

The ultraviolet spectrum of the CoCl_2 radical, studied at vibrational and rotational resolution

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The laser excitation spectrum of the 327 nm band system of CoCl_2 , formed in a free-jet expansion, has been recorded at a rotational temperature of approximately 10 K. The spectrum is congested and suffers extensive perturbations. A progression in the excited state symmetric stretching vibration has been identified. The decrease in the symmetric stretching vibrational wave number on excitation is considerable [$\nu'_1=195.7(12)$, $\nu''_1=358.1(17)$ cm^{-1}]. Despite widespread perturbations in the rotational structure of these vibronic bands, they can be confidently assigned to a parallel $\Omega=7/2-7/2$ transition, consistent with an inverted $^4\Delta_g$ ground electronic state. The rotational constant for $\text{Co}^{35}\text{Cl}_2$ in the ground state is determined to be $0.056\,65(11)$ cm^{-1} , which corresponds to a value for the zero-point averaged Co–Cl bond length r_0 of $2.062\,8(40)$ Å. The perturbations are found to be strongly isotopomer dependent. © 2006 American Institute of Physics. [DOI: 10.1063/1.2188937]

I. INTRODUCTION

The transition metal dichlorides are amongst the simplest molecular systems in which the d electrons are directly involved in chemical bonding. Despite this, their study is challenging for both theoreticians and experimentalists. The theoretical description of these molecules is complicated by the fact that the open d shell of the metal atom gives rise to several low-lying electronic configurations with similar energies, which leads to a high density of electronic states. The task of describing these electronic states is daunting. For experimentalists there is the added complication of reaching the high temperatures required to generate a sufficient vapor pressure to study these molecules in the gas phase. Under such conditions a very large number of vibrational and rotational levels are populated, and the resulting spectra are extremely congested and almost featureless.¹ Consequently, extracting structural information from these spectra is almost impossible. Our solution to this problem is to form the molecules in a free-jet expansion through a nozzle that can be heated up to 1000 °C.² The expansion provides effective vibrational and rotational cooling while avoiding condensation. Rotational temperatures of the order of 10 K can be obtained, allowing resolved rotational features to be recorded by laser excitation spectroscopy. We use a pulsed dye laser to identify bands from survey work at vibronic resolution and then use a continuous-wave ring dye laser to obtain rotationally resolved spectra of individual vibronic bands.

Although the transition metal dichlorides have been studied for many years,^{1,3} it is only recently that precise structural information has been obtained from recordings of

their spectra at rotational resolution. Those studied so far include NiCl_2 ,⁴ CuCl_2 ,⁵ and FeCl_2 .^{6,7} In this study we report the first high resolution study of CoCl_2 .

Previous experimental works on the CoCl_2 radical have involved either high-temperature gas phase absorption spectroscopy in the visible and ultraviolet regions^{1,8,9} or spectroscopy of the molecule trapped in a rare gas matrix.^{10–14} A low resolution study of CoCl_2 in the gas phase was reported by DeKock and Gruen.¹ They observed two strong transitions in the ultraviolet at 298 and 230 nm and several weak $d-d$ transitions in the red end of the visible spectrum. They also studied the absorption spectrum of the molecule isolated in a rare gas matrix.¹⁰ It appeared to reveal at least five transitions underlying the intense ultraviolet band between 330 and 260 nm in addition to three weaker transitions at 253, 238, and 218 nm. Jacox and Milligan¹² described a very similar investigation of CoCl_2 isolated in an argon matrix, essentially confirming the observations of DeKock and Gruen. Infrared studies by Thompson and Carlson¹¹ and Le-roi *et al.*³ have determined the bending (ν_2) and antisymmetric stretching (ν_3) wave numbers to be 94.5 and 493 cm^{-1} , respectively. However, the work by Thompson and Carlson was performed on CoCl_2 in an argon matrix, and subsequent high-temperature electron diffraction studies by Tremmel *et al.*¹⁵ suggested a lower value of 78 cm^{-1} for the bending fundamental of the gaseous molecule.

DeKock and Gruen, using ligand field theory to interpret their results, suggested that the electronic ground state of CoCl_2 was of $^4\Phi_g$ character. This was later challenged by Garner *et al.*,¹⁶ whose *ab initio* calculations revealed a $^4\Sigma_g^-$ state very close in energy. A density functional study by Bridgeman¹⁷ suggested that this $^4\Sigma_g^-$ state was in fact the ground state, an assignment supported by Wang and

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Schwarz.¹⁸ In a recent *ab initio* study, Sliznev *et al.*¹⁹ predicted that the molecule has a $^4\Delta_g$ ground state. In addition to this area of debate, the geometry of the molecule in its ground state is also uncertain. Most of the previous work on CoCl_2 has assumed a linear geometry in the ground state. The molecular beam electron deflection studies by Büchler *et al.*²⁰ and the electronic diffraction studies by Hargittai *et al.*²¹ conclude that the dichlorides from Mn to Cu are all linear in their ground states; on the other hand, an infrared study of a matrix-isolated sample¹⁴ has claimed that the molecule is slightly nonlinear, with a bond angle of 157° . The molecule has also been studied by photoelectron spectroscopy,²² but the interpretation of the resultant spectrum is limited.

II. EXPERIMENTAL DETAILS

The 327 nm band system of CoCl_2 was recorded by the technique of laser excitation spectroscopy, the sample being formed in a free-jet expansion through a heated nozzle. The details of the experiment have been given in full elsewhere.^{2,23} In the present work, CoCl_2 was produced in the gas phase by passing a mixture of 5% HCl in argon over high purity cobalt wire (Alfa Aesar, 99.995%) at a temperature of approximately 800 °C. The stagnation pressure was 1.5 atm, and the background pressure was maintained at approximately 80 mTorr under load by an Edwards EH 1200 Roots blower and a Leybold Trivac mechanical pump.

We investigated two additional methods of producing CoCl_2 in our heated nozzle; first by heating $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ slowly to 850 °C in a stream of Ar, and secondly by the reaction between cobalt powder and a mixture of 5% HCl in argon at 800 °C. Neither of these production methods was as effective as the reaction between cobalt wire and HCl. For $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ the signal strength was weak, the sample did not last long enough to permit a detailed recording of the spectrum, and the nozzle was easily clogged. Cobalt powder was a much more reliable source; however, the molecular concentration in the beam was considerably lower than for the analogous reaction with cobalt wire, and the signal intensities were correspondingly weaker. In the work reported here, all spectra were obtained by generating CoCl_2 in the reaction between cobalt wire and HCl. An interesting feature of this reaction is its dependence on the backing pressure of the HCl/Ar gas mixture. The optimum backing pressure was found to be 1.5 atm, and the signal strength decreased markedly as the backing pressure was raised, to the extent that, by 4 atm, the signal was barely above the level of the noise. A similar behavior was observed in the reaction between iron wire and HCl.^{6,7}

The present study consists of three separate experiments. First, a pulsed dye laser system was used to study the broadband, vibrationally resolved spectrum. The same system was then used in conjunction with a monochromator to disperse the fluorescence from individual vibronic transitions. Finally, the spectra of a number of individual vibrational bands were recorded at the rotational resolution using a continuous-wave ring dye laser system.

The spectra were obtained at vibrational resolution using

a Lambda Physik FL3002 dye laser pumped by a Lambda Physik 205i excimer laser, operating with XeCl at 308 nm. Rhodamine 101, rhodamine B, and rhodamine 6G dyes were used. The dye laser output was frequency doubled using a β -barium borate crystal and directed through a series of baffles to cross the molecular beam at right angles. The laser-induced fluorescence was focused onto a photomultiplier tube mounted at right angles to both the molecular beam and the laser beam. An Andover UG-11 filter located in front of the photomultiplier tube (PMT) greatly improved the signal-to-noise ratio by blocking out the majority of the blackbody radiation from the heated nozzle in the visible region while allowing the ultraviolet fluorescence to pass. The laser power was measured with a photodiode, and the laser wavelength was monitored using a Burleigh uv pulsed wavemeter (model WA55-00). At the end of the experiment the fluorescence signal was normalized to the laser power and the wavelength calibrated against the accurately determined positions of the *R*-branch heads in the rotationally resolved spectra. The dye laser scanning system was found to be highly linear in wavelength.

The dispersed fluorescence spectra were recorded by exciting the most intense *R*-branch head of individual vibronic bands with the FL3002 dye laser. The fluorescence was focused onto the entrance slit of a 0.5 m monochromator (Monospek 600) equipped with a 2400 lines/mm grating. A photomultiplier was mounted on the exit slit, and the signal was amplified before being sent to the Stanford Research Systems SR250 boxcar. The spectra were calibrated by first recording the spectrum of a hollow cathode lamp to acquire a calibration curve for the diffraction grating. There was an almost constant offset of 0.05 nm over the range of these experiments, and the spectra were subsequently calibrated with respect to the excitation band, and confirmed by the position of the 308 nm line of the excimer radiation.

The rotationally resolved spectra of CoCl_2 were recorded using a Coherent 899-21 continuous-wave ring dye laser, pumped by a Coherent Innova 100 argon ion laser operating on the 514 nm line. Dicyanmethylen (DCM) Special laser dye was used, and the output was frequency doubled using a lithium iodate crystal. The laser beam was chopped at 3 kHz, and the photomultiplier signal was demodulated using a Brookdeal 9503 lock-in amplifier. The spectra were calibrated by a simultaneous recording of the absorption spectrum of I_2 and the transmission fringes from a confocal étalon. A portion of the fundamental laser beam was diverted into a heated iodine cell, and a photodiode was used to detect the absorption signal. Another small portion was sent through a 1 m confocal étalon and onto another photodiode. The remainder of the fundamental beam was sent to the Burleigh pulsed wavemeter for a rough calibration. The absorption spectrum of iodine has been well characterized,^{24,25} and it provides the absolute wave number calibration. The étalon fringes were then used for an accurate interpolation. The limit on accuracy was determined by the measurement of the iodine spectrum; the iodine lines typically have a linewidth of 0.02 cm^{-1} . The estimated uncertainty in the CoCl_2 line positions is 0.002 cm^{-1} . The most significant contribution to the spectral linewidth in the rotationally resolved spectra is

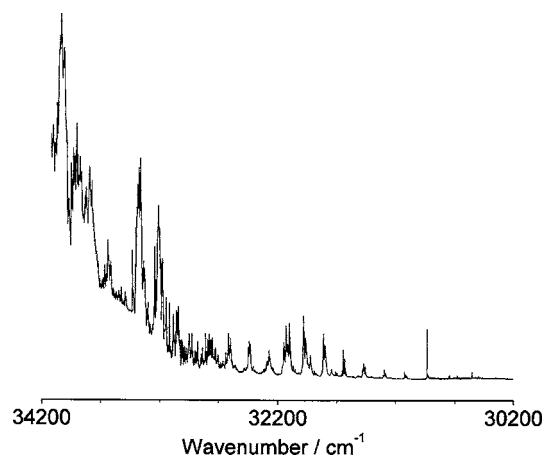


FIG. 1. The vibrationally resolved survey spectrum of CoCl_2 between 290 and 330 nm. The spectrum extends to a considerably higher wave number, but only the low wave number end has been analyzed in detail (shown in Figs. 2 and 3).

the Doppler effect resulting from the divergence of the molecular beam. This effect can be reduced by installing an iris before the photomultiplier tube, essentially reducing the viewing region. This was highly effective in reducing the linewidth from 800 down to 350 MHz for the recording of the most intense band; in the weaker bands, the much reduced signal-to-noise ratio far outweighed any benefits from the reduced linewidth, and it was necessary to open the iris. As has been explained elsewhere,⁴ when using the iris it was important to ensure that the nozzle was aligned so that the portion of the expanding jet from which the fluorescence was collected was as close to orthogonal to the laser beam as possible. If the iris were set so that a region of the jet with a nonzero velocity parallel to the laser beam was being sampled, the signals would all be Doppler shifted. At extreme orientations of the jet, this Doppler shift can be as large as 0.05 cm^{-1} . In these experiments, the position of the maximum intensity was established by successive adjustments of the jet position and laser frequency, and care was taken to ensure that the spectral line shapes were symmetric. When parts of the same band were recorded during different experimental runs, the measurements were standardized by ensuring an overlap between scans. This wave number shift was never more than 0.01 cm^{-1} , and it affects only the value of the band origin. The accuracy of the absolute wave numbers for these transitions is therefore lower than the precision.

III. RESULTS

A. Vibrational structure

The laser excitation spectrum was recorded at a resolution of 0.28 cm^{-1} in the 292–330 nm region and is shown in Fig. 1. The longer wavelength end of this survey spectrum is shown in Figs. 2 and 3, and the measured bandheads are given in Table I. Despite the relatively low vibrational and rotational temperatures achieved in the free-jet expansion, the spectrum obtained under these conditions is both exten-

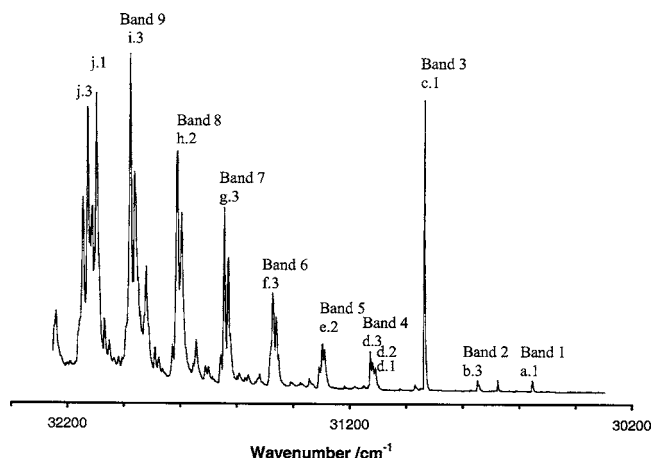


FIG. 2. A portion of the vibrationally resolved survey spectrum of the CoCl_2 band system at 327 nm. Vacuum wave numbers for the bandheads, and some tentative assignments, are given in Table I.

sive and congested. This is particularly apparent at the short wavelength end of this band system where the intense, broad transitions form a virtual continuum.

A progression with a band separation of approximately 200 cm^{-1} emerges at the long wavelength end of the region studied (Bands 1 to 9 in Figs. 2 and 3). However, this is clearly not a simple progression; the (0-0) band appears to be at $30\,555.2 \text{ cm}^{-1}$ (Band 1), yet the relative intensities and rotational contours in the five long wavelength bands do not change smoothly from one band to the next. In particular, the third band is anomalously strong. This progression is assumed to be a progression in the excited state symmetric stretching vibration ν'_1 .

A least-squares fit of the data to the expression

$$G(\nu_1) = \nu_1 \omega_1^0 + (\nu_1)^2 x_{11}^0 \quad (1)$$

yields vibrational parameters for the symmetric stretching vibration in the upper electronic state. These are given in Table II. Note that this expression is only valid if (i) the energy levels of the excited electronic state are not significantly perturbed and (ii) the bands belong to a single isotopomer.

Since the assignments of these bands are still tentative, those that make up this progression have been numbered in

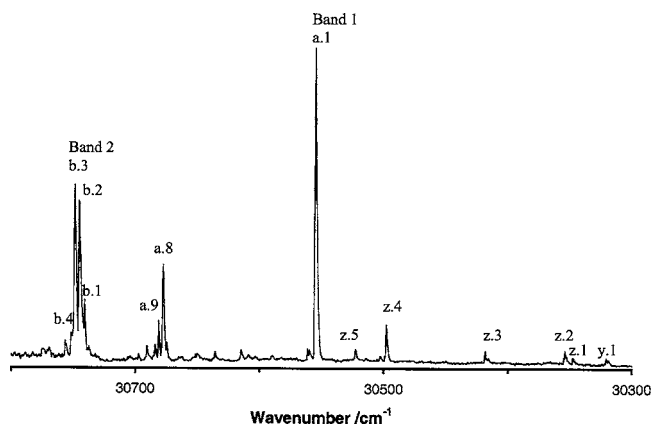


FIG. 3. The low wave number end of the survey spectrum of the 327 nm band system of CoCl_2 .

TABLE I. Vacuum wave numbers and assignments for the most intense bandheads in the 327 nm system of CoCl_2 . The peak labels refer to Figs. 2 and 3, but for the purposes of clarity, only those bands referred to in the text are labeled. These measurements are accurate to 0.2 cm^{-1} .

Assignment $\nu_1' \nu_2' \nu_3'$	Peak label	Wave number (cm^{-1})	Assignment $\nu_1' \nu_2' \nu_3'$	Peak label	Wave number (cm^{-1})
000 ^c	y.1	30 320.2		e.3	31 309.3
	z.1	30 348.1		e.4	31 343.8
	z.2	30 354.1	500 ^{a,b}	f.1	31 452.3
	z.3	30 418.2	500 ^{b,c}	f.2	31 462.0
	z.4	30 497.7	500 ^d	f.3	31 474.8
	z.5	30 522.2		f.4	31 518.7
	a.1	30 555.2		f.5	31 559.5
	a.2	30 559.9		f.6	31 591.5
	a.3	30 561.3	600 ^{a,b}	g.1	31 624.3
	a.4	30 614.8	600 ^{c,d}	g.2	31 631.9
	a.5	30 635.5	600 ^d	g.3	31 646.7
	a.6	30 650.1		g.4	31 656.9
	a.7	30 674.6		g.5	31 700.4
	a.8	30 676.9		g.6	31 711.8
020 ^d	a.9	30 681.0		g.7	31 744.7
020 ^{b,c}	a.10	30 683.9	700 ^{b,c}	h.1	31 798.1
020 ^{a,b}	a.11	30 690.6	700 ^d	h.2	31 813.2
100 ^a	b.1	30 740.9		h.3	31 828.1
100 ^c	b.2	30 745.5		h.4	31 890.4
100 ^d	b.3	30 748.7		i.1	31 922.0
	b.4	30 751.4	800 ^{b,c}	i.2	31 965.9
200 ^d	b.5	30 756.3	800 ^{b,d}	i.3	31 981.4
	c.1	30 938.5		i.4	31 995.0
	c.2	30 969.5		i.5	32 053.3
300 ^a	d.1	31 109.7		i.6	32 070.7
300 ^c	d.2	31 121.3		j.1	32 101.5
300 ^d	d.3	31 128.7		j.2	32 115.1
400 ^{b,c}	e.1	31 289.9		j.3	32 132.6
400 ^d	e.2	31 297.7		j.4	32 148.1

^a $\text{Co}^{37}\text{Cl}_2$.

^bSpeculative assignment.

^c $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$.

^d $\text{Co}^{35}\text{Cl}_2$ isotopomer.

order of increasing frequency, beginning at the band origin. Hence, throughout this paper the (0-0) band at $30\,555.2 \text{ cm}^{-1}$ is known as Band 1, while the band at $30\,748.7 \text{ cm}^{-1}$, thought to be the 1_0^2 band, is referred to as Band 3. Band 1 was given zero weight in the fit of vibrational parameters since its rotational structure only reveals transitions attributable to the $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$ isotopomer.

B. Lifetime measurements

The fluorescence lifetimes of the first eight bands in the progression were measured during the course of these experi-

TABLE II. Upper state band origin and vibrational parameters for the symmetric stretching vibration in the 327 nm system of $\text{Co}^{35}\text{Cl}_2$. The figures in parentheses represent one standard deviation of the least-squares fit in units of the last quoted decimal place.

Molecular parameter	Value (cm^{-1})
ν_0	30 552.4(15)
ω_1^0	198.4(12)
x_{11}^0	-2.68(16)

TABLE III. Radiative lifetimes for Bands 1–9 in the CoCl_2 band system at 327 nm.

Band	Number	Lifetime, τ (μs)
ν_0^0	1	0.928(11)
1_0^1	2	0.942(15)
1_0^2	3	0.964(10)
1_0^3	4	1.369(15)
1_0^4	5	1.374(15)
1_0^5	6	1.488(16)
1_0^8	9	1.776(19)

ments. The laser was fixed at the frequency of the maximum fluorescence intensity, and the fluorescence decay was recorded as a function of time following the excitation pulse. The decay curves were fitted using an equation of the form $I = I_0 e^{-t/\tau}$. The determined lifetimes are given in Table III. These lifetimes are considerably longer than 35 ns, which is approximately that expected for an excited state connected to a ground state by a fully allowed transition, indicating that these transitions are forbidden to some extent. The lifetimes might be expected to decrease as ν_1' increases because of the approach of predissociation, but just the opposite trend is observed. It is likely that these are formally forbidden transitions that gain intensity through perturbation with a nearby electronic state. The increasing lifetime observed in this progression is then explained by the decreasing strength of interaction with the perturbing state as ν_1' increases. This possibility will be discussed in more detail later.

Lifetime measurements were also performed on several of the weak spectral features in the region of the origin band; this region is shown in detail in Fig. 3. The transition labeled a.8 has a lifetime of $0.917 \mu\text{s}$. This is a strong candidate for the 2_0^2 band, resulting in an approximate value for $\tilde{\nu}_2$ of 60 cm^{-1} (in the 460 nm band system of NiCl_2 , $\tilde{\nu}_2$ is found to be approximately 59 cm^{-1} , a significant reduction from its ground state value of 85 cm^{-1}).² Figure 3 also shows the presence of several weak transitions to the red of Band 1, the supposed (0-0) band. In the past we have been able to check for the presence of hot band transitions by recording the spectra under both hot and cold conditions; the vibrational temperature can be increased by reducing the backing pressure behind the nozzle. However, as mentioned previously, the reaction we used to generate CoCl_2 is very dependent on the pressure of the HCl/Ar mixture, and these experiments were not totally conclusive. At lower backing pressures, the relative intensities of all these bands did not change, while at backing pressures above 2 atm, it was not possible to detect these signals above the experimental noise. We were, however, able to measure the fluorescence lifetimes of these transitions. Band z.2 has a lifetime of $2.69 \mu\text{s}$, which implies that it is a more strongly forbidden transition. The true lifetime may, in fact, be significantly higher than this value; this time scale is close to the upper limit of our ability to measure the lifetime. The molecules enter the beam chamber at about 1000 ms^{-1} , and the fluorescence is detected by a photomultiplier tube mounted on the roof of the reaction chamber. Molecules with a fluorescence decay lifetime of $3 \mu\text{s}$ or longer will have passed the field of view of the PMT before

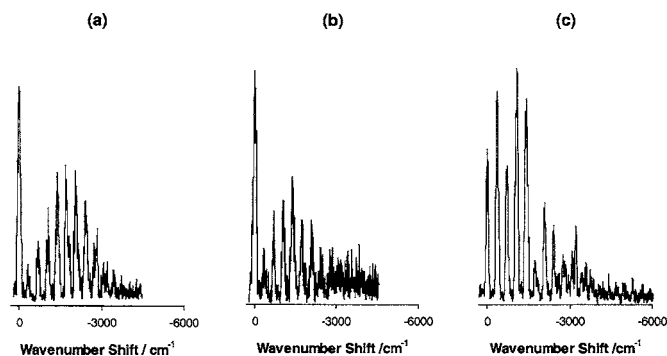


FIG. 4. Dispersed fluorescence spectra from (a) Band 1, (b) Band 2, and (c) Band 3 of the 327 nm CoCl_2 band system. The wave number shift is quoted relative to the excitation band.

they have finished fluorescing. The experimental evidence suggests that these are not hot band transitions, but transitions to another electronic state or set of states. There is clearly a very high density of states in this region.

C. Dispersed fluorescence

In order to obtain information on the molecule in its ground electronic state, we have recorded dispersed fluorescence spectra. By exciting at the wavelength of the maximum fluorescence, dispersed fluorescence spectra have been obtained for the first four bands in the progression. For the three bands studied at a high resolution, the maximum fluorescence intensity corresponded to the position of the head in the R branch.

The dispersed fluorescence spectra are dominated by a simple vibrational progression in the ν_1'' symmetric stretching vibration. The spectra for Bands 1–3 are shown in Fig. 4. Note that the intensity of the excitation peak is anomalously high due to the scattered laser light adding to the fluorescence signal at the laser wavelength. In these experiments, we are investigating the vibrational intervals of CoCl_2 in the ground electronic state. If we have excited the same isoto-

pomer in each band, the vibrational spacings should not change from band to band, and the intensity of each band is proportional to the square of the overlap integral between the ground and excited state vibrational wave functions. The absence of nodes in the intensity distribution of the spectrum from Band 1 and the absence of “anti-Stokes” transitions on the high frequency side of the laser line reinforce its assignment as the (0-0) band.

The intensity of the fluorescent emission from Band 3 was much stronger than that from the other bands. Consequently, we were able to work on this band with considerably narrower monochromator slits (1.5 mm), and we were able to obtain better resolved spectra. For this reason, only the dispersed fluorescence spectrum from Band 3 was used to calculate ground state vibrational constants. The value, $360.2(17) \text{ cm}^{-1}$ determined for $\omega_1^{0''}$ in this way is virtually indistinguishable from the value obtained by fitting the spectra from Bands 2–4 simultaneously. The details of the dispersed fluorescence fit are tabulated in Table IV. There was no indication of progressions in ν_2 or ν_3 in the dispersed fluorescence spectra.

The dispersed fluorescence results from Band 1 reveal slightly smaller vibrational separations than observed in the other three bands. $\omega_1^{0''}$ is determined to be $353.8(35) \text{ cm}^{-1}$. In the excitation spectrum, Band 4 appears to be comprised of three subbands with an approximate intensity ratio of 9:6:4. We have recorded dispersed fluorescence spectra resulting from an excitation into all three of these bandheads. Fitting of the spectra from the three subbands revealed distinct vibrational constants for each, in approximately the correct wave number ratio (within their uncertainties) to assign them to the $\text{Co}^{35}\text{Cl}_2$, $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$, and $\text{Co}^{37}\text{Cl}_2$ isotopomers. In the case of the $\text{Co}^{37}\text{Cl}_2$ isotopomer, the spectrum was obtained by exciting slightly off resonance to a longer wavelength than the fluorescence maximum on the low resolution scan. This was necessary to avoid the fluorescence from $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$ dominating the spectrum. The results of these experiments are displayed in Table V. From this evidence we

TABLE IV. Measurement of the dispersed fluorescence spectra of selected bands in the 327 nm system of CoCl_2 and results of the fit of Band 3. These results were obtained by pumping the most intense bandhead in Bands 1–4.

Band 1 ^a		Band 2		Band 3 ^b		Band 4	
ν_1', ν_1''	Wave number (cm^{-1})	ν_1', ν_1''	Wave number (cm^{-1})	ν_1', ν_1''	Wave number (cm^{-1})	ν_1', ν_1''	Wave number (cm^{-1})
0,0	30 555.2	1,0	30 748.7	2,0	30 938.5	3,0	31 128.7
0,1	30 206.1	1,1	30 390.7	2,1	30 576.0	3,1	30 765.6
0,2	29 856.7	1,2	30 044.0	2,2	30 230.0	3,2	30 416.2
0,3	29 490.8	1,3	29 687.4	2,3	29 887.6	3,3	30 067.5
0,4	29 151.8	1,4	29 345.0	2,4	29 536.8	3,4	29 713.3
0,5	28 801.8	1,5	28 992.7	2,5	29 194.2		
0,6	28 467.0	1,6	28 664.4	2,6	28 849.1		
0,7	28 142.8	1,7	28 332.0	2,7	28 523.1		
0,8	27 765.7						
$\omega_1^{0''} (\text{cm}^{-1})$				$x_{11}^{0''} (\text{cm}^{-1})$			
360.2(17) ^b				-2.13(30) ^b			

^aThe carrier of this spectrum is $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$.

^bThese results are for $\text{Co}^{35}\text{Cl}_2$.

TABLE V. Measurement of the bands in the dispersed fluorescence spectra of the three subbands which comprise Band 4 in the 327 nm band system of CoCl_2 . The results of the fit are reported below.

ν_1', ν_1''	Transition wave number (cm^{-1})		
	$\text{Co}^{35}\text{Cl}_2$	$\text{Co}^{35}\text{Cl}^{37}\text{Cl}$	$\text{Co}^{37}\text{Cl}_2$
3,0	31 128.7	31 121.3	31 109.7
3,1	30 765.6	30 762.1	30 751.2
3,2	30 416.2	30 415.2	30 411.5
3,3	30 067.5	30 069.5	30 074.6
3,4	29 713.3	29 719.8	29 722.2
ω_1'' (cm^{-1})	359.9(35)	356.8(29)	352.4(61)
x_{11}'' (cm^{-1})	-1.6(10)	-1.72(86)	-1.6(17)

can assign the species responsible for Band 3 to $\text{Co}^{35}\text{Cl}_2$, and that responsible for Band 1 to either $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$ or $\text{Co}^{37}\text{Cl}_2$. This surprising conclusion is fully supported by the rotational analysis, which reveals that only the fluorescence from the $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$ isotopomer is observed in Band 1.

D. Rotational structure

Of the bands recorded at vibrational resolution, Band 3 was by far the strongest, and consequently the best feature to study at high resolution. The rotationally resolved spectrum of Band 3 is shown in Fig. 5. The band is strongly red degraded with an obvious perturbation in the middle of the P branch between $P(9.5)$ and $P(20.5)$. The perturbation also manifests itself in a reduction in intensity of the corresponding R lines. In the first inspection, the rotational temperature of the species seems to be exceptionally cold. The R lines appear to pile on top of each other to produce a very sharp head, while no returning R lines are found between the Q branch and the R head. This is not due to the exceptional rotational cooling, but due to the strong J -dependent pertur-

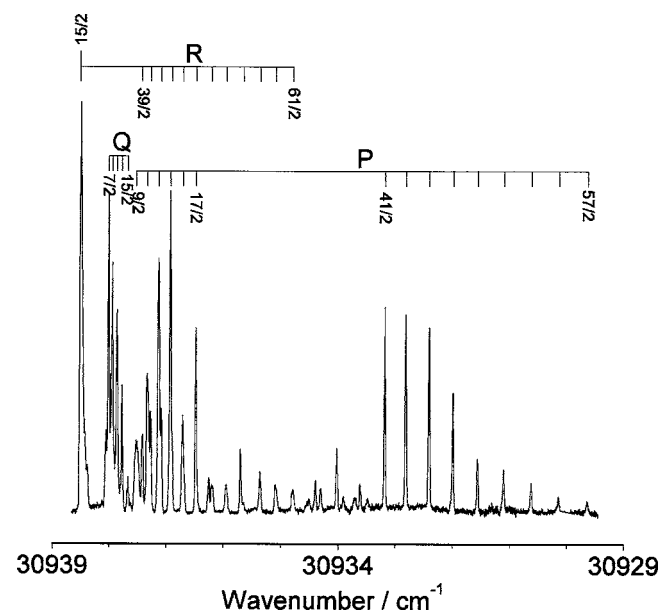


FIG. 5. The rotationally resolved spectrum of Band 3 of the CoCl_2 327 nm band system. Only transitions for the $\text{Co}^{35}\text{Cl}_2$ isotopomer are observed.

bation that is obvious in both the P and R branches of this spectrum. The R branch can be retraced after $R(18.5)/R(19.5)$, but the intensity distribution in this branch is somewhat irregular.

The higher- J lines, beyond the region of strong perturbation, are found to have shifted slightly from their expected frequencies. The assignments of these lines, given in Fig. 5 and Table VI, are based on a least-squares fit to a polynomial containing centrifugal distortion constants to account for the shift. The residuals for this fit are rather large (typically 0.0055 cm^{-1}), but we believe that these assignments are secure. The low- J region of this spectrum is, by comparison, well behaved and unperturbed. These lines were used to obtain a much more precise fit to a rigid-rotor model.

Bands 1 and 2 have also been recorded at rotational resolution. Band 1 has a very similar structure to Band 3, and it exhibits a similar region of strong perturbation around the $J'=8.5$ level. In this band the higher- J P lines were found to be below the level of the noise, and centrifugal distortion constants were not required in the least-squares fitting of these rotational lines. Band 2 consists of three subbands which can be tentatively assigned to the three isotopomers: $\text{Co}^{35}\text{Cl}_2$, $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$, and $\text{Co}^{37}\text{Cl}_2$. The branch structure in this band is highly fragmented, and a detailed rotational analysis is impossible at this stage.

A partial rotational analysis of both Bands 1 and 3 has been achieved; the detailed measurements and assignments are given in Table VI. The rotational analyses reveal that the ground state rotational constant for Band 1 is considerably smaller than that for Band 3. The ratio of these parameters confirms the dispersed fluorescence results: $\text{Co}^{35}\text{Cl}_2$ is responsible for Band 3, and $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$ for Band 1. Since there are relatively few unperturbed lines in these spectra, they have been fitted simultaneously to a rigid-rotor model, with their ground state B values constrained to their predicted ratio (0.972 65). The rotational constants obtained from this analysis are listed in Table VII. The residuals in this fit are slightly larger than the experimental uncertainty, indicating that the perturbation causes small, but significant, deviations from the rigid-rotor line positions, even for the rotational lines away from the region of obvious perturbation. Nevertheless, we have been able to obtain accurate values for the $\text{Co}-^{35}\text{Cl}$ bond length in the ground and excited states. These values are given in Table VII.

We attempted to record Bands 4 and 5 at rotational resolution, but their spectra were disappointingly weak, despite appearances to the contrary in the pulsed laser spectrum. Only the strongest features were visible in these spectra, and no rotational analysis was possible.

IV. DISCUSSION

In this paper we have reported the detection and identification of several bands in the electronic spectrum of CoCl_2 . By producing the molecule in a free-jet expansion, we have been able to generate CoCl_2 at low rotational temperatures (approximately 10 K). This has enabled the spectra to be recorded at a much higher resolution than achieved previ-

TABLE VI. Assignments and vacuum wave numbers for the rotational lines in Bands 1 and 3 of the CoCl₂ 327 nm band system. All data are in cm⁻¹ units.

Band 3						Band 1				
<i>J</i>	<i>P</i> (<i>J</i>)	<i>o</i> − <i>c</i> ^a	<i>Q</i> (<i>J</i>)	<i>o</i> − <i>c</i>	<i>R</i> (<i>J</i>)	<i>P</i> (<i>J</i>)	<i>o</i> − <i>c</i>	<i>Q</i> (<i>J</i>)	<i>o</i> − <i>c</i>	<i>R</i> (<i>J</i>)
3.5			30 938.0060					30 554.6574	−32	
4.5	30 937.5508	50 ^b	30 937.9462	25		30 554.1618	−30 ^b	30 554.6040	12	
5.5	30 937.3214	8	30 937.8642	−37		30 553.9958	−8	30 554.5362	43	
6.5	30 937.1320	5	30 937.7756	−28		30 553.8916	40	30 554.4488	7	
7.5	30 936.9300	12	30 937.6728	−23	30 938.4930 ^{b,c}	30 553.6170	−46	30 554.3544	29	30 555.1980 ^{b,c}
8.5	30 936.7132	10	30 937.5510	−72 ^b		30 553.4080	−67	30 554.2486	66	
9.5	30 936.4842	23				30 553.1972	21	30 554.1618	−40 ^b	
10.5						30 552.9730	105 ^b			
19.5					30 937.4164 ^d					
20.5	30 933.1838 ^d				30 937.2730 ^d					
21.5	30 932.8152 ^d				30 937.0898 ^d					
22.5	30 932.4048 ^d				30 936.8986 ^d					
23.5	30 931.9910 ^d				30 936.7132 ^d					
24.5	30 931.5604 ^d									
25.5	30 931.1062 ^d				30 936.1882 ^d					
26.5	30 930.6244 ^d				30 935.9516 ^d					
27.5	30 930.1410 ^d				30 935.6536 ^d					
28.5	30 929.6428 ^d									
29.5					30 935.0858 ^d					
30.5					30 934.7850 ^d					
Unassigned lines (Band 3)			30 938.4288		30 934.5036	Unassigned lines (Band 1)		30 555.1462		30 552.4830
			30 938.3812		30 934.3924			30 554.9850		30 552.1584
			30 938.1228		30 934.3006			30 554.7106		30 551.9920
			30 938.0526		30 934.0198			30 553.7800		30 551.8160
			30 936.4568		30 934.8986			30 553.2902		30 551.6148
			30 936.2546		30 933.6100			30 552.8120		30 551.4036
			30 935.7014					30 552.7388		30 551.1680
			30 935.3612					30 552.6918		30 550.9376
			30 934.5466					30 552.6062		

^aObserved minus calculated wave number × 10⁴.^bTransition given zero weight in the fit (e.g., overlapping lines).^cPosition of the *R*-branch head.^dHigher-*J* lines beyond the region of strong perturbation. These lines are found to be shifted somewhat from their expected frequencies and are not included in the fit.

ously. The rotational structure is fully resolved, and this is the first time this has been achieved for CoCl₂.

Although our understanding of this spectrum is far from complete, there can be no doubt that the carrier of the spectrum is CoCl₂. The absorbing species is only produced in the presence of both cobalt metal and HCl in the reaction mixture. The ground state symmetric stretching vibrational separation of 360 cm⁻¹ is entirely consistent with the value ex-

pected by analogy with FeCl₂, NiCl₂, and CuCl₂, and the ground state rotational constant of 0.056 65(11) cm⁻¹ is appropriate for a first-row transition metal dichloride. The cobalt used was 99.995% pure (Alfa Aesar), and the spectrum is inconsistent with either CoCl or CoCl₃. In addition, where isotope patterns are obvious in the shorter wavelength end of the region studied, they are as expected for a symmetric triatomic dichloride molecule.

A. Vibrational structure

The ultraviolet spectrum of CoCl₂ is complicated and congested. The short wavelength end of the spectrum appears to be a continuum, even at a resolution of 0.28 cm⁻¹ and a rotational temperature of 12 K (see Fig. 1). We have studied a relatively short progression at the long wavelength end of this system. This has been assigned as a progression in the excited state symmetric stretching vibration.

The dispersed fluorescence shows progressions with an interval of 360 cm⁻¹. These can be securely assigned to the symmetric stretching vibration in the ground electronic state

TABLE VII. Rotational parameters obtained from the least-squares fit of Bands 1 and 3 in the 327 nm system of CoCl₂.

Parameter	Value (in cm ⁻¹ units, unless stated)	
	Band 1 (Co ³⁵ Cl ³⁷ Cl)	Band 3 (Co ³⁵ Cl ₂)
<i>ν</i> ₀	30 554.762 2(26)	30 938.114 0(26)
<i>B</i> '	0.048 66(14)	0.049 76(15)
<i>r</i> ' ₀		2.200 8(65) Å
<i>B</i> ''	0.055 10 ^a	0.056 65(11)
<i>r</i> '' ₀		2.062 8(40) Å

^aThis parameter is constrained to be in the correct isotopic ratio with *B*'' for Band 3 (0.972 65).

TABLE VIII. Isotope shifts of $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$ bands relative to those of $\text{Co}^{35}\text{Cl}_2$ in the 327 nm system of CoCl_2 . All values are in cm^{-1} .

Band	Tentative assignment $\nu_1' \nu_2' \nu_3'$	Observed isotope shift	Calculated shift	Obs. – calc.
4	300	–7.4	–7.1	–0.3
5	400	–7.8	–9.8	2.0
6	500	–12.8	–12.5	–0.3
7	600	–14.8	–15.3	0.5

by comparison with NiCl_2 ,² CuCl_2 ,²⁶ and FeCl_2 .⁷ The progression in the excitation spectrum is clearly not simple. The intensity distribution is unusual, with Band 3 being anomalously strong; the lifetimes of the fluorescent emission from these bands do not vary smoothly through the progression (Table III); strong, isotopomer-dependent perturbations are obvious in the bands studied at rotational resolution. In spite of these complications, the progression has a fairly constant vibrational interval of approximately 200 cm^{-1} . This has been assigned to the excited state symmetric stretching vibration for the following reasons

- (1) This progression complements the progression in the symmetric stretching vibration identified in the dispersed fluorescence spectrum.
- (2) A very similar interval is observed in the 288 nm band system of FeCl_2 , where it has been confidently assigned to the excited state stretching vibration.⁷
- (3) The alternative assignment of a progression in two quanta of the ν_2 bending vibration is unsatisfactory. The long progression would imply that the molecule was significantly bent in at least one electronic state, and we see no evidence of this in the rotationally resolved spectra; nor do we observe bending mode progressions in the dispersed fluorescence spectra.
- (4) In the later bands in this progression (from Band 4 onwards), it is possible to assign *R*-branch heads to both the $\text{Co}^{35}\text{Cl}_2$ and $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$ isotopomers (Table I), and occasionally to $\text{Co}^{37}\text{Cl}_2$. It is therefore possible to compare the observed isotope shifts in each band with those calculated based on the symmetric stretching vibrational wave numbers (ω_1) in the ground and excited states (362.3 and 201.0 cm^{-1} , respectively). The results of this analysis are shown in Table VIII. The calculations assume that the molecule is linear in both states

and that there is no interaction between the bending and stretching vibrational modes. The difference in zero-point energies between the different isotopic species due to the antisymmetric stretching and bending vibrational modes has been ignored. Note also that the small reduction in ν_1 and the increase in ν_3 due to the interaction of these two modes in $\text{Co}^{35}\text{Cl}^{37}\text{Cl}$ (they both have the same symmetry, Σ^+ , in the $C_{\infty v}$ molecule) have not been included in this calculation; the shift is known to be small in closely related FeCl_2 (approximately 0.1 cm^{-1}).¹⁴ Since there are clearly local perturbations that affect the different isotopic species differently, a perfect agreement between experiment and theory is not expected, but it is reassuring that the isotope shifts seem to confirm our excited state vibrational assignments of these bands.

Table IX lists known vibrational wave numbers for a number of transition metal dichlorides. For CoCl_2 there is a very dramatic drop in ν_1' from its ground state value, implying a considerable weakening of the Co–Cl bonds. This behavior is also observed in the spectrum of FeCl_2 ,⁷ and it suggests that these electronic transitions involve a large change in the bonding character of the promoted electron.

In addition to the bands thought to make up the progression, many weak bands pervade this system. The fluorescence lifetimes of several of these bands in the vicinity of Band 1 have been measured and found to be much longer than those making up the progression in excited state ν_1 . The complexity of this spectrum suggests that there are several excited electronic states in this region, with considerable perturbations among them. It is perhaps not surprising that the rotational structure of these bands appears fragmented.

B. Rotational structure

Despite the obvious perturbations in Bands 1 and 3, their rotationally resolved spectra can be fitted to a rigid-rotor model with a reasonably high precision. In each case, the first *Q* line is found to be $Q(7/2)$, the first *P* line, $P(9/2)$, and the intensity distribution within the *Q* branch suggests a $\Delta\Omega=0$ transition. This evidence leads to the assignment of the transition as $\Omega=7/2-7/2$. This assignment is confirmed by simulations of the bands using the results of the least-squares fit with transition intensities given by the product of

TABLE IX. Selected vibrational wave numbers for the first-row transition metal dichlorides. All values are in cm^{-1} .

Molecule	Band system (nm)	ν_1''	ν_1'	ν_3''	ν_3'
$^{56}\text{Fe}^{35}\text{Cl}_2$	288 ^a	352.39(13)	200.43(18)	511 ^{b,c}	
$^{59}\text{Co}^{35}\text{Cl}_2$	327	358.1(17)	195.7(12)		
$^{58}\text{Ni}^{35}\text{Cl}_2$	460 ^d	360.24(10)	356.380(1)	520.4(10) ^c	530.9546(4)
$^{63}\text{Cu}^{35}\text{Cl}_2$	650 ^e	369.365(2)	331.041(5)	520.994(2) ^c	

^aReference 7.

^bApproximate value ($\pm 20 \text{ cm}^{-1}$).

^cOne half of the $2\nu_3$ interval.

^dReferences 2 and 4.

^eReferences 26 and 27.

TABLE X. Ground state rotational constants for the first-row transition metal dichlorides. These data refer to the most abundant isotopomer in each case.

Molecule	M ³⁵ Cl ₂	B_0'' (cm ⁻¹) M ³⁵ Cl ³⁷ Cl	M ³⁷ Cl ₂
FeCl ₂ ^a	0.053 029 6(95)	0.051 575(19)	0.050 148(33)
CoCl ₂	0.056 65(11)	0.055 10(11)	
NiCl ₂ ^b	0.057 178 8(80)	0.055 578(20)	
CuCl ₂ ^c	0.058 138(1)	0.056 561(2)	0.055 003(1)

^aReference 7.

^bReference 4.

^cReferences 26 and 28.

a Boltzmann population factor for $T=12$ K and a Hönl-London line strength factor. This value for Ω'' is consistent with the latest theoretical prediction that the ground state is an inverted $^4\Delta_g$.¹⁹ This is contrary to earlier suggestions of a $^4\Sigma_g^-$ ground state.^{17,18}

The Co–Cl bond length r_0 has been determined to be 2.062 8(40) Å in the ground electronic state and 2.200 8(65) Å in the excited state. The large increase on excitation is entirely consistent with the suggested drop in the symmetric stretching frequency on excitation. Our value is considerably lower than the equilibrium bond distance r_e of 2.090(7) Å determined by Hargittai *et al.*²¹ from electron diffraction and vibrational spectroscopy.

C. Deciphering the isotopic structure

The HCl used in these experiments contained Cl in natural abundance. In all vibronic bands, absorptions attributable to each of the three isotopomers, Co³⁵Cl₂, Co³⁵Cl³⁷Cl, and Co³⁷Cl₂, are expected in a 9:6:1 intensity ratio. It is strange but significant that there is a single, but different, isotopomer clearly present in the rotationally resolved spectra of Bands 1 and 3. In this section we review the evidence that led to these isotopic assignments.

- (1) Table X lists the ground state rotational constants determined in our laboratory for a series of first-row transition metal dichlorides. The trend across the series is clear: the increase in rotational constant reflects a shortening of the M–Cl bond. Interpolation confirms that our assignment of the carrier of the Band 3 spectrum as Co³⁵Cl₂ is entirely reasonable.
- (2) The value determined for $\omega_1^{0''}$ of 360.2(17) cm⁻¹ from the dispersed fluorescence spectrum of Band 3 is greater than the value obtained from the Co³⁵Cl³⁷Cl subband in Band 4 and is comparable with the Band 4 results from the Co³⁵Cl₂ bandhead. It is also comparable with that obtained for other transition metal dichlorides [for Ni³⁵Cl₂: $\omega_1^{0''}=360.24(10)$ cm⁻¹].⁴ The value of $\omega_1^{0''}$ determined from the dispersed fluorescence spectrum of Band 1 is significantly lower: 353.8(35) cm⁻¹.
- (3) The rotational analysis of Band 1 reveals that the ground state rotational constant for this isotopic species is smaller than for the Co³⁵Cl₂ value determined from

Band 3. The ratio of the two values (0.9727) confirms our assignments.

The evidence from the ground state vibrational and rotational analyses leads to the same conclusion: Only the Co³⁵Cl₂ isotopomer is observed in Band 3, while only the Co³⁵Cl³⁷Cl isotopic form is observed in Band 1.

D. The nature of the perturbation

There is substantial evidence that this system of CoCl₂ is heavily perturbed. The radiative lifetimes suggest that these may be formally forbidden transitions that gain intensity through perturbation by a nearby electronic state (or states). The rotational analyses reveal that the transition involved in Bands 1 and 3 is $\Omega=7/2-7/2$. However, this need not be a spin-allowed transition. These may be intercombination bands involving excitation from the ground $^4\Delta$ state to a sextet or doublet excited state, perturbed by a nearby state of quartet multiplicity. The influence of the perturbing state is clearly observed in the rotationally resolved spectra of Bands 1 and 3; it has a strong J -dependence. The unusual intensity distribution of the bands in this progression, and the anomalously large intensity of Band 3, can be explained through their varying extents of interaction with the perturbing state. In addition, the relatively long fluorescence lifetimes observed for these bands, and the increase in lifetime with increasing ν_1' , are supported by this theory. The apparent absence of any direct manifestation of the perturbing states themselves remains something of a mystery, however.

The mechanism by which the Co³⁵Cl₂ or Co³⁵Cl³⁷Cl isotopomers are favored in the spectrum can only be guessed at. Since the symmetric and asymmetric isotopomers differ in symmetry, the perturbing state may selectively mix with either the excited state wave function of the symmetric isotopomer or that of the asymmetric isotopomer, depending on its symmetry properties. This may be the process by which the asymmetric form is preferentially selected in Band 1. It is also conceivable that both symmetric forms are excited in these experiments, and that the excitations due to Co³⁷Cl₂ are simply too weak to be observed under these experimental conditions. Another possibility is that there is a nearby dissociative state of appropriate symmetry to interact with the asymmetric Co³⁵Cl³⁷Cl isotopomer, which causes the dissociation of this species. These suggestions are all highly speculative; it is especially hard to explain the fact that a single, but different, isotopomer is exclusively present in Bands 1 and 3.

V. CONCLUSION

More work needs to be done before we can hope to understand this band system of CoCl₂ fully. It is essential to improve the sensitivity of the experiment even further to enable more of the weaker bands to be studied at rotational resolution. We hope this will provide more information about the electronic states in this congested system and the interactions between them. Experiments have been carried out to look for other band systems of CoCl₂ at longer wavelengths, but none has been observed out to 420 nm.

This paper reports a study of the electronic spectrum of CoCl_2 around 327 nm at a considerably higher resolution than was achieved previously. Vibrational and rotational structures are observed for the first time. The spectrum is revealed to be extremely complicated with obvious and extensive perturbations. Many aspects are not presently well understood, but a number of our results are unambiguous. The wave number in the symmetric stretching vibration (ν_1) for $\text{Co}^{35}\text{Cl}_2$ in the ground electronic state is determined to be $358.1(17) \text{ cm}^{-1}$. The Ω value for the lowest spin component of the ground electronic state is determined to be $7/2$; this is consistent with an inverted $^4\Delta_g$ ground state.¹⁹ The rotational constant for $\text{Co}^{35}\text{Cl}_2$ in this component is determined to be $0.056\,65(11) \text{ cm}^{-1}$, corresponding to a value for the bond length r_0 of $2.062\,8(40) \text{ \AA}$.

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