The laser magnetic resonance spectrum of HCl+†

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Pure rotational spectra have been obtained for only a very limited number of molecular ions [1]. Both microwave spectroscopy and millimetre wave astronomy have been employed for the study of CO^+ [2], HCO^+ [3], HNN^+ [4] and HCS^+ [5]. In a previous paper [6] the first detection of rotational transitions of a molecular ion (HBr^+) by far-infrared laser magnetic resonance spectroscopy of a longitudinal d.c. discharge was reported. In this article we describe the first detection of the pure rotational spectrum of HCl^+ with a laser magnetic resonance spectrometer employing a transverse intracavity positive column discharge.

The HCl^+ molecular ion has received considerable attention in recent years. Its electronic spectra have been the subjects of several theoretical treatments aimed at establishing the relationship between the electron spin–nuclear rotation interaction and centrifugal distortion of the spin–orbit interaction and their respective isotopic and vibrational dependences [7, 8]. While a chlorine-containing molecule has not yet been observed in an interstellar dust cloud [9], it has been suggested that both HCl^+ and H_2Cl^+ might be detectable interstellar molecules that are important in the thermochemistry of such clouds [10]. The rates of the chemical reactions relevant to this question, $Cl^+ + H_2 \rightarrow HCl^+ + H$ and $HCl^+ + H_2 \rightarrow H_2Cl^+ + H$, have been measured in flowing afterglow experiments [11]. The information resulting from a detailed analysis of the pure rotational spectrum of HCl^+ will prove valuable both for examining the aforementioned theoretical predictions in detail and for providing the accurate rest frequencies needed to search for HCl^+ in interstellar sources.

The principles of laser magnetic resonance spectroscopy have been discussed in detail elsewhere [12] and will not be described here. The L.M.R. spectrometer developed by our group consists essentially of a transversely pumped far-infrared laser, a 15 in. Varian electromagnet and associated electronics and vacuum equipment. The FIR laser is a 1·15 m Fabry–Perot cavity with a symmetric near-confocal resonator structure. It is separated into two regions by a 12·5 μm polypropylene beam splitter, which can be rotated to provide either σ or π orientations of the laser electric field relative to the transverse d.c. magnetic field. The 0·58 m gain cell of the FIR laser is pumped transversely by a 3 m CO_2 laser with a maximum output near 70 W. A pair of transverse planar pumping mirrors are oriented to be parallel with adjustable spacing to optimize the pumping for each laser line. A micrometer-driven mirror

($R = 1\cdot0$ m) is translated to select a single longitudinal mode of the desired laser line while a concentrically-mounted iris is used to eliminate higher order transverse modes.   Another identical mirror is mounted on a piezoelectric translator (Vernitron PZT 5–H) which is driven by a dither stabilization system used to lock the far-infrared laser on the peak of its gain curve.   The intracavity FIR laser power is monitored by coupling a fraction of it out through a polyethylene window into the detector with a 45° copper mirror ($d = 12$ mm) that can be inserted a desired distance into the laser mode pattern.   The detector is a gallium-doped germanium bolometer (Infrared Laboratories) mounted in a liquid helium dewar (Infrared Laboratories HD–3(L)).   The detector system exhibits an NEP of $2\cdot4 \times 10^{-13}$ W/Hz$^{1/2}$.   The magnetic field is provided by a Varian 15 in. electromagnet system capable of reaching 2 T within the $7\cdot0$ cm air gap between the tapered pole pieces.   The flux density is measured with an N.M.R. Gaussmeter (Cyclotron Corp Model 5300).   A sinusoidal modulation field of up to 5 mT at a frequency of $2\cdot5$ kHz is produced by a pair of Helmholtz coils mounted on the pole tips.   The L.M.R. signals are demodulated by a lock-in amplifier (PAR HR–8) and displayed on an XY recorder (HP 7044B) in first derivative mode versus the magnetic flux density.   Molecular ions are produced in the sample region by a positive column discharge maintained between two brass shim-stock electrodes mounted in a teflon holder with a separation of $5\cdot7$ cm. The vacuum in the sample chamber is provided by a 760 l/min rotary pump (Leybold-Heraeus D30A).

This configuration possesses two major advantages over the solenoid magnet system employed previously [6] for the study of HBr$^+$: (1) either σ or π orientation of the laser electric field relative to the d.c. magnetic field can be used whereas only σ orientation is possible with a solenoid ; (2) fields up to 2 T are obtained, compared with the $0\cdot6$ T maximum available with the liquid nitrogen cooled solenoid.   These advantages have allowed us to measure over 130 lines of HBr$^+$ at high fields and/or in π polarization that could not be observed before [6]. The complete set of 230 HBr$^+$ transitions is presently being analysed and interpreted using the $^2\Pi$ hamiltonian of Brown *et al.* [13].   Similarly, the HCl$^+$ spectra reported in this paper could not have been detected with the solenoid system.

The energy level diagram of the $^2\Pi$ ground state of HCl$^+$ calculated with the hamiltonian of Brown *et al.* [13] and the molecular constants obtained by Brown *et al.* [8] from the analysis of optical data of Matthews and co-workers [14] is shown in figure 1.   The $J = 5/2 \to 7/2$ transition of H ^{35}Cl$^+$ in the $\Omega = 3/2$ state was predicted to be 7 GHz below the frequency ($2027\cdot7526$ GHz) of the $147\cdot9$ μm laser line of CH$_3$NH$_2$ pumped by the 9P24 line of the CO$_2$ laser [15].   The transitions shown in figure 2 were detected in a discharge containing ~ 2 mTorr of HCl (Matheson, Commercial Grade) and $\sim 1\cdot5$ Torr of helium (99·999 per cent) at currents near 20 mA.   In all, 24 transitions, consisting of 3 magnetic sublevels (M_J), each split into pairs of quartets by the lambda doubling and the hyperfine interactions of the ^{35}Cl nucleus, have been observed for H ^{35}Cl$^+$. The less intense H ^{37}Cl$^+$ lines have not yet been observed with this laser line, but its $J = 7/2 \to 9/2$ transition has been detected with the $115\cdot8$ μm line of ^{13}CH$_3$OH.   Precise flux densities have not yet been measured for these weak spectra.   The hyperfine patterns, lambda doubling and isotope shifts observed are all as expected, based on optical data and on the HBr$^+$ results.   All lines
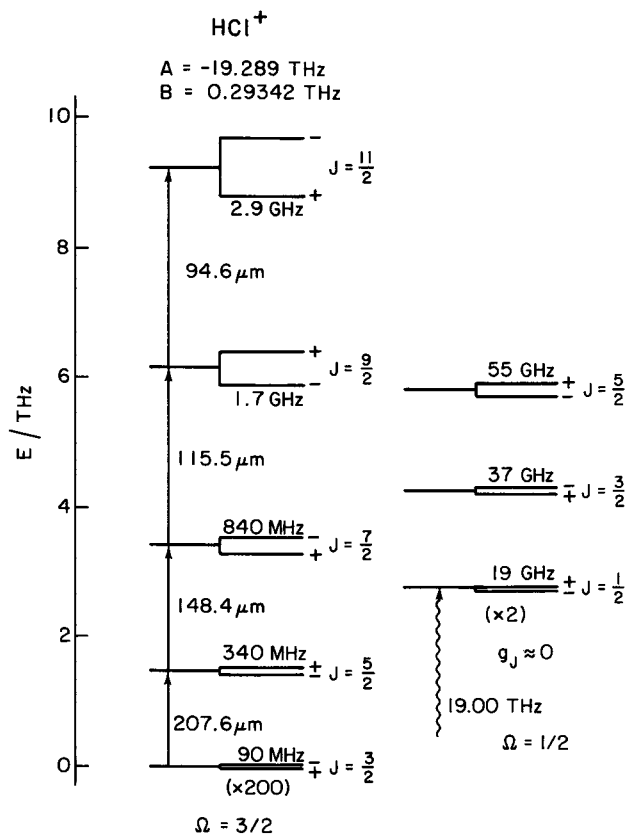
Figure 1. Energy level diagram for the $^2\Pi$ ground state of HCl$^+$ calculated from molecular constants given in [8].
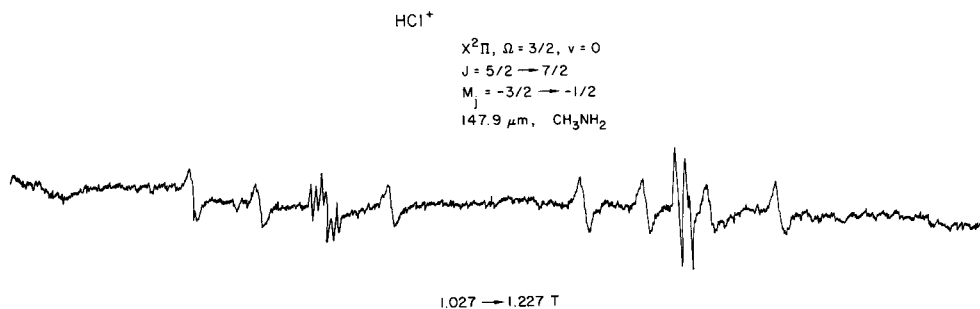

Figure 2. The laser magnetic resonance spectrum of $X\,^2\Pi_{3/2}$ H ^{35}Cl$^+$, $J=5/2\to7/2$ obtained in a positive column discharge through ~ 2 mTorr HCl in 1·5 Torr He at a current of 20 mA using the 147·9 μm laser line of CH$_3$NH$_2$. The quartet structure is due to the $I=3/2$ spin of the ^{35}Cl nucleus, while the large doublet splitting arises from lambda doubling. The additional features observed are due to NH and NH$_2$ formed from impurities.

attributable to HCl$^+$ were found to disappear when HCl was replaced by DCl. By shifting the laser frequency slightly and observing the consequent shift in the resonance lines, the sign of the tuning rate $(\partial H/\partial \nu_L)$ was determined to be negative, indicating that the $J = 5/2 \rightarrow 7/2$ transition occurs at a frequency below that of the $147\cdot9\,\mu m$ laser line, as predicted. Addition of small amounts of O_2 and H_2 resulted in the disappearance of all HCl$^+$ lines, as did raising the amount of HCl in the helium carrier above about 1 per cent. This is consistent with the known rapid reaction rates of HCl$^+$ with H_2 and HCl to form H_2Cl^+ [11].

The 24 measured lines of H ^{35}Cl$^+$ were analysed by non-linear least squares regression techniques employing the hamiltonian given in detail in [13] with the exception of the electric quadrupole terms, which were derived both by ourselves and by Carrington *et al.* [16]. This data set was sufficient to determine the Hund's Case (a) parameters q (lambda doubling), $h = a + \frac{1}{2}(b+c)$ (magnetic hyperfine), eq_0Q (electric quadrupole hyperfine) and its off-diagonal counterpart eq_2Q, and B_0, the rotational constant. The centrifugal distortion constant D_0, the spin–rotation constant γ, the spin–orbit constant A and its centrifugal correction A_D were fixed at values given by Brown *et al.* [8]. The higher order g-factors given by Brown [13] were fixed at values appropriate for HCl$^+$. The results of this analysis are given in the table. Our fitted parameters are in good agreement with those given by Brown *et al.* [8] but are substantially more precise. With this new set of parameters, which reproduce the experimental frequencies with an average residual of $1\cdot9$ MHz, we have calculated the r.f. lambda-doubling intervals in low-J $\Omega = 3/2$ states with a precision of ~ 2 MHz. These calculations will provide for a search for interstellar HCl$^+$.

It would be interesting to compare our HCl$^+$ results and those to be obtained shortly for HBr$^+$ with presently unavailable *ab initio* calculations, since these

Molecular parameters for HCl$^+$ in $X\,^2\Pi_{3/2}$ ground state. Uncertainties are given in parentheses as 1 standard deviation.

Parameter	This work	Brown *et al.* [8]
B_0/MHz	$293438\cdot14\ (0\cdot08)$	$293420\cdot56\ (12\cdot14)$
h/MHz	$365\cdot2\ (2\cdot0)$	
q/MHz	$-336\cdot83\ (0\cdot97)$	$-342\cdot96\ (1\cdot1)$
eq_0Q/MHz	$7\cdot65\ (18\cdot2)$	
eq_2Q/MHz	$-131\cdot8\ (56\cdot4)$	
D_0/MHz	$F\dagger$	$16\cdot2095$
A/MHz	$F\dagger$	$-1\cdot929 \times 10^7\ (1\cdot29 \times 10^3)$
A_D/MHz	F	$45\cdot3\ (4\cdot2)$
γ/MHz	F	$-8\cdot9 \times 10^3\ (1\cdot65 \times 10^2)$
p/MHz	F	$1\cdot8467 \times 10^4\ (39\cdot0)$
g_l	$2\cdot226 \times 10^{-2}\ddagger$	
g_s	$2\cdot00129\ddagger$	
g_r	$-1\cdot6 \times 10^4\ddagger$	

$\dagger$ Parameter fixed at values given in [8].
$\ddagger$ Calculated from matrix elements in [13].

are the first cases for which such a detailed study of hyperfine interactions in open-shell molecular ions has been made. Comparisons between these species and the isoelectronic molecules SH and SeH will be of interest in ascertaining the effects of a net positive charge on the electron distribution, particularly with regard to the anomalously small value for eq_0Q. The greatly extended tuning range of this new spectrometer should permit similar measurements to be made for a number of additional molecular ions in the future.

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