

Fourier transform emission spectroscopy of the $g^4\Delta$ – $a^4\Delta$ system of FeCl[☆]

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Abstract

The emission spectrum of FeCl has been investigated at high resolution in the near infrared. The molecule was excited in a microwave discharge lamp using a mixture of FeCl₃ vapor and 4.9 Torr of He, and the spectra were recorded in the 3000–12 200 cm⁻¹ region using a Fourier transform spectrometer. New bands with *R* heads near 7725, 8149, 8577, 8949, 9319, 9686, and 10 050 cm⁻¹ have been assigned as the 0–2, 0–1, 0–0, 1–0, 2–0, 3–0, and 4–0 bands (respectively) of a new $^4\Delta$ – $^4\Delta$ system of FeCl. The strong bands of this system consist of four sub-bands assigned as $^4\Delta_{1/2}$ – $^4\Delta_{1/2}$, $^4\Delta_{3/2}$ – $^4\Delta_{3/2}$, $^4\Delta_{5/2}$ – $^4\Delta_{5/2}$, and $^4\Delta_{7/2}$ – $^4\Delta_{7/2}$. This transition is analogous to the 1 μm transitions of FeH and FeF. A rotational analysis of a number of bands in each sub-band has been obtained and spectroscopic constants extracted. The lower $a^4\Delta$ state is affected by perturbations from a nearby electronic state, while the excited $g^4\Delta$ state is free from perturbation. This work represents the first observation of a transition involving quartet states of FeCl.

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1. Introduction

Iron is an important element in chemistry and astronomy. Spectroscopic studies of small iron-containing molecules provide valuable data on iron–ligand bonding and on the electron distribution. Such data are of particular interest in the study of corrosion and iron plays an important role in catalytic processes [1–3]. Iron has a high cosmic abundance and is a prominent constituent of stars [4,5]. The observation of some metal halide molecules such as AlF, AlCl, and KCl [6] in the circumstellar envelope of the late-type carbon star IRC + 10 216 strengthens the possibility of detection of iron-containing molecules, including FeF and FeCl. The cosmic abundance of iron is five times that of aluminum. So far none of the iron halides have been detected,

partly because of the lack of high resolution data needed for a meaningful search.

Only limited work is available on iron-containing species because of the complexity of their spectra. Since the iron atom has six *d* electrons in its valence shell, small molecules involving iron have ground and low-lying excited states of high spin multiplicity, and high orbital angular momentum. The electronic spectra resulting from transitions between the low-lying electronic states are, therefore, very complex. The large spin–orbit interaction causes additional complications and induces frequent local and global perturbations. Among the iron-containing molecules, the electronic spectra of FeO [7–9], FeH [10–13], FeC [14], and FeN [15] have been studied in the past decade. Some limited work has also been carried out on the diatomic iron halides, FeF [16–18], and FeCl [19,20].

The electronic spectrum of FeCl has been known for several decades [19] and three electronic transitions have been identified in the near ultraviolet region between 27 000 and 32 000 cm⁻¹. Two transitions with the 0–0 bands located near 28 000 and 29 000 cm⁻¹ have been assigned as $^6\Pi$ – $X^6\Delta$ and $^6\Phi$ – $X^6\Delta$, with the common

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lower state, $X^6\Delta$, being the ground state of FeCl [19]. Each of these transitions consists of six sub-bands and all the six sub-bands of the 0–0 band were rotationally assigned for the ${}^6\Phi-X^6\Delta$ transition. For the ${}^6\Pi-X^6\Delta$ transition only the ${}^6\Pi_{7/2}-X^6\Delta_{9/2}$ and ${}^6\Pi_{5/2}-X^6\Delta_{7/2}$ sub-bands of the 0–0 band were rotationally analyzed by Delaval et al. [19]. A third transition with its 0–0 band near $31\,200\text{ cm}^{-1}$ has tentatively been assigned as a quartet–quartet transition [19], although this assignment has yet to be confirmed by rotational analysis. The ${}^6\Pi-X^6\Delta$ transition of FeCl has also been recorded recently in a laser-excitation experiment of a molecular beam of photolyzed $\text{Fe}(\text{CO})_5$ diluted in seed gases containing CCl_4 [20]. In this experiment the laser-excitation spectra of several bands of the $\Delta v = 1, 0, -1$, and -2 sequences with vibrational levels up to $v = 4$ were recorded and sub-bands with $\Omega'' = 9/2, 7/2$, and $5/2$ were rotationally analyzed.

The ground state of FeCl has been studied recently by millimeter/sub-millimeter wave spectroscopy. Tanimoto et al. [21] observed the rotational spectrum for the two lowest energy spin components $X^6\Delta_{9/2}$ and $X^6\Delta_{7/2}$, while Allen et al. [22] observed all six spin components of the ground state, and provided precise spectroscopic constants. Allen et al. [22] were also able to resolve the Λ -doubling in the $\Omega = 3/2, 1/2$, and $-1/2$ spin components and from the relatively large Λ -doubling constants, they concluded that the ground state is affected by interactions with some nearby excited electronic states.

The thermochemical data for FeCl and FeCl_2 along with some other transition metal chlorides of Cr, Mn, Co, and Ni were derived by Hildenbrand [23] by high temperature mass spectrometry, and the dissociation energy of $D_0 = 78.8\text{ kcal/mol}$ at 298 K was determined for FeCl. Recent values of $\omega_e = 409\text{ cm}^{-1}$ and $D_0 = 82.5\text{ kcal/mol}$ were computed in high-level ab initio calculations by Bach et al. [24]. The spectroscopic properties of the low-lying ${}^6\Delta$ and ${}^4\Delta$ electronic states of FeF and FeCl have also been calculated by Bauschlicher [25] using the coupled cluster approach with a large basis set. Bauschlicher has confirmed the assignment of a ${}^6\Delta$ ground state for FeCl. This calculation has also provided the values of $D_0 = 86 \pm 3\text{ kcal/mol}$ and $\omega_e = 394\text{ cm}^{-1}$ for the ground state of FeCl, in reasonable agreement with values obtained previously [23,24].

In the present work we report the first observation of a ${}^4\Delta-{}^4\Delta$ electronic transition of FeCl with the 0–0 band located near 8577 cm^{-1} . This transition is found in the near infrared and is analogous to the $g^4\Delta-a^4\Delta$ system of FeF [16]. The spectra consists of a number of bands including vibrational levels up to $v' = 6$ and $v'' = 3$ in different sub-bands. A rotational analysis of a number of bands of the new transition will be reported in this paper.

2. Experimental details

The FeCl molecules were excited in a microwave discharge through a flowing mixture of about 4.9 Torr of helium and a trace of FeCl_3 vapor. The spectra were recorded using the 1-m Fourier transform spectrometer associated with the Mc-Math Pierce Telescope of the National Solar Observatory at Kitt Peak. The spectra in the $3500\text{--}10\,000\text{ cm}^{-1}$ region were recorded using liquid nitrogen-cooled InSb detectors and green glass filters. A total of eight scans were co-added in about 60 min of integration at a resolution of 0.02 cm^{-1} . The spectrum in the $8700\text{--}12\,200\text{ cm}^{-1}$ region was recorded using mid-range Si-diode detectors at a resolution of 0.02 cm^{-1} . This time 21 scans were coadded in about 3 h of integration.

The spectral line positions were measured using a data reduction program called PC-DECOMP developed by J. Brault. The peak positions were determined by fitting a Voigt lineshape function to each line. The spectra were calibrated using the measurements of Fe atomic lines provided by Nave et al. [26]. The molecular lines appear with a width of 0.032 cm^{-1} and a maximum signal-to-noise ratio of about 13:1. The line positions are expected to be accurate to about $\pm 0.003\text{ cm}^{-1}$. However, because there is considerable overlapping and blending caused by the presence of different sub-bands in the same region, the error in the measurement of blended and weak lines is expected to be somewhat higher.

3. Observations and analysis

The new emission bands of FeCl are located in the $7000\text{--}11\,000\text{ cm}^{-1}$ spectral region. The observed spectra consist of a number of band sequences having the higher wavenumber R heads at $7725, 8149, 8577, 8949, 9319, 9686$, and $10\,050\text{ cm}^{-1}$. These bands have been assigned as the 0–2, 0–1, 0–0, 1–0, 2–0, 3–0, and 4–0 bands (respectively) of a new ${}^4\Delta-{}^4\Delta$ system of FeCl analogous to the electronic transition of FeF that we analyzed previously [16]. A number of higher vibrational bands were also identified in each sequence. A compressed portion of the near infrared bands is presented in Fig. 1, where the high wavenumber R heads of the sequence bands have been marked.

In the $8580\text{--}8700\text{ cm}^{-1}$ region there are a number of weak bands which are degraded towards higher wavenumbers. At least 10 heads located near $8581.7, 8585.1, 8787.2, 8589.5, 8598.4, 8602.2, 8606.6, 8513.6, 8619.5$, and 8626.9 cm^{-1} can be marked, but the analysis of these bands was not possible because of their weak intensity and the high density of lines. The rotational line spacing in these bands is very small near the heads compared to that in the other FeCl bands indicating that

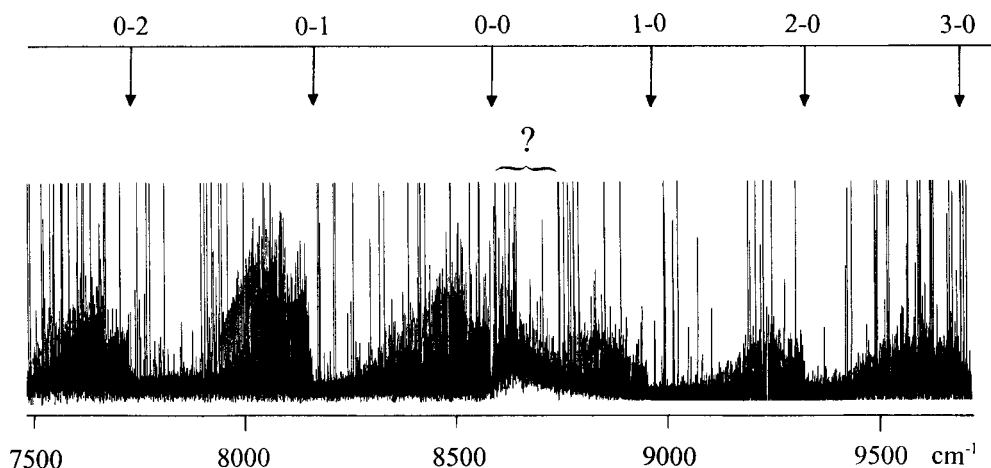


Fig. 1. A compressed portion of the $g^4\Delta$ - $a^4\Delta$ system of FeCl with the high wavenumber heads of each sequence marked. Complex violet degraded bands marked by a question mark may be due to a larger molecule such as FeCl_2 or to another transition of FeCl.

these bands might belong to a larger molecule such as FeCl_2 [27]. These bands could be attributed to FeCl only if the rotational constants in the lower and upper states are of similar magnitude and the band heads are formed in the P branches, e.g., for a ${}^6\Delta$ - $X^6\Delta$ transition. This assignment to FeCl could not be confirmed because no connecting R branches could be marked with certainty because of strong overlapping. A definite assignment can be made only by high resolution analysis of these bands, which is not possible with our current spectra. To higher wavenumbers, two additional weak unanalyzed bands with a similar dense structure have been observed near 11 161 and 11 350 cm^{-1} .

The FeCl bands were easily identified by the expected line spacing based on the rotational constants reported from the analysis of the near ultraviolet transitions [19]. Because of the overlapping from the structure of different sub-bands associated with this transition, the structure of each band appears to be very complex. The overlapping from sequence bands involving the higher vibrational levels also contributes to the inherent com-

plexity. A band of a ${}^4\Delta$ - ${}^4\Delta$ transition should consist of four sub-bands: ${}^4\Delta_{1/2}$ - ${}^4\Delta_{1/2}$, ${}^4\Delta_{3/2}$ - ${}^4\Delta_{3/2}$, ${}^4\Delta_{5/2}$ - ${}^4\Delta_{5/2}$, and ${}^4\Delta_{7/2}$ - ${}^4\Delta_{7/2}$, which should be separated by substantial spin-orbit interactions in the lower and upper excited electronic states. At first glance, it is difficult to identify the band heads due to the four sub-bands and it is difficult to draw any conclusion about the nature of the electronic states. But a careful inspection of each band using a color Loomis-Wood program helped us identify and assign the rotational structure of all four sub-bands. The Ω -assignment of different bands was achieved using the observed Ω -doubling in one sub-band, which was assigned as the ${}^4\Delta_{1/2}$ - ${}^4\Delta_{1/2}$ sub-band. The Ω -assignment in the other spin components was made on the basis of the size of their B_v values. Since the low-lying electronic states of FeCl are inverted as also observed for FeF [16–18], the B_v values in the different spin components of a ${}^4\Delta$ state of FeCl are expected to vary as $B({}^4\Delta_{7/2}) < B({}^4\Delta_{5/2}) < B({}^4\Delta_{3/2}) < B({}^4\Delta_{1/2})$.

A compressed part of the 1-0 band of FeCl is presented in Fig. 2, where the R heads due to the four

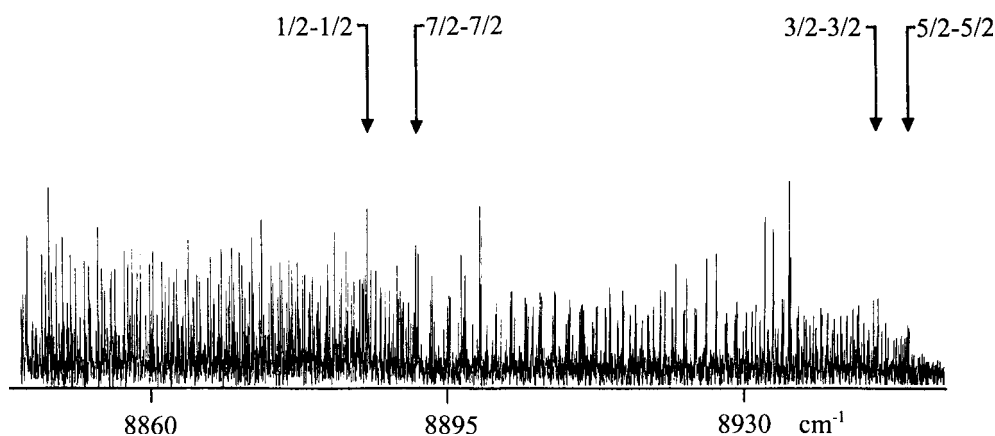


Fig. 2. A portion of the 1-0 band of the $g^4\Delta$ - $a^4\Delta$ system of FeCl with the R heads of the four sub-bands marked.

sub-bands have been marked. The structure of each of these sub-bands consists of a *R* and a *P* branch consistent with a $\Delta\Omega = 0$ transition. No *Q*-branches, which are expected to be very weak for a $\Delta\Omega = 0$ transition, have been observed in any of the sub-bands. The observation of large Ω -doubling in the lower ${}^4\Delta_{1/2}$ spin components indicates that the ${}^a\Delta$ state is probably interacting strongly with a nearby state. Our rotational analysis indicates that very small Ω -doubling is present in the excited $g^4\Delta_{1/2}$ spin component suggesting that the $g^4\Delta$ state is relatively free from similar interactions. Since the different sub-bands are not located either in increasing or decreasing order of Ω , the structure of each sub-bands will be described separately.

3.1. The $g^4\Delta_{7/2}$ – ${}^a\Delta_{7/2}$ sub-band

A band with an origin near 8519 cm^{-1} has been identified as the 0–0 band of the $7/2$ – $7/2$ sub-band. We have been able to assign the rotational structure in ten bands of this sub-band involving vibrational levels up to $v' = 5$ and $v'' = 3$. No Ω -doubling has been observed even at the highest *J* values. The rotational analysis indicates that the lower ${}^a\Delta_{7/2}$ spin component is affected by perturbations. The $v'' = 0$ vibrational level is perturbed at $J'' = 59.5$ and all rotational lines with $J'' > 56.5$ have been given lower weights. The $v'' = 1$ vibrational level is perturbed near $J'' = 41.5$, while $v'' = 2$ and 3 vibrational levels are perturbed near $J'' = 89.5$ and 79.5 , respectively. A number of rotational lines in the vicinity of the perturbations have been de-weighted in the final fit. These perturbations affect each line of the Ω -doublet in the same way because no

Ω -doubling or extra lines were detected in the perturbed regions. The excited state vibrational levels are free from perturbations as apparent from the observed minus calculated differences for the lines in different bands.

3.2. The $g^4\Delta_{5/2}$ – ${}^a\Delta_{5/2}$ sub-band

A 0–0 band with an origin near 8575 cm^{-1} has been assigned as the $5/2$ – $5/2$ sub-band. We have obtained a rotational analysis of 11 bands, 6–2, 5–2, 5–1, 4–1, 3–0, 2–0, 1–3, 1–0, 0–2, 0–1, and 0–0, belonging to this sub-band. The structure of these bands also consists of a single *R* and a single *P* branch, both appearing with nearly the same intensity. Ω -doubling is not observed. An expanded portion of the spectrum near the *R* head has been provided in Fig. 3, where the *R* lines of the closely lying $g^4\Delta_{3/2}$ – ${}^a\Delta_{3/2}$ sub-band have also been marked. The analysis of the 0–0 band indicates that the $v'' = 0$ vibrational level is locally perturbed near $J'' = 20.5$. Similar perturbations have been observed in the $v'' = 1$ and 2 vibrational levels near $J'' = 79.5$ and 71.5 , respectively. The $v'' = 3$ vibrational level of the lower state appears to be unaffected by perturbations over the observed range of *J* values. Again, the lines in the vicinity of perturbations were de-weighted in the final fit and the excited $g^4\Delta_{5/2}$ spin component is not perturbed.

3.3. The $g^4\Delta_{3/2}$ – ${}^a\Delta_{3/2}$ sub-band

The band with a 0–0 origin near 8571 cm^{-1} has been assigned to the $3/2$ – $3/2$ sub-band. In spite of overlapping from the $5/2$ – $5/2$ sub-band, a sufficient number of *R* and *P* lines have been identified. We have been able to assign

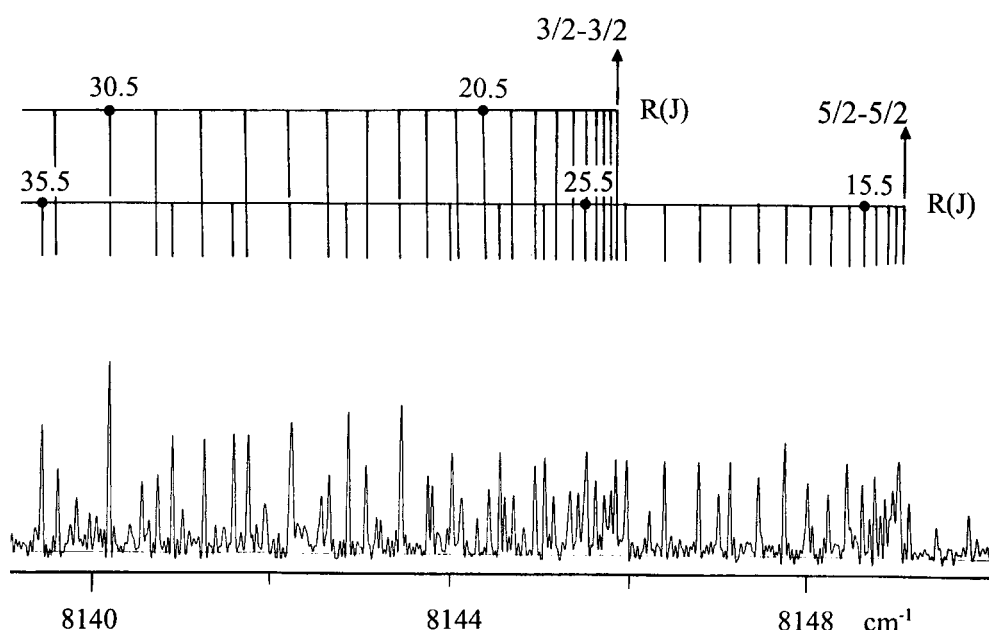


Fig. 3. An expanded portion of the 0–1 band near the *R* heads of the $g^4\Delta_{3/2}$ – ${}^a\Delta_{3/2}$ and $g^4\Delta_{5/2}$ – ${}^a\Delta_{5/2}$ sub-bands.

the lines in the 5–1, 4–1, 3–0, 2–0, 1–0, 0–1, and the 0–0 bands of this sub-band. The Ω -doubling is not resolved in the bands involving the $\Omega = 3/2$ spin component, although an Ω -splitting was seen in the $\Omega = 3/2$ spin component of the $a^4\Delta$ state of FeF [16]. Rotational perturbations have also been observed in the lower state vibrational levels. The $v'' = 0$ level is perturbed near $J'' = 69.5$, while the $v'' = 1$ vibrational level is also affected by perturbations near $J'' = 64.5$. Again the rotational lines in the vicinity of these perturbations were deweighted and the excited $g^4\Delta_{3/2}$ spin component is not perturbed.

3.4. The $g^4\Delta_{1/2}$ – $a^4\Delta_{1/2}$ sub-band

The 1/2–1/2 sub-band is weakest in intensity and only the 0–1, 0–0, and 1–0 bands could be identified in our spectra. In spite of weak intensity and strong overlapping, the use of our Loomis–Wood program allowed us to identify the rotational lines. Once the branches of the other three sub-bands were picked out, then the lines due to the 1/2–1/2 sub-band became clearly visible. Even then the band heads were not distinct, although the band head positions can be obtained by extrapolation. The 0–0 band has an origin at 8511 cm^{-1} , while the 1–0 band is located near 8883 cm^{-1} . Each band consists of two P and two R branches as expected for a 1/2–1/2 transition. The splitting in the branches is largely due to Ω -doubling in the lower state $a^4\Delta_{1/2}$ spin component, although Ω -doubling constants of very small magnitude have been determined for the $g^4\Delta_{1/2}$ spin component.

Our analysis indicates that the $v'' = 0$ vibrational level is perturbed at very low J values, and it was noted that inclusion of the low J lines distorts the fit considerably. In the final fit, therefore, the lines with $J'' \leq 47.5$ were deweighted. The $v'' = 1$ vibrational level is not affected by perturbations. The Ω -doubling constants p_v and p_{Dv} have been determined for both the $v'' = 0$ and 1 vibrational levels of the $a^4\Delta_{1/2}$ spin component.

The rotational assignment in different bands was made by comparing the combination differences for the common vibrational levels. It is difficult to make a definite e - and f -parity assignment in the bands with resolved Ω -doubling. We have therefore chosen to label the branches arbitrarily by placing e levels above the f parity levels in the lower $a^4\Delta$ state. The observed $^4\Delta$ electronic states probably belong to Hund's case (a), however, in the absence of $\Delta\Omega = \pm 1$ transitions it is difficult to obtain Hund's case (a) constants for the observed electronic states. A Hund's case (a) fit is possible only if we fix some important molecular parameters, such as A in at least one state, to estimated values. We decided to obtain a fit by using the usual Hund's case (c) empirical term energy expression for each of the spin components

$$F_v(J) = T_v + B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 + L_v [J(J+1)]^4 \pm 1/2 [p_v (J+1/2) + p_{Dv} (J+1/2)^3 + p_{Hv} (J+1/2)^5]. \quad (1)$$

Initially, band-by-band fits were obtained. Once the lines in each of the observed bands were assigned, final fits were carried out by combining the lines of all the

Table 1
Rotational constants^a (in cm^{-1}) for the $a^4\Delta$ state of FeCl

State	Constants	$v = 0$	$v = 1$	$v = 2$	$v = 3$
$a^4\Delta_{7/2}$	T_v	0.0 ^b	428.7024(11)	854.1481(13)	1276.7899(16)
	B_v	0.1776302(40)	0.1766151(36)	0.1758506(36)	0.1748930(45)
	$10^7 \times D_v$	1.426(39)	0.513(17)	1.758(17)	1.989(26)
	$10^{11} \times H_v$	1.83(19)	–1.408(37)	1.067(39)	1.889(72)
	$10^{15} \times L_v$	–4.58(30)	0.661(28)	–1.364(31)	–3.403(66)
$a^4\Delta_{5/2}$	T_v	0.0 ^b	428.0408(11)	852.7274(12)	1274.4443(18)
	B_v	0.1781894(24)	0.1771236(25)	0.1761158(35)	0.1749078(71)
	$10^7 \times D_v$	1.5011(80)	1.2042(75)	2.146(27)	2.93 (10)
	$10^{11} \times H_v$	0.574(18)	–0.781(10)	1.605(99)	1.81(54)
	$10^{14} \times L_v$	–0.0613(14)	–	–0.569(12)	–1.783(95)
$a^4\Delta_{3/2}$	T_v	0.0 ^b	427.2277(15)	–	–
	B_v	0.1785095(53)	0.1770731(67)	–	–
	$10^7 \times D_v$	2.226(33)	4.485(63)	–	–
	$10^{11} \times H_v$	3.46(12)	7.80(29)	–	–
	$10^{14} \times L_v$	–0.850(15)	–4.855(45)	–	–
$a^4\Delta_{1/2}$	T_v	0.0 ^b	429.644(13)	–	–
	B_v	0.1786891(64)	0.1777457(88)	–	–
	$10^7 \times D_v$	1.0803(64)	0.898(19)	–	–
	$10^{12} \times H_v$	–	–2.74(15)	–	–
	$10^2 \times p_v$	–1.1898(70)	–1.2534 (46)	–	–
	$10^7 \times p_{Dv}$	3.01(29)	0.91(22)	–	–

^a The numbers in parentheses are one standard deviation in the last two digits.

^b Each spin component was fitted separately. The $a^4\Delta$ spin–orbit intervals are unknown as is the $a^4\Delta$ – $X^6\Delta$ interval.

Table 2
Rotational constants^a (in cm^{-1}) for the $g^4\Delta$ state of FeCl

State	Constants	$v = 0$	$v = 1$	$v = 2$	$v = 3$	$v = 4$	$v = 5$	$v = 6$
$g^4\Delta_{7/2}$	T_v	8518.74455(79) ^b	8889.94079(99)	9258.30900(91)	9623.86899(98)	9986.63870(83)	10346.6282(12)	—
	B_v	0.1618283(26)	0.1609328(29)	0.1600458(30)	0.1591625(30)	0.1582808(27)	0.1574244(28)	—
	$10^7 \times D_v$	1.1956(41)	1.1819(54)	1.1811(65)	1.1820(63)	1.1714(50)	1.2072(42)	—
$g^4\Delta_{5/2}$	T_v	8575.16895(86) ^b	8947.7118(13)	9317.46740(94)	9684.44957(87)	10048.68051(12)	10410.1881(11)	10768.9899(13)
	B_v	0.1620511(21)	0.1611298(22)	0.1602194(22)	0.1593169(22)	0.1584220(21)	0.1575272(22)	0.1566317(24)
	$10^7 \times D_v$	1.1983(29)	1.1928(30)	1.1910(30)	1.1902(32)	1.1941(29)	1.1942(34)	1.1820(43)
$g^4\Delta_{3/2}$	T_v	8571.1326(10) ^b	8944.1074(17)	9314.2879(12)	9681.71859(98)	10046.4041(11)	10408.3723(17)	—
	B_v	0.1622815(44)	0.1613769(46)	0.1604912(44)	0.1595958(45)	0.1587125(44)	0.1578350(53)	—
	$10^7 \times D_v$	1.2621(96)	1.245(10)	1.2616(95)	1.2445(99)	1.2443(97)	1.254(15)	—
$g^4\Delta_{1/2}$	T_v	8511.381(13) ^b	8883.548(19)	—	—	—	—	—
	B_v	0.1625373(85)	0.1616548(14)	—	—	—	—	—
	$10^7 \times D_v$	1.519(17)	1.550(30)	—	—	—	—	—
	$10^{12} \times H_v$	2.28(12)	2.45(21)	—	—	—	—	—
	$10^7 \times p_{Dv}$	-7.09(16)	—	—	—	—	—	—
	$10^{11} \times p_{Hv}$	5.48(30)	-3.59(31)	—	—	—	—	—

^aThe numbers in parentheses are one standard deviation in the last two digits.

^bRelative to $v'' = 0$ of the corresponding spin component of the $a^4\Delta$ state.

bands in each sub-band. This merged fit provided a single set of constants for each vibrational level in each sub-band. The observed lines positions in different bands are deposited with the Journal of Molecular Spectroscopy's Electronic Depository, which is available on the World Wide Web. The molecular constants for the lower and upper $^4\Delta$ states are provided in Tables 1 and 2, respectively.

4. Results and discussion

In our previous studies of several transition metal halides and hydrides, we have noted that the electronic structure of halides closely resembles to that of hydrides. For example, we have found strong similarity in the electronic structure of CoF [28]/CoH [29]; TiCl [30], TiF [31]/TiH [32]; and FeF [16]/FeH [33,34]. We expect that the electronic structure of FeCl should also be similar to that of FeF and FeH. In our previous work on FeF [16] we have reported on the $^4\Delta$ - $^4\Delta$ system near $1 \mu\text{m}$. This transition was labeled as the $g^4\Delta$ - $a^4\Delta$ based on the correlation of FeF electronic states to the states of FeH predicted by the high quality ab initio calculations on FeH by Langhoff and Bauschlicher [23]. The spectroscopic properties of the low-lying electronic states of FeF and FeCl have recently been calculated by Bauschlicher [25] using the coupled cluster approach with a large basis set. This calculation has confirmed the assignment of a $^6\Delta$ state as the ground state of FeF and FeCl. This calculation has also provided the equilibrium bond lengths, r_e , dissociation energies, D_0 , vibrational frequencies, ω_e and the electronic term energies, T_e , for the $X^6\Delta$ and $a^4\Delta$ states of FeF and FeCl. According to Bauschlicher [25] the $a^4\Delta$ state of FeF is 5210 cm^{-1}

above the ground state, while for FeCl this state is 3606 cm^{-1} above the ground $X^6\Delta$ state. The present $^4\Delta$ - $^4\Delta$ transition of FeCl is analogous to the $g^4\Delta$ - $a^4\Delta$ system of FeF [16] and the $F^4\Delta$ - $X^4\Delta$ system of FeH.

The spectroscopic constants for the different spin components of FeCl states (Tables 1 and 2) suggest that the $a^4\Delta$ state of FeCl is affected by interactions from a close-lying electronic state. Due to perturbations, the higher order spectroscopic constants H_v and L_v are required in the $a^4\Delta$ state, while these constants are not needed for the $g^4\Delta$ state. The determination of larger Ω -doubling constants p_v and p_{Dv} in the $a^4\Delta_{1/2}$ spin component, the abnormal location of different sub-bands and the irregular intervals between the spin components are the reflection of interaction with the nearby states. If we use the energy level diagram for FeF electronic states [16], we notice that the $A^6\Pi$ and $B^6\Sigma^+$ states are located in the same region as the $a^4\Delta$ state. The observed perturbations in the $a^4\Delta$ state could be due to interaction with the $A^6\Pi$ state or higher vibrational levels of the $X^6\Delta$ state. Unfortunately the $A^6\Pi$ state has yet to be observed experimentally and the higher vibrational levels of the $X^6\Delta$ ground state have not been characterized at high resolution.

Since the spectroscopic constants for the four spin components of the $^4\Delta$ states were determined by treating each spin components as individual states [Hund's case (c)], the "true" Hund's case (a) constants have been determined from the effective constants of the four spin components using the relations provided in our previous paper on FeF [16]. The approximate Hund's case (a) constants obtained in this manner are $B_0 = 0.17825 \text{ cm}^{-1}$, $B_1 = 0.17714 \text{ cm}^{-1}$, $A_0 = -88 \text{ cm}^{-1}$, and $A_1 = -83 \text{ cm}^{-1}$ for the lower $a^4\Delta$ state. The values of $B_0 = 0.16217 \text{ cm}^{-1}$, $B_1 = 0.16128 \text{ cm}^{-1}$, $A_0 = -125 \text{ cm}^{-1}$,

and $A_1 = -108 \text{ cm}^{-1}$ have been determined for the upper $g^4\Delta$ state. The spin-orbit splitting constants of the FeCl state compare reasonably well with the values of $A_0'' = -100 \text{ cm}^{-1}$ and $A_0' = -160 \text{ cm}^{-1}$ obtained for the FeF states using the same procedure [16]. Since the excited state is relatively free from perturbations, we attempted to obtain Hund's case (a) constants for the $v' = 0$ vibrational level by using the combination differences from the four spin components in a Hund's case (a) fit. This fit provides $A_0'' = -55 \pm 4 \text{ cm}^{-1}$, $B_0' = 0.1621463(29) \text{ cm}^{-1}$, and $D_0' = 1.2112(31) \times 10^{-7} \text{ cm}^{-1}$. Although the case (a) rotational and distortion constants obtained from this fit are determined precisely, the spin-orbit splitting constant (as well as the computed uncertainty) are unreliable since a small change in the weights of a few combination differences results in very different values for the A_0' constant.

The rotational constants for $v'' = 0$ and 1 vibrational levels of the lower state provide equilibrium constants of $B_e'' = 0.17881 \text{ cm}^{-1}$, $\alpha_e'' = 0.00111 \text{ cm}^{-1}$, and $r_e'' = 2.093 \text{ \AA}$ for the $a^4\Delta$ state, while the excited state equilibrium constants obtained in a similar manner are $B_e' = 0.16262 \text{ cm}^{-1}$, $\alpha_e' = 0.00089 \text{ cm}^{-1}$, and $r_e' = 2.195 \text{ \AA}$ for the $g^4\Delta$ state. The lower state bond length of $r_e'' = 2.093 \text{ \AA}$ compares well with the bond length of $r_e'' = 2.115 \text{ \AA}$ calculated by Bauschlicher [25]. Although vibrational levels up to $v'' = 3$ and $v' = 6$ have been observed in different sub-bands, all the four spin components have been observed only for the $v = 0$ and 1 vibrational levels of the upper and lower states. In order to evaluate the "true" values of vibrational intervals we have averaged the values from the four spin components. The values of $\Delta G''(1/2) = 428.40 \text{ cm}^{-1}$ and $\Delta G'(1/2) = 372.22 \text{ cm}^{-1}$ have been obtained for the lower and upper states of FeCl. In order to determine the Hund's case (a) vibrational constants, we have assumed that the $\omega_e x_e$ constants for the four spin components of a $^4\Delta$ state are similar. Since all four spin components were not observed for the higher vibrational levels of the lower and upper states, the values of $\omega_e x_e'' = 1.65 \text{ cm}^{-1}$, and $\omega_e x_e' = 2.79 \text{ cm}^{-1}$ were estimated by averaging the values obtained from the observed spin components. These values combined with the averaged $\Delta G_{1/2}$ intervals given above provide the vibrational frequencies of $\omega_e'' = 431.70 \text{ cm}^{-1}$ and $\omega_e' = 377.80 \text{ cm}^{-1}$ for the lower and upper states.

Rotational lines belonging to the minor isotopomer, Fe³⁷Cl, were identified for the highest wavenumber sub-bands of the strong bands. For example, the *R* heads of the 0–0, 0–1 and 0–2 bands of the 5/2–5/2 sub-band of Fe³⁷Cl are located at 8577.55 cm⁻¹, 8156.97 cm⁻¹, and 7724.48 cm⁻¹ while the corresponding Fe³⁵Cl heads are located at 8576.96, 8149.04, and 7739.67 cm⁻¹. This provides isotopic shifts of 0.59, 7.93, and 15.19 cm⁻¹, respectively, for the 0–0, 0–1 and 0–2 bands. These values can be compared with the calculated values of 0.47, 7.59, and 14.60 cm⁻¹ using the approximate

vibrational constants for Fe³⁵Cl provided above and the isotopic relations.

In previous work Delaval et al. [19] observed a transition near 31 200 cm⁻¹ which they tentatively assigned as a $^4\Pi-^4\Sigma$ transition although no rotational analysis was obtained. This transition has a lower state vibrational interval of 428 cm⁻¹, which is precisely the vibrational interval for our new $a^4\Delta$ state. This suggests that the 31 200 cm⁻¹ bands probably involve the $a^4\Delta$ lower state and belong either to a $^4\Pi-a^4\Delta$ or a $^4\Phi-a^4\Delta$ transition. The actual assignment has to be confirmed by rotational analysis.

5. Conclusions

The near infrared emission spectrum of FeCl has been recorded at high resolution using a Fourier transform spectrometer and a number of new bands have been detected in the 7000–11 000 cm⁻¹ region. The bands with *R* heads near 7725, 8149, 8577, 8949, 9319, 9686, and 10 050 cm⁻¹ have been assigned as the 0–2, 0–1, 0–0, 1–0, 2–0, 3–0, and 4–0 bands (respectively) of a new $^4\Delta-^4\Delta$ system of FeCl. This transition is analogous to the $g^4\Delta-a^4\Delta$ transition of FeF [16] and the $F^4\Delta-X^4\Delta$ system of FeH [33] both observed near 1 μm . A rotational analysis of a number of bands has been obtained and spectroscopic constants for the new quartet states of FeCl have been determined.

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