, the relativistic correction to $g_s$ also has to be taken into account, and it can be shown (7) that to a good approximation the value of $g_s$ in Eq. (24) is given by

$$g_s = 1 - \frac{2\langle T \rangle}{mc^2},$$

where $\langle T \rangle$ denotes the expectation value of the kinetic energy of one of the unfilled shell electrons. An ab initio calculation of $\langle T \rangle$ is available for SH (7); for $^3\text{Cl}^+$, estimates from atomic values are of sufficient accuracy for the present purpose. The values of $\langle T \rangle / mc^2$ are included in Table VI.

The derived values of the parameter $\Delta g_6$ of Eq. (25) are also included in Table VI. This parameter gives direct information about the interaction between the $^2\Pi$ ground state and excited $^2\Delta$ states, information that seems to be inaccessible from zero-field spectra. It is interesting to note that the value found for $\Delta g_6$ is numerically smaller for SH than for $^3\text{Cl}^+$, and as shown in (8) the same relation also applies to SeH and $^7\text{Br}^+$. These results indicate that the excitation energies of the $^2\Delta$ states are lower in the ions than in the isoelectronic neutral molecules.

To get a better idea of the importance of the interaction between the $X^2\Pi$ ground state and the excited $^2\Delta$ states, we multiply $\Delta g_6$ by 2B, obtaining a quantity which can be compared directly with the $\Lambda$-doubling constant $q$. For $^3\text{Cl}^+$ the results are $2B\Delta g_6 = -405$ MHz, $q = -334.5$ MHz, indicating that the $^2\Delta$ states are making important contributions to the wavefunction of the ground state. In view of this considerable interaction with $^2\Delta$ states, estimates of the $g$ factor $g_I$ of Eq. (21) will be rather unreliable, and no value of the rotational $g$ factor $g_R$ or the true orbital $g$ factor $g_L$ can be extracted from the fitted parameters.

Because only the linear combinations of individual magnetic hyperfine parameters
represented by $h = a + 1/2(b + c)$ and $b = b_F - 1/3c$ could be determined accurately, a description of the unpaired electron density cannot be obtained from the LMR results above (39). However, the quadrupole coupling constants obtained can be interpreted to yield interesting qualitative information about the bonding in HCl$^+$. Small values of $eQq_0$ were observed for both isotopes. Despite the large uncertainties, it is clear that the small axial field gradients $q_0$ favor a description of HCl$^+$ as a neutral chlorine atom strongly perturbed by a proton.

An analysis using Townes and Dailey theory (45) distinguishes between a covalently bonded electronic configuration ($\text{H}$··Cl$^+$) and an ionic configuration (H$^+$·Cl). Assuming the unpaired $\pi$ electron is in a $p$ orbital localized on the Cl atom, the field gradient is given by

$$q_0 = (i + s - is - \frac{1}{2}) q_{\text{atom}},$$

where $i$ represents the fraction of ionic bonding, and $s$ gives the contribution of the Cl 3$s$ atomic orbital to the $\sigma$ covalently bonding orbital. The effects of hybridization and ionicity cannot be separated, but by setting $s = 0$, the maximum ionic contribution can be found. Using $eQq_{\text{atom}} = 109.746$ (86.510) MHz for $^{35}\text{Cl}$ ($^{37}\text{Cl}$) (46) the maximum ionicity is $i = 43\%$ (39\%).

The off-diagonal quadrupole coupling constant $eQq_2$ is proportional to the radial field gradient (40), and thus depends only on the $\pi$ electron density. If the unpaired $\pi$ electron is localized in an atomic 3$p$ orbital on the Cl atom, then from Townes and Dailey theory, one expects $eQq_2 = -eQq_{\text{atom}}$. The observed values show that the Cl 3$p$ orbital makes the dominant contribution to the $\pi$ nonbonding molecular orbital, justifying the assumption made above. A more quantitative description of the electron distribution in HCl$^+$ will be possible when the spectra of the $\Omega = \frac{1}{2}$ spin component are analyzed.

The detailed analysis of the rotational spectrum of HCl$^+$ presented here makes it possible to calculate precise energy levels for the ground vibrational state of $X^2\Pi$. These eigenvalues can be used to compute accurate partition functions or to provide rest frequencies for astronomical or aeronomical searches for HCl$^+$. Dalgarno (24) has postulated that HCl$^+$, formed by the exothermic process Cl$^+$ + H$_2$ $\rightarrow$ HCl$^+$ + H, may be important in the radiative cooling of interstellar clouds. The detection of HCl$^+$ could most probably be achieved with radiofrequency searches for its low-$J$ $\Lambda$-doubling transitions in $\Omega = \frac{3}{2}$, or far-infrared detection of the $J = \frac{3}{2} \leftarrow \frac{1}{2}$ rotational transition. Relatively precise ($\pm 2$ MHz) values for the hyperfine components of these transitions can be calculated from the parameters of Tables II and IV and may serve as a useful guide in searching for interstellar HCl$^+$.

ACKNOWLEDGMENTS

This work was supported by the Structure and Thermodynamics Program of the National Science Foundation (Grant No. CHE-8402861). We thank Dr. Sheldon Green for his calculations on the quadrupole constants.

RECEIVED: July 26, 1988

REFERENCES


29. D. J. Knight, unpublished results.


