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Fourier Transform Spectroscopy of the $A^2\Delta$–$X^2\Pi$ Electronic Transition of the Jet-Cooled CCl Free Radical

Introduction. The $A^2\Delta$–$X^2\Pi$ transition of CCl has been studied in emission by several groups. It was first observed in 1937 in an electric discharge through CCl_4 (*1*). In 1961 the 0–0 and 0–1 vibrational bands of this transition were recorded at high resolution and rotationally analyzed by Gordon and King (*2*) and Verma and Mulliken (*3*). They both concluded that the ground state was a regular $^2\Pi$ state and that the excited state was an inverted $^2\Delta$ state. However, several years later Merer *et al.* (*4*) concluded that the $^2\Delta$ was regular, by observing some of the first lines and from the relative branch intensities.

The matrix isolation infrared spectrum of CCl was reported by Jacox and Milligan (*5*). Quite recently CCl was observed by diode laser spectroscopy by Yamada *et al.* (*6*) and by microwave spectroscopy by Endo *et al.* (*7*). Several ab initio quantum chemical calculations are available for CCl (*8–11*).

In 1983 Melen *et al.* (*12*) published their analysis of emission spectra of the $A^2\Delta$–$X^2\Pi$ 0–0 and 1–0 vibrational bands of CCl with $J_{max} \sim 70.5$. They confirmed that the $^2\Delta$ state was regular. However, due to the high rotational temperature many lines were blended and the low J lines had poor intensity. The spectra proved inadequate to resolve any low J Q_1 and Q_2 lines (Q_{12} and Q_{21} branches were not observed), but Λ-doubling was observed at high J.

Quite recently, rotationally cool CCl (15 K) has been observed using multiphoton ionization from a pulsed supersonic jet (*13*). R_{21}, R_1, and P_1 lines, with an accuracy of approximately 0.05 cm^{-1}, were assigned in the 1–0 and 2–0 bands of the $^2\Delta$–$^2\Pi$ electronic system.

The CCl radical is a component of the plasma produced when CCl_4 is discharged. This plasma is utilized in the etching of Si, Al, GaAs, GaP, and InP in the semiconductor industry (*14*). Gottscho *et al.* (*14*) have used laser-induced fluorescence of the $A^2\Delta$–$X^2\Pi$ transition as an optical diagnostic of the plasma etching process and have measured the radiative lifetime of the $A^2\Delta$ state.

Presented here is the rotationally cool (30 K) spectrum of the 0–0 vibrational band of the $A^2\Delta$–$X^2\Pi$ electronic transition. The spectrum was recorded in emission at high resolution (accuracy of 0.004 cm^{-1} for the strongest lines) using the Fourier transform spectrometer associated with the McMath Solar Telescope. The first rotational lines of the six strongest branches (P_1, Q_1, R_1, P_2, Q_2, and R_2) were observed. Transitions in three other branches were also detected (R_{12}, Q_{21}, and R_{21}), and Λ-doubling was detected in the $^2\Pi_{1/2}$ component of the ground state.

Experimental details. The CCl radicals were observed during an unsuccessful attempt to make ultracold CCl_2 radicals. CCl radicals were produced in a corona discharge through a supersonic expansion of CCl_4 seeded in helium. This technique has been described in detail by Droege and Engelking (*15*) and Engelking (*16*). Briefly, a tungsten electrode was positioned near (200 microns) the tip of a glass nozzle of about 150 microns diameter. A mixture of several Torr of CCl_4 seeded in three atmospheres of helium was expanded through the nozzle into a vacuum chamber. A high voltage (36 kV) was applied between the tungsten electrode and the vacuum chamber through a series of load resistors (17 MΩ). These conditions produced rotationally cool but electronically excited CCl radicals. The resulting fluorescence was detected with the Fourier transform spectrometer associated with the National Solar Observatory of the National Optical Astronomy Observatory at Kitt Peak. The unapodized resolution was set at 0.05 cm^{-1}. The spectral range was limited to 30 000–38 000 cm^{-1} by a band-pass filter.

Two separate scans were recorded using different nozzle diameters. In the first spectrum eight scans were coadded in 40 min of integration. The rotational temperature was determined to be ~20 K. In the second spectrum four scans were coadded in 20 min of integration. The rotational temperature of this scan was found to be ~30 K. The helium atomic line at 31 361.075 ± 0.003 cm^{-1} was used to provide the absolute calibration of our spectra. The wavenumber of this line was measured from two hollow cathode emission spectra (He/Ti and Ar/Ti) as described previously (*17*). A Doppler shift of 0.022 cm^{-1}, due to the trajectory

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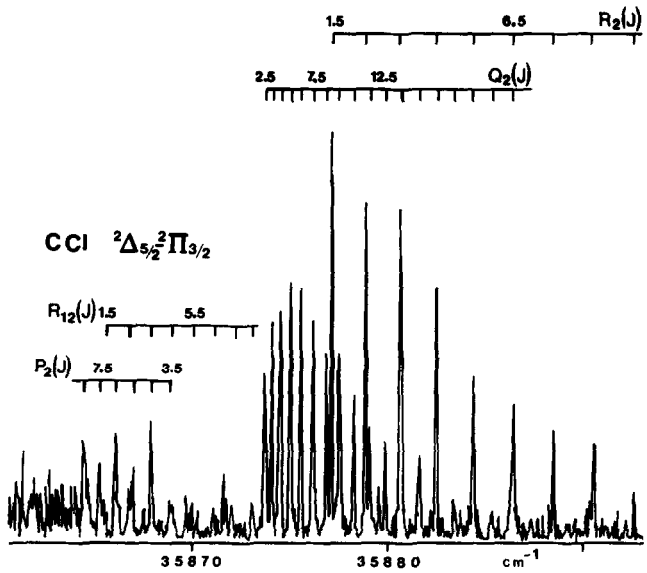

FIG. 1. Fourier transform emission spectrum of the $A^2\Delta_{5/2}$–$X^2\Pi_{3/2}$ transition of CCl.

of the supersonic jet, was observed between the two CCl scans. The main difficulty with the radical source was finding and maintaining stable operating conditions.

Results and discussion. The interferograms were transformed by G. Ladd of the National Solar Observatory. The linewidth of the CCl emission features was about 0.11 cm^{-1} (FWHM). The line positions were determined with the aid of a data reduction program called DECOMP developed at Kitt Peak. A Voigt lineshape function was fit to the CCl lines in a nonlinear least-squares procedure. The peak position of lines with a

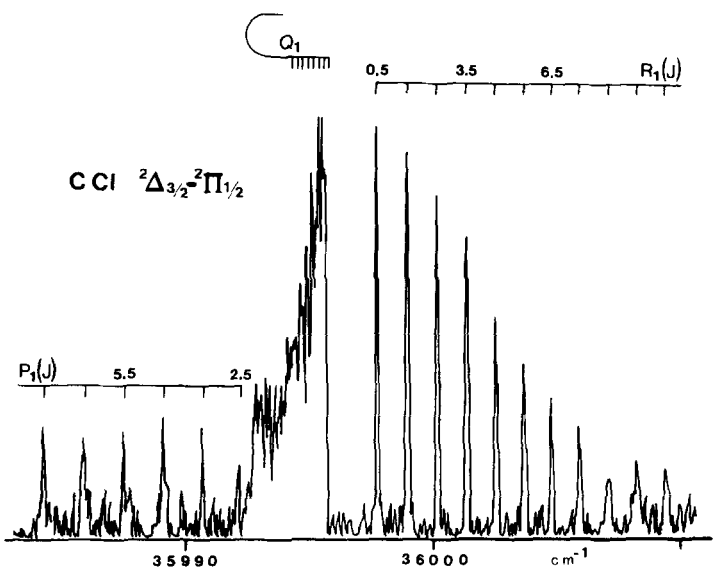

FIG. 2. Fourier transform emission spectrum of the $A^2\Delta_{3/2}$–$X^2\Pi_{1/2}$ transition of CCl.

TABLE I

Observed Line Positions in the 0–0 Band of the $A^2\Delta$–$X^2\Pi$ Transition of CCl (cm^{-1})

J	$P_1(J)$	O-C	$Q_1(J)$	O-C	$R_1(J)$	O-C
0.5					35 997.681	0.011
1.5			35 995.592	-0.008	35 998.919	0.002
2.5	35 992.143	-0.008	35 995.467	-0.000	36 000.123	0.000
3.5	35 990.633	-0.005	35 995.309	0.014	36 001.293	-0.004
4.5	35 989.072	-0.013	35 995.088	-0.002	36 002.445	-0.006
5.5	35 987.459	-0.005[a]	35 994.870	0.005	36 003.564[a]	0.010
	35 987.515	-0.025			36 003.619	-0.011
6.5	35 985.848	-0.005	35 994.581	-0.001[b]	36 004.681	-0.002
	35 985.925	-0.018	35 994.672	-0.000	36 004.774	0.000
7.5	35 984.216	-0.015	35 994.326	-0.007	36 005.823	0.006
	35 984.330	-0.003	35 994.436	0.000	36 005.918	-0.000
8.5	35 982.625	0.020	35 994.085	-0.002	36 006.935	-0.020
	35 982.737	0.017	35 994.212	0.009	36 007.066	-0.004
9.5	35 980.980	0.000	35 993.844	-0.004	36 008.120	0.013
	35 981.110	0.002	35 993.971	-0.004	36 008.225	-0.008
10.5	35 979.378	0.015			36 009.284	0.012
	35 979.519	0.015			36 009.371	-0.040
11.5	35 977.744	-0.015			36 010.474	0.019
	35 977.915	0.002			36 010.577	-0.029
12.5	35 976.167	-0.003				
	35 976.338	0.002				
13.5	35 974.610	0.009				
	35 974.780	0.002				
14.5	35 973.056	0.004				
	35 973.252	0.010				
15.5	35 971.527	0.001				
	35 971.735	0.006				
16.5	35 970.028	0.004				
	35 970.227	-0.011				

J	$P_2(J)$	O-C	$Q_2(J)$	O-C	$R_2(J)$	O-C
1.5					35 877.014	0.003
2.5			35 873.521	-0.006	35 878.756	-0.001
3.5	35 868.670	0.019	35 873.889	0.007	35 880.583	-0.004
4.5	35 867.615	0.003	35 874.322	0.004	35 882.475	-0.013
5.5	35 866.646	-0.009	35 874.837	0.010	35 884.442	-0.012
6.5	35 865.764	-0.007	35 875.405	0.005	35 886.483	0.007
7.5	35 864.172	-0.017	35 876.024	-0.004	35 888.565	0.018
8.5	35 863.464	-0.012	35 876.708	0.001	35 890.682	0.021
9.5	35 862.794	-0.013	35 877.432	0.002	35 892.824	0.009
10.5	35 862.174	-0.005	35 878.184	-0.008	35 895.018	0.014
11.5	35 861.577	-0.010	35 878.993	0.002	35 897.237	0.010
12.5	35 861.021	-0.009	35 879.806	-0.016	35 899.493	0.013
13.5	35 860.479	-0.025	35 880.712	0.025	35 901.775	0.013
14.5	35 860.021	0.011	35 881.574	-0.005	35 904.086	0.015
15.5	35 859.084	-0.019	35 883.448	-0.000	35 906.411	0.005
16.5			35 885.394	-0.024	35 908.781	0.015
17.5			35 887.454	-0.031	35 911.152	0.003
18.5			35 889.611	-0.033	35 913.568	0.012
19.5			35 891.860	-0.031	35 915.989	0.003
20.5					35 918.509	0.071

J	$R_{12}(J)$	O-C	$R_{21}(J)$	O-C	$Q_{21}(J)$	O-C
2.5	35 866.509	0.055	36 012.504	0.096		
3.5	35 867.610	0.028	36 014.366	0.087		
4.5	35 868.686	0.012	36 016.324	0.087		
5.5	35 869.724	-0.014	36 018.275	0.004		
6.5	35 870.824	0.037				
7.5	35 871.817	-0.004			36 010.070	0.046
8.5	35 872.882	0.032			36 010.791	-0.020

[a] Upper (lower) number for each J corresponds to the f-f (e-e) transition.
[b] Upper (lower) number for each J corresponds to the e-f (f-e) transition where e and f are defined by J.M. Brown et al. J. Mol. Spectrosc. 55, 500-503 (1975).

signal-to-noise ratio less than ~2 were determined by eye. The absolute accuracy and relative precision of strong unblended lines is estimated to be ±0.004 cm^{-1}.

The $X^2\Pi$ ground state has a large positive spin–orbit coupling constant ($A \sim 135$ cm^{-1}). Thus it follows Hund's case (a) coupling and there are two distinct spin–orbit components $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ with the $^2\Pi_{1/2}$ component lowest in energy.

The $A^2\Delta$ excited state has a relatively small spin–orbit coupling constant ($A \sim 7.0$ cm^{-1}). Since the rotational constant, B, is ~0.7 cm^{-1} this state will exhibit Hund's case (a) coupling only for the first few rotational lines. For a Hund's case (a) to case (a) transition, $\Delta\Omega = \Delta\Lambda = 1$ for $^2\Delta$–$^2\Pi$. Thus the strongest transitions are the $^2\Delta_{5/2}$–$^2\Pi_{3/2}$ and the $^2\Delta_{3/2}$–$^2\Pi_{1/2}$ transitions, shown in Figs. 1 and 2. The first lines of all six main branches (P_1, Q_1, R_1, P_2, Q_2, and R_2) were observed in the spectra making the J rotational assignment trivial.

At higher J the cross transitions between spin components become fully allowed as the case (a) $|^2\Delta_{5/2}\rangle$ and $|^2\Delta_{3/2}\rangle$ basis functions become mixed by spin uncoupling. Several R_{12}, Q_{21}, and R_{21} lines were detected and were included in the fit. These lines allowed the spin–orbit coupling constants for both the $A^2\Delta$ and $X^2\Pi$ states to be determined.

Λ-doubling was observed only in the $^2\Pi_{1/2}$ component so only one Λ-doubling parameter, p, could be determined. The other Λ-doubling parameter, q, was set to the value obtained from the combined fit of the infrared and microwave data (*7*).

The observed CCl transition wavenumbers used in the fit are listed in Table I. The standard effective $^2\Pi$ and $^2\Delta$ Hamiltonians of Brown *et al.* (*18*) were used to extract the molecular constants in Table II. An explicit listing of the matrix elements of this Hamiltonian evaluated with Hund's case (a) basis functions is available in the literature (Ref. (*19*) for $^2\Pi$, Ref. (*20*) for $^2\Delta$). The fit required eight parameters to achieve a standard deviation of 0.005 cm^{-1}, comparable to the estimated precision of the measurements. In the final fit the parameters D_0, A_D ($=2A_J$) and q_0 of the $X^2\Pi$ state were fixed to the values determined by Endo *et al.* (*7*).

The $C^{37}Cl$ isotope structure was only resolved for the R_2 branch. Calculation of the vibrational and rotational isotope effects show that $C^{37}Cl$ contributes to line broadening in the other branches.

The B_0 and p_0 constants of the $X^2\Pi$ state (Table II) are in reasonable agreement with the more accurate values of Endo *et al.* ((*7*), $B_0 = 0.6937190(13)$ cm^{-1}, $p_0 = 0.01339914(83)$ cm^{-1}). The molecular constants for the $v = 0$ level of the $A^2\Delta$ state agree with the "solution 1" of Melen *et al.* (*12*). Note that the Hamiltonian used in our work differs from the Hamiltonians employed in Refs. (*7, 12*).

Conclusion. The free radical source developed by Engelking and co-workers (*15, 16*) can be combined with a high-resolution Fourier transform spectrometer. The ultracold emission spectrum of the 0–0 band of the $A^2\Delta$–$X^2\Pi$ transition of CCl was recorded with the McMath Fourier transform spectrometer. The rotational cooling achieved in the source reduced the spectral congestion and allowed the first lines of the

TABLE II

The Moleculear Constants for the 0–0 Band of the $A^2\Delta$–$X^2\Pi$ Transition of CCl (cm^{-1})

Constant	$X^2\Pi$	$A^2\Delta$
T_0	0.0	35934.3812(14)
A_0	135.000(17)[a]	7.0636(87)
A_{D0}	-0.309885×10^{-3} [b]	$-0.414(58) \times 10^{-3}$
B_0	0.693266(92)	0.70615(10)
D_0	0.1758×10^{-5} [b]	$0.1739(72) \times 10^{-5}$
q_0	0.39227×10^{-4} [b]	-
p_0	0.01277(38)	-

[a] One standard deviation uncertainty.
[b] Fixed to the value in Ref. 7.

band to be resolved. The combination of a free radical jet source and a Fourier transform spectrometer promises to be a very powerful tool in unraveling complex polyatomic emission spectra.

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REFERENCES

1. R. K. ASUNDI AND S. M. KARIM, *Proc. Indian Acad. Sci. Sect. A* **6,** *328–333 (1937).*
2. R. D. GORDON AND G. W. KING, *Canad. J. Phys.* **39,** 252–262 (1961).
3. R. D. VERMA AND R. S. MULLIKEN, *J. Mol. Spectrosc.* **6,** 419–437 (1961).
4. A. J. MERER, D. N. TRAVIS, AND J. K. G. WATSON, *Canad. J. Phys.* **44,** 447 (1966).
5. M. E. JACOX AND D. E. MILLIGAN, *J. Chem. Phys.* **53,** 2688–2701 (1970).
6. C. YAMADA, K. NAGAI, AND E. HIROTA, *J. Mol. Spectrosc.* **85,** 416–426 (1981).
7. Y. ENDO, S. SAITO, AND E. HIROTA, *J. Mol. Spectrosc.* **94,** 199–207 (1982).
8. B. A. HESS AND R. J. BUENKER, *Chem. Phys.* **101,** 211–218 (1986).
9. L. G. M. PETTERSSON AND P. E. M. SIEGBAHN, *J. Chem. Phys.* **83,** 3538–3546 (1985).
10. S. P. KARNA AND F. GREIN, *Int. J. Quantum Chem.* **29,** 755–766 (1986).
11. M. LARSSON, M. R. A. BLOMBERG, AND P. E. M. SIEGBAHN, *Mol. Phys.* **46,** 365–382 (1982).
12. F. MELEN, Y. HOUBRECHTS, I. DUBOIS, AND H. BREDOHL, *J. Phys. B* **16,** 2523–2530 (1983).
13. S. W. SHARPE AND P. M. JOHNSON, *J. Mol. Spectrosc.* **116,** 247–250 (1986).
14. R. A. GOTTSCHO, R. H. BURTON, AND G. P. DAVIS, *J. Chem. Phys.* **77,** 5298–5301 (1982).
15. A. T. DROEGE AND P. C. ENGELKING, *Chem. Phys. Lett.* **96,** 316–318 (1983).
16. P. C. ENGELKING, *Rev. Sci. Instrum.* **57,** 2274–2277 (1986).
17. C. R. BRAZIER, R. S. RAM, AND P. F. BERNATH, *J. Mol. Spectrosc.* **120,** 381–402 (1986).
18. J. M. BROWN, E. A. COLBOURN, J. K. G. WATSON, AND F. D. WAYNE, *J. Mol. Spectrosc.* **74,** 294–318 (1979).
19. C. AMIOT, J. P. MAILLARD, AND J. CHAUVILLE, *J. Mol. Spectrosc.* **87,** 196–218 (1981).
20. C. R. BRAZIER AND J. M. BROWN, *Canad. J. Phys.* **62,** 1563–1578 (1984).

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