

High-Resolution Fourier Transform Emission Spectroscopy of the $A^6\Sigma^+ - X^6\Sigma^+$ System of CrD

R. S. RAM AND P. F. BERNATH*

*Department of Chemistry, University of Arizona, Tucson, Arizona 85721; and *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

The CrD molecule has been investigated at high resolution in the 700 nm–1 μm spectral region using a Fourier transform spectrometer. The CrD molecules were formed in a chromium hollow cathode lamp operated with neon gas and a trace of deuterium. Compared with the previous work on this molecule the present spectra provide greatly improved measurements of line positions and allow the analysis of several new bands. The rotational analysis of the 0–1, 0–0, 1–0, and 1–2 bands has been performed providing the following principal molecular constants for the ground $X^6\Sigma^+$ state:

$$\omega_e = 1183.1958(21) \text{ cm}^{-1}, \omega_e x_e = 15.6006(9) \text{ cm}^{-1},$$

$$B_e = 3.175443(21) \text{ cm}^{-1}, \text{ and } r_e = 1.654730(5) \text{ \AA}.$$

The excited $A^6\Sigma^+$ state, with principal constants $T_{00} = 11559.7206(6) \text{ cm}^{-1}$, $\Delta G(\frac{1}{2}) = 1066.4202(10) \text{ cm}^{-1}$, $B_e = 2.762705(13) \text{ cm}^{-1}$, and $r_e = 1.774034(4) \text{ \AA}$, is involved in several perturbations. The observed perturbations in the $v = 0$ and $v = 1$ vibrational levels are similar to those observed previously in the $v = 0$ vibrational level of the $A^6\Sigma^+$ state of CrH. These perturbations arise from interactions with a nearby $a^4\Sigma^+$ state with preliminary molecular constants: $T_{00} = 11\,176 \text{ cm}^{-1}$, $B_e = 3.19 \text{ cm}^{-1}$. This state located below the $A^6\Sigma^+$ state and is the lowest excited state of this molecule, supporting the conclusions of our previous work on CrH. © 1995

Academic Press, Inc.

INTRODUCTION

CrH is one of the best-characterized molecules of the 3d transition metal hydride family. This molecule has been known since 1937 when Gaydon and Pearse (1) first observed a complex band at 368 nm. The extensive work on CrH has been reviewed in our previous paper (2). Much less work is available for CrD and the only rotational analysis carried out so far is the 0–0 band of the $A^6\Sigma^+ - X^6\Sigma^+$ system (3).

Part of the interest in CrH arises because it is of astrophysical importance (4). This molecule has been identified in the spectra of the sun (5) and cool stars in general (6).

Recently we published an analysis of the high-resolution spectra of the 0–0 band of the $A^6\Sigma^+ - X^6\Sigma^+$ transition of CrH (2) by Fourier transform emission spectroscopy of a hollow cathode lamp. In this work we have corrected several misassignments in the F_1 and F_6 spin components in the previous analysis (7). From the analysis of the observed perturbations in the excited state we have assigned the perturbing electronic state as a $^4\Sigma^+$ state which lies below the $A^6\Sigma^+$ state. In the present work we provide an analysis of the 0–1, 0–0, 1–0, and 1–2 bands of the analogous transition of CrD. The results in this work are consistent with the previous results obtained for CrH.

There are several ab initio calculations on CrH, predicting the dissociation energy and other molecular properties of ground $X^6\Sigma^+$ state (8–10). In general the experimental and theoretical values are in good agreement. Very recently Dai and Balasu-

bramanian (11) completed a CAS-MCSCF calculation followed by second-order CI (SOC1) on the low-lying states of CrH. Their results are, in general, in good accord with our observations on CrH and CrD.

EXPERIMENTAL DETAILS

The spectrum of CrD molecule was observed in a chromium hollow cathode lamp. The cathode was prepared by inserting a 1-mm thick cylindrical foil of chromium metal into a hole in a copper block. The foil was tightly pressed against the inner wall of the cathode to provide a close and uniform contact between the metal and the copper. The lamp was operated at 300 V and 310 mA current, and a steady flow of 2.0 Torr Ne and about 100 mTorr of D₂ was maintained through the lamp during the experiment.

The spectra were recorded using the 1-m Fourier transform spectrometer associated with the McMath Solar Telescope of the National Solar Observatory. The spectrometer was operated with a red pass filter (OG-570) and photodiode detectors. The use of OG-570 filters and Si-diode detectors limited the observed spectral region to the 10 000–17 500 cm⁻¹ interval. A total of five scans were coadded in approximately 40 min of integration at a resolution of 0.02 cm⁻¹.

The spectral line positions were extracted from the observed spectra using a data reduction program called PC-DECOMP developed by Brault. The peak positions were determined by fitting a Voigt lineshape function to each spectral feature. Cr has four naturally occurring isotopes ⁵⁰Cr (4.8%), ⁵²Cr (83.8%), ⁵³Cr (9.5%), and ⁵⁴Cr (2.4%), of which ⁵²Cr is the most abundant. The data reported in this paper are for the most abundant ⁵²CrD isotopomer.

In addition to the CrD bands, the final spectra also contained Cr and Ne atomic lines. The spectra were calibrated using the measurements of Ne atomic lines made by Palmer and Engleman (12). The absolute accuracy of the wavenumber scale is expected to be better than ±0.001 cm⁻¹. The CrD lines have a typical width of about 0.045 cm⁻¹ and appear with a maximum signal-to-noise ratio of about 30. Therefore the precision of our measurements of the line positions of the strong and unblended lines is expected to be better than ±0.001 cm⁻¹. The 0–1 and 1–0 bands are much weaker in intensity than the 0–0 band. There are many strong Cr atomic lines present which frequently overlap the relatively weaker molecular lines. This, as well as blending caused by the unassigned 2–3 and 2–1 bands of CrD, limits the precision of measurement of the blended and weaker lines to ±0.003 cm⁻¹.

OBSERVATION AND ANALYSIS

The spectrum of CrD is much stronger than the spectrum of CrH (2) and consists of $\Delta v = -1, 0,$ and 1 sequence bands. The intensities of the 1–2, 1–1, and 2–1 bands are much weaker than the corresponding first members (0–1, 0–0, and 1–0) of each sequence. In the present work we have obtained a rotational analysis of the 0–1, 0–0, 1–0, and 1–2 bands.

The analysis of the 0–0 band of this molecule has earlier been reported by O'Connor (3), using data obtained with a grating spectrometer. He observed perturbations in two regions, one at $N = 18$ and the other at $N = 32$ or 33 . The $N = 18$ perturbation was observed in the $F_1, F_2,$ and F_3 spin components but the higher N perturbation was not assigned in detail. The very weak intensity of the high J lines coupled with the sharp fall in the plate sensitivity toward the infrared prevented him from definitely assigning the rotational lines in the higher N perturbation region.

As expected for a ${}^6\Sigma^+ - {}^6\Sigma^+$ transition, each band of this transition consists of six R and six P branches. The lines of each branch were picked out using an interactive color Loomis-Wood program running on a 486/33 microcomputer. The assignments of the rotational lines of the new bands were made by comparing the combination differences for the common vibrational levels.

A part of the spectrum of the 0-0 band near the R heads is presented in Fig. 1. As observed in the case of CrH (2) our spectra show that the $A^6\Sigma^+$ ($v = 0$) level is perturbed in two regions. A local perturbation observed at $N = 18$ affects the F_1 , F_2 , and F_3 spin components of the excited state. To higher N a strong perturbation has been observed at $N = 30$ of the excited state which affects the F_2 , F_3 , F_4 , and F_5 spin components. The F_6 spin component is not perturbed. These perturbations arise from interactions between the $A^6\Sigma^+$ state and a nearby ${}^4\Sigma^+$ state as has been observed in the case of CrH (2). The 0-1 band has a structure similar to the 0-0 band. In some of the branches of this band the rotational lines could not be identified in the perturbed regions because of their very weak intensity.

On the higher wavenumber side of the 0-0 band, a band at $12\,652\text{ cm}^{-1}$ with about 30% of the intensity of the 0-0 band has been identified as the 1-0 band. The analysis of this band shows that the excited state $A^6\Sigma^+$ ($v = 1$) vibrational level is also perturbed in two regions. The lower N perturbation is observed at $N = 13$ and affects the F_1 , F_2 , and F_3 spin components while the higher N perturbation observed at $N = 24$ affects the F_2 , F_3 , F_4 , and F_5 spin components. Again, the F_6 spin component is not perturbed. The rotational analysis of the 1-2 band confirms the excited state vibrational and rotational assignments.

The observed wavenumbers were fitted with the usual N^2 Hamiltonian for a ${}^6\Sigma$ state, as given by Brown and Milton (13). An explicit listing of most of the necessary matrix elements is given by Gordon and Merer (14). The complete Hamiltonian

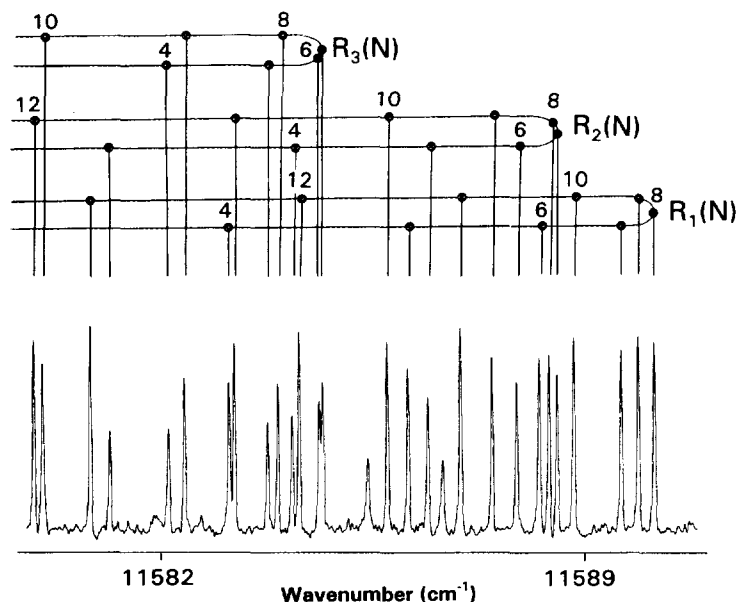


FIG. 1. A portion of the spectrum of CrD near the R_1 , R_2 , and R_3 heads of the 0-0 band of the $A^6\Sigma^+ - X^6\Sigma^+$ transition.

TABLE I

Observed Transition Wavenumbers (in cm^{-1}) of the 0-0 Band of the $A^6\Sigma^+ - X^6\Sigma^+$ System of CrD

N	R1	O-C	P1	O-C	R2	O-C	P2	O-C	R3	O-C	P3	O-C
0	11563.255	2										
1	11569.447	-0	11550.687	2								
2	11574.798	-2	11544.671	-0	11577.376	6						
3	11579.353	-2	11538.092	-3	11581.137	3	11541.785	3	11579.696	-1	11541.083	0
4	11583.108	-2	11530.819	-1	11584.151	0	11533.547	5	11582.105	3	11532.455	1
5	11586.066	0	11522.800	-2	11586.392	-2	11524.702	4	11583.745	0	11523.127	0
6	11588.219	3	11514.022	-0	11587.848	-4	11515.155	-3	11584.598	-1	11513.052	-0
7	11589.567	5	11504.473	-0	11588.513	-4	11504.885	-1	11584.657	0	11502.212	-5
8	11590.111	9	11494.154	2	11588.379	-6	11493.862	-3	11583.914	2	11490.613	-1
9	11589.850	12	11483.067	5	11587.449	-6	11482.087	-2	11582.371	5	11478.243	1
10	11588.787	18	11471.212	8	11585.722	-4	11469.552	-4	11580.025	7	11465.107	1
11	11586.925	25	11458.597	13	11583.197	-2	11456.264	-2	11576.882	11	11451.210	3
12	11584.266	34	11445.226	19	11579.880	1	11442.220	-7	11572.940	13	11436.558	6
13	11580.816	46	11431.104	25	11575.773	7	11427.439	-1	11568.214	24	11421.158	11
14	11576.583	67	11416.241	34	11570.882	18	11411.916	2	11562.700	35	11405.016	16
15	11571.581	105	11400.646	48	11565.219	40	11395.662	9	11556.403	48	11388.141	23
16	11565.867	213	11384.327	67	11558.812	97	11378.686	19	11549.337	72	11370.541	33
17	11557.428	-1630	11367.309	107	11552.120	643	11361.004	41	11541.554	152	11352.229	48
18			11349.654	221	11543.260	-213	11342.650	99	11532.735	-37	11333.216	72
19	11543.469	-93	11329.335	-1629	11534.610	-96	11324.087	647	11523.434	52	11313.562	153
20	11534.610	-66	11311.617	-186	11525.117	-70	11303.429	-212	11513.330	91	11292.949	-35
21	11525.003	-40	11291.871	-90	11514.876	-46	11283.058	-104	11502.481	131	11271.937	55
22	11514.640	-29	11271.395	-55	11503.889	-29	11261.949	-67	11490.901	177	11250.203	90
23	11503.542	-22	11250.237	-44	11492.174	-11	11240.170	-45	11478.611	241	11227.823	134
24	11491.717	-18	11228.440	-25	11479.761	28	11217.745	-25	11465.625	329	11204.802	182
25	11479.182	-12	11205.999	-17	11466.646	78	11194.692	0	11451.977	464	11181.166	244
26	11465.941	-8	11182.933	-12	11452.868	164	11171.028	32	11437.712	682	11156.937	332
27	11452.011	-0	11159.259	-7	11438.502	353	11146.776	83	11422.995	1137	11132.146	462
28	11437.387	-5	11134.986	-5	11423.882	967	11121.968	169	11408.591	2584	11106.855	684
29	11422.098	-1	11110.134	-2	11403.823	-3188	11096.681	354	11384.946	-4543	11081.221	1141
30	11406.150	1	11084.714	0	11389.444	-1009	11071.258	967	11370.642	-1674	11056.013	2586
31	11389.552	1	11058.740	1	11372.590	-659	11040.517	-3187	11353.506	-994	11021.683	-4542
32	11372.322	5	11032.229	1	11354.888	-526	11015.576	-1008	11335.361	-693	10996.815	-1676
33	11354.463	-0	11005.195	1	11336.498	-463	10988.284	-661	11316.470	-520	10969.245	-995
34	11336.003	5	10977.653	-1	11317.478	-424	10960.272	-532	11296.924	-399	10940.788	-698
35	11316.941	1	10949.627	3	11297.850	-403	10931.707	-469			10911.725	-522
36	11297.305	4	10921.119	-1	11277.641	-385	10902.648	-429	11256.004	-230	10882.134	-405
37	11277.097	2	10892.156	-3	11256.859	-377	10873.116	-408	11234.674	-167	10852.063	-316
38	11256.338	0	10862.758	-0	11235.525	-375	10843.145	-390	11212.796	-107	10821.544	-241
39	11235.046	0	10832.932	-3	11213.666	-365	10812.732	-395	11190.381	-55	10790.596	-178
40	11213.233	-0	10802.708	3	11191.274	-372	10781.938	-380	11167.467	11	10759.251	-112
41	11190.917	-0	10772.087	-3	11168.389	-374	10750.753	-374			10727.519	-53
42	11168.104	-10	10741.106	1	11145.012	-385					10695.424	5
43	11144.834	-6	10709.787	17							10662.990	67
44			10678.116	11							10630.216	112
45			10646.129	1							10597.107	127
46			10613.872	14							10563.791	217
47			10581.321	4							10530.259	354
48			10548.538	13							10496.325	330

matrix including some additional matrix elements such as those for H , L , γ_H , and γ_L are provided in our previous paper on CrH (2). The presence of perturbations affecting most of the branches does not allow the determination of molecular parameters from a free fit. To avoid the effects of the perturbation in the final fit we included only the unperturbed transition wavenumbers and the ground state combination differences corresponding to the perturbed transitions. The perturbed transitions were excluded from the final fit. The observed transition wavenumbers of the 0-0, 0-1, 1-0, and 1-2 bands are listed in Tables I, II, III, and IV, respectively. The observation of high N transitions (up to $N = 48$ in the 0-0 band and $N = 35$ in the 1-0 band) provides high N ground state combination differences which enable us to determine a very precise set of molecular constants in the ground state. In the final fit the molecular parameters B , D , H , γ , γ_D , γ_S , λ , λ_D , and θ for the ground state and T_0 , B , D , H ,

TABLE I—Continued

N	R4	O-C	P4	O-C	R5	O-C	P5	O-C	R6	O-C	P6	O-C
3	11575.205	-2										
4	11577.296	0	11527.558	-1	11570.693	5						
5	11578.508	0	11518.447	-2	11571.498	4			11563.894	-6		
6	11578.873	2	11508.157	2	11571.378	6	11501.539	3	11563.079	-8	11494.803	-8
7			11496.936	1	11570.381	6	11489.933	5			11482.451	4
8			11484.867	-0	11568.535	6	11477.389	3	11558.915	-1	11469.188	-6
9	11574.998	0	11471.986	-1	11565.867	14	11463.987	3	11555.591	0	11455.106	-4
10	11572.075	-2	11458.310	-2	11562.359	3	11449.766	3			11440.220	-4
11	11568.348	-3	11443.854	-3	11558.049	2	11434.747	1	11546.517	3	11424.552	-2
12	11563.817	-6	11428.634	-2	11552.937	2	11418.947	-4	11540.777	1	11408.112	-3
13	11558.497	-4	11412.652	-4	11547.024	-0	11402.390	-2	11534.248	4	11390.920	-1
14	11552.384	-4	11395.922	-6	11540.322	-1	11385.078	-2	11526.931	3	11372.981	0
15	11545.488	-4	11378.456	-6	11532.836	-2	11367.024	-4	11518.835	3	11354.308	2
16	11537.814	-3	11360.262	-5	11524.573	-1	11348.242	-3	11509.965	3	11334.909	2
17	11529.370	0	11341.351	-4	11515.541	1	11328.741	-3	11500.328	1	11314.799	5
18	11520.167	8	11321.734	0	11505.749	6	11308.534	-2	11489.933	-1	11293.982	3
19	11510.206	16 *	11301.418	1	11495.205	15	11287.632	2	11478.787	-2	11272.477	5
20	11499.503	31 *			11483.917	28 *	11266.048	9	11466.898	-2	11250.284	1
21	11488.066	53 *	11258.750	19 *	11471.896	47 *	11243.792	17	11454.275	-2	11227.429	2
22	11475.914	94 *	11236.422	35 *	11459.169	91 *	11220.880	32 *	11440.926	-2	11203.909	-3
23	11463.049	145 *	11213.451	59 *	11445.714	128 *	11197.326	54 *	11426.857	-5	11179.754	2
24	11449.503	230 *	11189.852	94 *	11431.585	203 *	11173.143	84 *	11412.085	-4	11154.961	1
25	11435.311	373 *	11165.647	151 *	11416.802	326 *	11148.356	133 *	11396.615	-4	11129.551	2
26	11420.545	636 *	11140.857	235 *	11401.420	542 *	11122.983	208 *	11380.453	-9	11103.532	1
27			11115.526	378 *			11097.059	329 *	11363.626	-4	11076.923	0
28	11389.918	2107 *	11089.730	642 *	11370.028	2375 *	11070.651	548 *	11346.129	-4	11049.734	-0
29	11364.646	-6119 *	11063.669	1211 *	11343.774	-6274 *	11043.910	1004 *	11327.985	1	11021.983	-1
30	11350.336	-2735 *			11329.335	-2462 *	11017.536	2381 *	11309.196	1	10993.686	2
31	11332.858	-1883 *	11001.425	-6115 *	11311.303	-1611 *	10980.599	-6267 *	11289.780	2	10964.850	0
32	11314.250	-1538 *	10976.551	-2733 *	11292.139	-1271 *	10955.591	-2462 *	11269.751	4	10935.497	-1
33	11294.862	-1364 *	10948.638	-1880 *	11272.209	-1091 *	10927.127	-1605 *	11249.119	5	10905.644	-0
34	11274.801	-1266 *	10919.722	-1535 *	11251.608	-990 *	10897.653	-1267 *	11227.901	6	10875.303	-1
35	11254.112	-1215 *	10890.156	-1363 *	11230.398	-918 *	10867.539	-1095 *	11206.111	6	10844.494	-0
36	11232.839	-1181 *	10860.051	-1268 *	11208.598	-874 *	10836.897	-992 *	11183.757	1	10813.236	2
37	11210.981	-1181 *	10829.456	-1218 *	11186.228	-851 *	10805.779	-925 *	11160.873	7	10781.535	-3
38	11188.583	-1183 *	10798.415	-1189 *	11163.320	-834 *	10774.215	-881 *	11137.453	5	10749.425	-0
39	11165.599	-1252 *	10766.947	-1179 *	11139.897	-817 *	10742.232	-851 *	11113.525	3	10716.911	-3
40	11142.214	-1218 *	10735.072	-1185 *	11115.961	-812 *	10709.846	-838 *	11089.096	-5	10684.017	-5
41	11118.284	-1242 *	10702.786	-1231 *	11091.544	-806 *	10677.100	-818 *	11064.205	-1	10650.760	-9
42	11093.887	-1264 *	10670.208	-1216 *	11066.659	-803 *	10643.992	-811 *	11038.840	-13	10617.162	-13
43	11069.021	-1303 *	10637.264	-1234 *	11041.349	-780 *	10610.556	-803 *	11013.075	15	10583.258	-0
44	11043.731	-1334 *	10603.996	-1263 *			10576.815	-792 *			10549.038	-2
45	11018.017	-1373 *	10570.435	-1291 *			10542.805	-763 *				
46			10536.673	-1248 *			10508.619	-642 *	10933.244			
47			10502.948	-917 *			10474.169	-540 *	10905.882			
48			10469.039	-538 *								

L , γ , γ_D , γ_H , γ_L , γ_S , γ_{SD} , λ , λ_D , θ , and θ_D for the excited state were required in order to obtain a satisfactory fit.

RESULTS AND DISCUSSION

The molecular constants obtained for the different vibrational levels of the ground state of CrD are provided in Table V and the corresponding data for the excited state are provided in Table VI. The molecular constants for the different vibrational levels enable us to determine equilibrium constants for the ground and excited states (Tables VII). The equilibrium rotational constants for the ground state of CrD are: $B_e = 3.175443(21) \text{ cm}^{-1}$ and $\alpha_e = 0.065908(23) \text{ cm}^{-1}$ and using the usual isotopic relationships (15), $B_e^i = \rho^2 B_e$ and $\alpha_e^i = \rho^3 \alpha_e$, the B_e and α_e values for CrH were predicted to be 6.227349 and 0.181003 cm^{-1} , respectively. This provides a predicted B_0 value for CrH of 6.136847 cm^{-1} , in good agreement with our experimental value of $6.1317406(19) \text{ cm}^{-1}$ reported earlier (2). Using the ground state vibrational constants

TABLE II

Observed Transition Wavenumbers (in cm^{-1}) of the 0-1 Band of the $A^6\Sigma^+-X^6\Sigma^+$ System of CrD

N	R1	O-C	P1	O-C	R2	O-C	P2	O-C	R3	O-C	P3	O-C
0	10411.253	-2										
1	10417.581	3	10398.812	-3	10421.066	0						
2	10423.190	-5	10393.063	-3	10425.800	10						
3	10428.143	-3	10386.880	-7	10429.950	3	10390.600	4				
4	10432.430	-3			10433.488	-2	10382.873	-9	10431.442	0		
5			10372.791	4	10436.383	-10	10374.698	1	10433.743	-1		
6	10439.001	5	10364.795	-7	10438.651	8	10365.949	-1	10435.379	-11	10363.843	-0
7	10441.270	1	10356.177	-3	10440.229	-4	10356.604	2	10436.383	13	10353.931	1
8	10442.873	4	10346.918	-1	10441.166	9	10346.634	-3	10436.687	7		
9	10443.802	6	10337.018	-3	10441.412	-4			10436.325	4	10332.192	-5
10	10444.062	9	10326.488	-0	10441.004	-4	10324.835	-3			10320.383	3
11	10443.652	11	10315.319	-7	10439.933	-4	10312.996	-7	10433.609	12	10307.935	3
12			10303.536	-3	10438.198	-4	10300.549	-1	10431.253	18		
13	10440.842	19	10291.132	-1	10435.807	-1	10287.469	-13	10428.236	22	10281.167	-4
14					10432.757	-1			10424.561	26	10266.882	11
15	10435.418	47	10264.494	-0	10429.069	13			10420.242	38	10251.980	12
16	10431.832	162	10250.288	12	10424.773	66			10415.281	56	10236.486	17
17									10409.735	130		
18			10220.225	138								

N	R4	O-C	P4	O-C	R5	O-C	P5	O-C	R6	O-C	P6	O-C
3	10423.996	-3										
4	10426.618	-1										
5	10428.499	8										
6	10429.647	0	10358.923	-7			10352.287	-0	10413.820	12		
7	10430.098	-1	10348.632	-1	10422.064	17	10341.593	-8	10413.068	8	10334.086	-3
8	10429.862	2	10337.633	13	10421.265	9	10330.109	-3	10411.602	-6	10321.885	-3
9	10428.934	-1	10325.922	-1	10419.764	-1	10317.892	-3	10409.473	6	10308.983	-3
10	10427.333	1	10313.566	-0	10417.581	-3	10304.996	6	10406.647	1	10295.418	4
11	10425.050	-4	10300.549	-11	10414.722	-1		0	10403.146	-5		
12	10422.113	6	10286.933	14	10411.191	3	10277.209		10398.995	6	10266.331	2
13	10418.495	-1	10272.649	-1	10406.987	-1	10262.356	1	10394.170	3	10250.848	5
14	10414.220	-7	10257.765	-2	10402.124	-5	10246.887	1	10388.694	3	10234.745	2
15	10409.296	-9	10242.271	-4	10396.614	-2	10230.800	-6	10382.547	-19	10218.043	3
16	10403.733	-3	10226.182	-5	10390.454	-2	10214.125	-2	10375.803	3	10200.735	-8
17	10397.522	-5			10383.656	-1	10196.859	-2	10368.392	-5	10182.867	2
18	10390.685	1	10192.249	-11	10376.228	3	10179.019	1	10360.369	1	10164.410	-3
19	10383.223	9	10174.433	-7	10368.199	31	10160.609	1	10351.717	0	10145.400	0
20	10375.147	21	10156.064	0	10359.516	24	10141.649	6	10342.452	-1	10125.837	1
21	10366.467	42	10137.148	5	10350.259	51			10332.582	-2	10105.733	1
22	10357.198	77			10340.404	83	10102.130	38	10322.111	-6	10085.102	1
23	10347.353	131			10330.111	269	10081.585	56	10311.054	-9	10063.954	0
24	10336.953	216			10319.156	377	10060.545	88	10299.431	1		
25	10326.035	360					10039.135	247	10287.239	13		

$\omega_e = 1183.1958 \text{ cm}^{-1}$ and $\omega_e x_e = 15.6006 \text{ cm}^{-1}$ and the isotopic relations, one predicts $\omega_e = 1656.9372 \text{ cm}^{-1}$ and $\omega_e x_e = 30.5943 \text{ cm}^{-1}$ for CrH, which are also in general agreement with $\omega_e = 1656.0515 \text{ cm}^{-1}$ and $\omega_e x_e = 30.4914 \text{ cm}^{-1}$, as reported by Lipus *et al.* (16). The equilibrium rotational constants obtained for the ground and the excited states were used to determine the equilibrium bond lengths in the ground and excited states. The observed equilibrium bond lengths for the ground and excited states are $1.654730(5)$ and 1.774034 \AA which can be compared with the corresponding values of $r_e = 1.655409 \text{ \AA}$ (16) and $r_0 = 1.798420 \text{ \AA}$, respectively, for CrH.

The electronic configurations of different low-lying electronic states have been discussed in detail in our previous paper on CrH (2). The ground $X^6\Sigma^+$ state of this molecule arises from the configuration $(1\sigma)^2(2\sigma)^1(1\delta)^2(1\pi)^2$ which is derived from the combination of a ground state 7S Cr atom with a 2S H atom. This combination also results in an $^8\Sigma^+$ state which is expected to be a repulsive state since it arises by the promotion of a bonding (1σ) electron to an antibonding $(3\sigma^*)$ orbital. The $A^6\Sigma^+$

TABLE III

Observed Transition Wavenumbers (in cm^{-1}) of the 1-0 Band of the $A^6\Sigma^+ - X^6\Sigma^+$ System of CrD

N	R1	O-C	P1	O-C	R2	O-C	P2	O-C	R3	O-C	P3	O-C
0	12629.291	4										
1	12635.263	1										
2	12640.294	1	12610.705	-1	12643.246	2			12642.749	5		
3	12644.425	-0	12603.909	-1	12646.596	2	12607.978	6	12645.393	0	12607.560	0
4	12647.657	-1	12596.314	0	12649.098	1	12599.418	2	12647.286	1	12598.578	4
5	12649.992	1	12587.846	-27			12590.156	-1	12648.340	19	12588.823	1
6	12651.425	4	12578.570	-0	12651.473	-2	12580.104	-1	12648.473	2	12578.238	2
7	12651.950	4	12568.394	-5	12651.325	-5	12569.227	6	12647.727	0	12566.797	3
8	12651.578	11	12557.355	-2	12650.297	9	12557.487	-2	12646.087	6	12554.484	-2
9	12650.297	14	12545.452	6	12648.340	-8	12544.896	-5	12643.533	-2	12541.312	1
10	12648.141	45	12532.679	10	12645.522	13	12531.457	-1	12640.087	-0	12527.271	-3
11	12645.136	126	12519.056	25	12641.821	47	12517.163	3	12635.756	14	12512.374	-1
12	12639.931	-1093	12504.578	44	12637.482	339	12502.024	14	12630.544	44	12496.624	3
13	12635.983	-162	12489.311	122	12631.455	-166	12486.063	49	12624.262	-105	12480.027	9
14	12630.266	-108	12471.907	-1092	12625.124	-85	12469.514	336	12617.319	-26	12462.620	46
15	12623.654	-65	12455.822	-151	12617.856	-58	12451.348	-160	12609.430	-10	12444.205	-89
16	12616.133	-49	12438.036	-83	12609.696	-43	12432.931	-80	12600.658	1	12425.164	-25
17	12607.731	-40	12419.381	-65	12600.658	-33	12413.642	-56	12591.017	16	12405.256	-10
18	12598.462	-29	12399.913	-49	12590.761	-15	12393.535	-40	12580.503	24	12384.542	6
19	12588.325	-24	12379.641	-37	12579.998	-2	12372.628	-26	12569.146	48	12363.021	14
20	12577.336	-16	12358.578	-25	12568.394	23	12350.933	-11	12556.949	84	12340.720	28
21	12565.501	-9	12336.730	-19	12555.936	40	12328.453	-2	12543.940	152	12317.652	54
22	12552.823	-5			12542.671	85	12305.222	22	12530.173	300	12293.829	90
23	12539.321	4	12290.741	-7	12528.736	289	12281.254	64	12516.240	1110	12269.283	157
24	12525.002	15	12266.628	3	12513.205	-285	12256.534	97	12499.024	-543	12244.080	310
25	12509.854	10	12241.785	15	12497.642	-82	12231.246	293	12482.831	-359	12218.784	1102
26	12493.917	15	12216.206	10	12481.105	-55	12204.501	-252	12465.791	-218	12190.320	-555
27	12477.176	6	12189.936	20	12463.807	-2	12177.767	-82	12447.900	-131	12163.011	-348
28	12459.657	-1	12162.952	8	12445.678	-1	12150.217	-39	12429.204	-60	12134.932	-216
29	12441.370	-6			12426.777	-8	12121.973	-13	12409.734	18	12106.126	-127
30	12422.329	-7			12407.137	2	12093.048	-7	12389.497	105	12076.626	-58
31					12386.755	13	12063.481	4	12368.513	214	12046.466	14
32					12365.631	15	12033.266	-0	12346.773	331	12015.674	107
33					12343.787	20	12002.444	6				
34					12321.196	-12						
35					12297.946	1						

N	R4	O-C	P4	O-C	R5	O-C	P5	O-C	R6	O-C	P6	O-C
5			12584.150	-1					12628.139	-5		
6	12642.775	-9	12573.363	4	12635.160	3	12566.569	1	12626.660	-9	12559.598	-11
7	12641.518	-3	12561.544	1	12633.388	7	12554.392	2	12624.239	2	12546.686	-5
8	12639.337	2	12548.784	3	12630.662	5	12541.172	0	12620.866	-2	12532.772	-6
9	12636.231	-1	12535.105	-1	12627.003	5	12526.990	-1	12616.580	3	12517.925	-3
10	12632.214	-4	12520.533	-5	12622.423	2	12511.891	1			12502.172	-4
11	12627.292	-7	12505.088	-3	12616.940	9	12495.885	-7	12605.273	8	12485.541	2
12	12621.476	-3	12488.773	-3	12610.538	1	12479.017	2	12598.262	3	12468.034	0
13	12614.760	-3	12471.597	-6	12603.245	-1	12461.274	-0	12590.360	-1	12449.675	3
14	12607.155	-3	12453.573	-10	12595.063	-3	12442.679	-3	12581.583	5	12430.470	6
15	12598.669	-1	12434.722	-2			12423.246	-3	12571.919	3	12410.421	-2
16	12589.305	3	12415.038	0	12576.091	30	12402.981	-7	12561.379	-4	12389.562	5
17	12579.075	11	12394.536	3	12565.258	8	12381.930	22	12549.970	-14	12367.881	2

N	R4	O-C	P4	O-C	R5	O-C	P5	O-C	R6	O-C	P6	O-C
18	12567.984	21	12373.226	6	12553.596	18	12360.055	33	12537.730	3	12345.402	3
19	12556.048	45	12351.126	16	12541.080	30	12337.352	12	12524.615	-3	12322.114	-13
20	12543.280	87	12328.241	26	12527.739	64	12313.895	21	12510.662	-6	12298.083	6
21	12529.682	140	12304.591	48	12513.607	146	12289.668	32	12495.885	5	12273.257	1
22	12515.548	491	12280.200	92	12498.777	363	12264.708	73	12480.260	-5	12247.673	-6
23			12255.076	155			12239.035	150			12221.350	-6
24			12229.494	500				363	12446.578	-0	12194.293	-4
25									12428.541	20	12166.516	1
26											12138.029	8
27											12108.847	22

TABLE IV

Observed Transition Wavenumbers (in cm^{-1}) of the 1-2 Band of the $A^6\Sigma^+-X^6\Sigma^+$ System of CrD

N	R1	O-C	P1	O-C	R2	O-C	P2	O-C	R3	O-C	P3	O-C
0	10356.505	10										
1	10362.725	-2										
2	10368.287	1	10338.702	4								
3			10332.690	-7	10375.425	3	10336.800	-0				
4	10377.501	-3	10326.156	-3	10378.977	-3	10329.297	-3	10377.164	2		
5	10381.158	-2	10319.040	-2	10381.926	-5	10321.362	1	10379.517	-1	10320.020	1
6	10384.177	1	10311.320	-5	10384.257	-5	10312.888	-4	10381.252	1	10311.021	5
7	10386.556	3	10303.003	-2	10385.960	-4	10303.846	-9	10382.352	-1	10301.422	3
8	10388.299	12 *	10294.078	1	10387.033	-0	10294.231	-3			10291.223	1
9	10389.402	21 *	10284.545	1	10387.474	6	10284.012	-10	10382.647	3	10280.421	0
10	10389.881	46 *	10263.696	23 *	10387.283	15 *	10273.218	1	10381.837	4	10269.017	-2
11	10389.777	125 *	10252.386	41 *	10386.485	50 *	10261.823	2	10380.397	10	10257.021	1
12	10387.740	-1094 *			10385.284	315 *	10249.847	12 *	10378.353	45 *		
13	10387.233	-151 *			10382.711	-162 *	10237.318	50 *	10375.507	-93 *	10231.260	9
14			10226.836	-1094 *	10380.067	-86 *	10224.454	333 *	10372.231	-35 *	10217.537	44 *
15	10382.547	-59 *			10376.744	-65 *	10210.236	-168 *	10368.287	-23 *	10203.067	-97 *
16	10379.235	-51 *			10372.791	-59 *	10196.038	-85 *	10363.731	-8 *	10188.236	-35 *
17	10375.307	-46 *			10368.239	-39 *	10181.217	-68 *	10358.555	-2 *	10172.800	-23 *
18	10370.771	-42 *			10363.068	-33 *	10165.846	-55 *	10352.783	12 *	10156.819	-8 *
19	10365.638	-34 *			10357.306	-19 *	10149.932	-47 *	10346.420	34 *	10140.289	-6 *
20	10359.912	-26 *			10350.951	-4 *	10133.491	-37 *	10339.482	72 *	10123.248	12 *
21	10353.591	-25 *					10116.539	-21 *	10331.977	127 *	10105.690	30 *
22	10346.918	202 *			10336.585	115 *	10099.080	-4 *	10323.990	279 *	10087.646	69 *
23											10069.126	127 *
24											10050.215	279 *

N	R4	O-C	P4	O-C	R5	O-C	P5	O-C	R6	O-C	P6	O-C
4					10365.526	8						
5					10367.075	-1						
6	10375.528	-4	10306.104	-2	10367.862	3	10299.266	-3	10359.309	-11		
7	10376.115	0	10296.139	2	10367.925	-2	10288.937	2	10358.727	1		
8	10376.036	-1	10285.484	2	10367.308	1	10277.821	-2				
9	10375.307	2			10366.023	4	10266.012	1	10355.531	-2	10256.879	-6
10	10373.924	-1	10262.244	-1	10364.075	3	10253.543	2	10352.957	0		
11	10371.901	-2	10249.682	-12	10361.481	5			10349.748	8	10230.008	-6
12	10369.237	-5	10236.539	-1	10358.243	3	10226.716	-2	10345.888	1		
13	10365.949	-0	10222.784	-5	10354.369	1	10212.395	-1			10200.735	21
14	10362.029	-0	10208.449	-4	10349.865	-3	10197.481	-4	10336.305	6		
15			10193.527	-15	10344.741	-6	10181.994	-2	10330.577	-0		
16	10352.321	-8	10178.059	-5			10165.929	-10	10324.241	-3	10152.422	3
17	10346.571	9	10162.025	-4			10149.313	-13	10317.290	-18	10135.205	1
18	10340.206	16 *	10145.446	-2	10325.732	8			10309.774	-2	10117.449	1
19	10333.266	42 *	10128.337	5	10318.211	26 *	10114.479	4	10301.649	-2	10099.146	-15
20			10110.702	15 *	10310.118	59 *	10096.270	11	10292.941	-4	10080.360	6
21			10092.565	36 *			10077.556	28 *				
22							10058.364	69 *			10041.212	-12
23											10020.922	-1

state arises from the $(1\sigma)^1(2\sigma)^2(1\delta)^2(1\pi)^2$ configuration resulting from the promotion of one electron from the (1σ) orbital to the (2σ) orbital. This state is accompanied by a $^4\Sigma^+$ state arising from the same nominal configuration.

The observed perturbations in the excited $A^6\Sigma^+$ state provide significant insight into the nature of the perturbing state. As in CrH (2), the $v = 0$ vibrational level of the $A^6\Sigma^+$ state of CrD is also perturbed in two N regions. The lower N perturbation affects the F_1 , F_2 , and F_3 spin components while the higher N perturbation affects the F_2 , F_3 , F_4 , and F_5 spin components. The F_6 spin component is not involved in any perturbation and the F_1 spin component is not perturbed at higher N . The perturbation in the $v = 1$ vibrational level also follows the same pattern. These results are very similar to the results obtained for CrH (2). These observations confirm that these

TABLE V

Rotational Constants (in cm^{-1}) for the $X^6\Sigma^+$ State of CrD

Constants	v=0	v=1	v=2
T_v	0.0	1151.9947(10)	2272.7883(11)
B_v	3.1424893(63)	3.076592(17)	3.010674(22)
$10^5 \times D_v$	9.08803(71)	9.1147(70)	9.0509(97)
$10^9 \times H_v$	1.5934(23)	2.110(74)	1.94(12)
γ_v	0.026484(68)	0.025232(88)	0.023829(85)
$10^6 \times \gamma_{Dv}$	-1.002(24)	-3.53(19)	-1.58(20)
λ_v	0.23756(42)	0.23094(45)	0.22598(48)
$10^5 \times \lambda_{Dv}$	-0.594(75)	0.51(18)	-1.32(27)
$10^4 \times \gamma_s$	0.723(97)	1.08(11)	0.72(12)

perturbations are caused by a nearby $a^4\Sigma^+$ state. The lower N perturbations are due to a $\Delta N = 2$ interaction and the higher N perturbations are caused by a $\Delta N = 0$ interaction between the rotational levels of the $a^4\Sigma^+$ and $A^6\Sigma^+$ states (see Fig. 3 in Ref. 2). These interactions occur through the microscopic form of the spin-spin operator (17).

As mentioned in our CrH paper (2), the peak at $11\,200\text{ cm}^{-1}$ in the photoelectron spectrum of CrH^- left unassigned by Miller *et al.* (18) can be assigned to $v = 0$ of the $a^4\Sigma^+$ state. This observation is consistent with a $\Delta v = 0$ interaction between the $a^4\Sigma^+$ and $A^6\Sigma^+$ states. The perturbations observed in the $v = 0$ and $v = 1$ vibrational levels have been used to estimate the approximate spectroscopic constants for the $v = 0$ and $v = 1$ vibrational levels of the perturbing state. A simple energy level expression

$$E_{vN} = T_v + B_{pv}N(N+1) - 9.1 \times 10^{-6} [N(N+1)]^2 \quad (1)$$

was used for the perturbing state. The resulting term values of the perturbing state are $T_0 = 11\,176\text{ cm}^{-1}$ and $T_1 = 12\,371\text{ cm}^{-1}$ with a $\Delta G(\frac{1}{2}) = 1195\text{ cm}^{-1}$, while the rotational constants are $B_{p0} = 3.19\text{ cm}^{-1}$ and $B_{p1} = 3.15\text{ cm}^{-1}$.

For CrH the perturbing $a^4\Sigma^+$ state has a $T_0 = 11\,186\text{ cm}^{-1}$ and $B_{p0} = 6.10\text{ cm}^{-1}$ so that our CrD analysis confirms the vibrational assignments. The isotopic relation predicts that $B_{p0} = 3.11\text{ cm}^{-1}$ from the corresponding CrH value. The rotational constants for the $a^4\Sigma^+$ state are greater than those of the $A^6\Sigma^+$ state ($B_{pv} > B'_v$) so the perturbing state crosses from below. The $a^4\Sigma^+$ rotational and vibrational constants are similar to those of the $X^6\Sigma^+$ state where $B_e = 3.175443\text{ cm}^{-1}$, $\alpha_e = 0.065908\text{ cm}^{-1}$, and $\Delta G(\frac{1}{2}) = 1151.9947\text{ cm}^{-1}$ while the perturbing $a^4\Sigma^+$ state has $B_e = 3.21\text{ cm}^{-1}$, $\alpha_e = 0.04\text{ cm}^{-1}$, and $r_e = 1.646\text{ \AA}$.

In the previous work on CrD, O'Connor (3) could not draw any conclusions about the nature of the perturbing state because of a lack of data in the perturbed regions. However, in the work on CrH by Kleman and Uhler (7) they concluded that an $^8\Sigma^+$ state was responsible for the perturbation. This conclusion was based on the erroneous observation of perturbations in all six spin components. Our present results on CrD and our previous work on CrH (2) suggest that a $^4\Sigma^+$ state is responsible for the

TABLE VI

Rotational Constants (in cm^{-1}) for the $A^6\Sigma^+$ State of CrD

Constants	v=0	v=1
T_v	11559.7206(6)	12626.1407(8)
B_v	2.7378616(87)	2.688175(16)
$10^5 \times D_v$	7.0381(19)	7.1069(65)
$10^9 \times H_v$	1.130(12)	2.710(99)
$10^{12} \times L_v$	0.0434(28)	-1.166(67)
γ_v	0.665796(83)	0.655206(92)
$10^5 \times \gamma_{Dv}$	-2.303(12)	-1.794(36)
$10^8 \times \gamma_{Hv}$	0.448(15)	-2.18(18)
$10^{11} \times \gamma_{Lv}$	-0.0919(40)	2.40(16)
λ_v	1.55966(39)	1.63451(41)
$10^4 \times \lambda_{Dv}$	-1.884(14)	-2.001(17)
$10^3 \times \theta_v$	1.915(95)	3.31(10)
$10^5 \times \theta_{Dv}$	-1.921(58)	-1.126(80)
$10^4 \times \gamma_S$	5.49(12)	7.15(12)
$10^7 \times \gamma_{SD}$	6.85(25)	5.47(17)

perturbations. This conclusion is also supported by recent theoretical work on this molecule (11). The ab initio calculation of the spectroscopic properties of CrH by Dai and Balusubramanian (11) predicts a low-lying $4\Sigma^+$ excited state at $11\,206\text{ cm}^{-1}$ with a bond length $r_e = 1.693\text{ \AA}$. This is in excellent agreement with our value of $T_{00} = 11\,186\text{ cm}^{-1}$ and $r_0 = 1.672\text{ \AA}$ for CrH (2) and present $T_{00} = 11\,176\text{ cm}^{-1}$ and r_e

TABLE VII

Equilibrium Constants (in cm^{-1}) for the $X^6\Sigma^+$ and $A^6\Sigma^+$ States of CrD

Constants	$X^6\Sigma^+$	$A^6\Sigma^+$
ω_e	1183.1958(21)	[1066.4202(10)]*
$\omega_e x_e$	15.6006(9)	--
B_e	3.175443(21)	2.762705(13)
α_e	0.065908(23)	0.049687(18)
$r_e(\text{\AA})$	1.654730(5)	1.774034(4)

* $\Delta G(1/2)$ value.

= 1.646 Å for CrD. The $^8\Sigma^+$ state which correlates to the Cr(7S) + H(2S) atomic limits is predicted to be a repulsive state (11).

CONCLUSION

The high resolution spectrum of the $A^6\Sigma^+ - X^6\Sigma^+$ system of CrD has been observed using a Fourier transform spectrometer. The analysis of the 0-0, 0-1, 1-0, and 1-2 bands of this transition provides a much improved set of molecular constants for the ground and the excited states. The $v = 0$ and $v = 1$ vibrational levels of the $A^6\Sigma^+$ state are perturbed by interaction with a close-lying $^4\Sigma^+$ state. Preliminary molecular constants have been derived for the perturbing state. The results of this analysis are consistent with the data previously reported for CrH (2).

ACKNOWLEDGMENTS

The National Solar Observatory is operated by the Association for Research in Astronomy, Inc., under contract with the National Science Foundation. We thank J. Wagner and C. Plymate for assistance in acquiring the spectra. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Some support was also provided by the Natural Sciences and Engineering Research Council of Canada.

RECEIVED: December 29, 1994

REFERENCES

1. A. G. GAYDON AND R. W. B. PEARSE, *Nature* **140**, 110-110 (1937).
2. R. S. RAM, C. N. JARMAN, AND P. F. BERNATH, *J. Mol. Spectrosc.* **161**, 445-454 (1993).
3. S. O'CONNOR, *Proc. R. Irish Acad. Sect. A* **65**, 95-111 (1967).
4. J. M. BROWN, S. P. BEATON, AND K. M. EVENSON, *Astrophys. J.* **414**, L125-L127 (1993).
5. O. ENGVOLD, H. WÖHL, AND J. W. BRAULT, *Astron. Astrophys. Suppl. Ser.* **42**, 209-213 (1980).
6. B. LINDGREN AND G. S. OLOFSSON, *Astron. Astrophys.* **84**, 300-303 (1990).
7. B. KLEMAN AND U. UHLER, *Can. J. Phys.* **37**, 537-549 (1959).
8. D. P. CHONG, S. R. LANGHOFF, C. W. BAUSCHLICHER, S. P. WALCH, AND H. PARTRIDGE, *J. Chem. Phys.* **85**, 2850-2860 (1986).
9. S. P. WALCH AND C. W. BAUSCHLICHER, *J. Chem. Phys.* **78**, 4597-4605 (1983).
10. G. DAS, *J. Chem. Phys.* **74**, 5766-5774 (1981).
11. D. DAI AND K. BALASUBRAMANIAN, *J. Mol. Spectrosc.* **161**, 455-465 (1993).
12. B. A. PALMER AND R. ENGLEMAN, Atlas of the Thorium Spectrum, Los Alamos National Laboratory, Los Alamos, 1983 (unpublished).
13. J. M. BROWN AND D. J. MILTON, *Mol. Phys.* **31**, 409-422 (1978).
14. R. M. GORDON AND A. J. MERER, *Can. J. Phys.* **56**, 642-656 (1980).
15. G. HERZBERG, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950.
16. K. LIPUS, E. BACHEM, AND W. URBAN, *Mol. Phys.* **73**, 1041-1050 (1991).
17. H. LEFEBVRE-BRION AND R. W. FIELD, "Perturbations in the Spectra of Diatomic Molecules," Academic Press, Orlando, 1986.
18. A. E. S. MILLER, C. S. FEIGERLE, AND W. C. LINEBERGER, *J. Chem. Phys.* **87**, 1549-1556 (1987).