JOURNAL OF MOLECULAR SPECTROSCOPY **89**, 107–124 (1981)

Vibration–Rotation and Deperturbation Analysis of $A^2\Pi$–$X^2\Sigma^+$ and $B^2\Sigma^+$–$X^2\Sigma^+$ Systems of the CaI Molecule

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Doppler-limited laser excitation spectroscopy employing narrow-band fluorescence detection was used to obtain a rotational and vibrational analysis in the (0, 0) and (1, 1) bands of the $A^2\Pi$–$X^2\Sigma^+$ system and the (4, 2) (3, 1), (0, 0), (0, 1), (1, 2), (2, 3), and (3, 4) bands of the $B^2\Sigma^+$–$X^2\Sigma^+$ system of CaI. The A and B states are deperturbed to obtain spectroscopic constants and Franck–Condon factors. Deperturbation was necessary because of the small separation of the A and B states relative to the $A \sim B$ interaction strength and the $A^2\Pi$ spin–orbit splitting. The main deperturbed constants (in cm^{-1}) are

	$X^2\Sigma^+$	$A^2\Pi$	$B^2\Sigma^+$
T_e	0	15 624.67(5)	15 700.52(12)
ω_e	238.7496(33)	241.19(7)	242.63(17)
$\omega_e x_e$	0.62789(64)	0.53(5) (Pekeris)	1.17(12) (Pekeris)
B_e	0.0693254(84)	0.070460(14)	0.071572(22)
$\alpha_e \times 10^4$	2.640(35)	2.15(10)	3.95(2)
A_e	—	45.8968(52)	—
R_e (Å)	2.8286(2)	2.8057(3)	2.7839(4)

where 1σ uncertainties are given in parentheses. The molecular constants provide insight into the orbital composition of the A and B states.

I. INTRODUCTION

The first CaI $A^2\Pi$–$X^2\Sigma^+$ and $B^2\Sigma^+$–$X^2\Sigma^+$ spectra were observed in absorption by Walters and Barratt in 1928 (*1*). Several vibrational analyses of the A–X and B–X bandheads have been performed (*2*), the most recent of which was by Rao *et al.* in 1978 (*3*). CaI has also been tentatively identified in the spectra of certain cool stars (*4*). In spite of the early and frequent observation of CaI spectra, no rotational analysis has been reported.

CaI is a very ionic molecule so the charge distribution is well represented by Ca^+I^-. The remaining Ca^+ valence electron resides in a nonbonding metal-centered orbital (*5*). Transitions from the $X^2\Sigma^+$ state correspond to excitations of the $4s\sigma$ nonbonding electron to higher nonbonding metal-centered orbitals, resulting in nearly identical potential curves for the X, A, and B states. The similarity of the rotational and vibrational constants in the ground and excited states causes the spectrum to be highly congested, precluding the possibility of correct rotational

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0022-2852/81/090107-18$02.00/0

or vibrational analyses by classical techniques. Earlier attempts at vibrational bandhead analyses, including the most recent, were not entirely correct (*2, 3*). The technique of laser excitation spectroscopy using a tunable single-mode cw dye laser, coupled with selective, narrow-bandpass fluorescence detection, has enabled rotation–vibration assignment of over 1600 lines.

The $A\,^2\Pi$ and $B\,^2\Sigma^+$ states are separated by only about 90 cm^{-1}. This separation is similar to the $^2\Pi_{3/2}$–$^2\Pi_{1/2}$ separation (60 cm^{-1}) and the $^2\Pi \sim {}^2\Sigma^+$ interaction matrix element (40 cm^{-1}), thus the usual expressions for Λ doubling (*7*), derived using second-order perturbation theory, are inadequate.

Nevertheless, the usual $^2\Sigma^+$ energy level expressions (Ref. (*6*, p. 249)) adequately reproduce the line positions of the $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ transition. However, the spin–rotation constant of the B state is larger than the rotational constant because of the strong interaction with the nearby $A\,^2\Pi$ state. Thus, the effective rotational constant of the $B\,^2\Sigma^+$ state has no mechanical significance (*8*).

In order to fit the A–X transition and obtain mechanically significant A–X and B–X constants, $A\,^2\Pi \sim B\,^2\Sigma^+$ interaction matrix elements were explicitly included in a "direct approach" fit (*7*). The (0, 0) A–X and B–X bands were fitted simultaneously, as were the (1, 1) A–X and (1, 2) B–X bands, in order to deperturb the A and B state constants. For the $B\,^2\Sigma^+$ state, two sets of constants are presented in order to provide effective constants for convenient calculation of energy levels as well as to provide deperturbed constants for the calculation of potential energy curves.

II. EXPERIMENTAL DETAILS

CaI was produced in a Broida-type oven (*9*) by the reaction of ethyl iodide, C_2H_5I, with calcium vapor produced by heating calcium metal in an alumina crucible. Operating pressure was typically 1 Torr of argon carrier gas. Four watts of 514-nm radiation from a Coherent CR 10 Ar^+ laser pumped a Coherent Model 599-21 dye laser (1-MHz bandwidth) operated with rhodamine 6G (50 mW) or rhodamine 101 (30 mW). The dye laser was used to excite fluorescence in the $\Delta v = 0$ band sequence of the A–X system and the $\Delta v = 2$, 0, and -1 band sequences of the B–X system.

Fluorescence was viewed (*10, 11*) through a 1-m monochromator (spectral slitwidth, 1–2 cm^{-1}) which provided the narrow bandwidth detection necessary to isolate transitions in a selected branch. While fluorescence detection was generally done in the same band in which the laser excitation occurred, on occasion it was advantageous to view fluorescence in another band sequence, which might possess more convenient bandhead separations or more favorable Franck–Condon factors.

Each of the bands in the B–X system displays double heads, as expected from the large spin–rotation constant in the B state, and is shaded to the violet. The single-mode dye laser was scanned through a selected P or R branch and fluorescence was detected exclusively in the corresponding R or P branch (of the same parity), respectively. The spectral bandwidth of the monochromator could be adjusted to discriminate against, or controllably allow for, detection of fluorescence from other bands of the sequence. Similar scans were made for the A–X system.

Although many branches occur in the same spectral region, overlapped lines coming from different branches often have different N values. This difference in N means that the separations between resultant $P(N + 1)$ and $R(N - 1)$ fluorescence lines are different, permitting the lines in a given small spectral region to be sorted into branches. The different branches in the same spectral region give rise to fluorescence that occurs in distinct spectral regions. By using the monochromator as a narrow-bandpass filter, fluorescence arising from excitation in a specific branch can be detected selectively. When the laser is scanned and the monochromator used as a filter, the excitation spectrum is simplified.

Overlapping sequence bands can result in more than 100 lines/cm^{-1}. Without the simplification provided by narrow-band detection, our analysis would have been impossible. The technique is illustrated by Figs. 1 and 2 of Ref. (*11*).

The fluorescence excitation spectrum was calibrated with respect to I_2 B 0_u^+–$X^1\Sigma_g^+$ lines (*12*) by simultaneously recording I_2 and CaI excitation spectra as well as fringes from a 300-MHz FSR semiconfocal Fabry–Perot etalon. The absolute accuracy of unblended lines is ±0.003 cm^{-1}. The estimated precision, from rms error of the fit, is 0.003 cm^{-1}. The line positions and band origins given have not been corrected by subtraction of 0.0056 cm^{-1}, contrary to the suggestion by Gerstenkorn and Luc (*13*).

III. RESULTS AND DISCUSSION

Initial fluorescence excitation spectra of CaI were recorded in the $\Delta v = 2, 0$, and -1 sequences of the B–X system. Attempts to analyze the $\Delta v = 1$ bands were

TABLE I

$B^2\Sigma^+$–$X^2\Sigma^+$ Bandheads (cm^{-1})

	$B^2\Sigma^+$ - $X^2\Sigma^+$			Band Heads (in cm^{-1})	
(v',v'')	P_{1e}	P_{2f}	(v',v'')	P_{1e}	P_{2f}
(2,0)	16 191.70	16 187.44	(4,3)	15 950.47	15 953.57
(3,1)	16 190.06	16 186.14	(5,4)	15 950.28	--
(4,2)	16 188.36	16 184.79	(6,5)	15 950.00	--
(5,3)	16 186.61	16 183.36	(7,6)	15 949.61	--
(6,4)	16 184.79	16 181.82	(8,7)	15 949.11	--
(7,5)	16 182.91	16 180.20	(0,0)	15 712.22	15 716.29
(8,6)	16 180.95	16 178.47	(1,1)	15 713.59	15 717.28
(9,7)	16 178.92	--	(0,1)	15 475.17	15 478.85
(1,0)	15 950.59	15 954.68	(1,2)	15 477.79	15 481.10
(2,1)	15 950.59	15 954.36	(2,3)	15 480.33	15 483.32
(3,2)	15 950.54	15 953.97	(3,4)	15 482.79	--

Accuracy ± 0.01 cm^{-1}.

TABLE II

Franck–Condon Factors Calculated from Deperturbed Constants

$B^2\Sigma^+ - X^2\Sigma^+$

v_B \ v_X	0	1	2	3	4	5
0	0.814	0.159	0.023	0.003	--	--
1	0.175	0.530	0.232	0.053	0.009	0.001
2	0.010	0.286	0.348	0.256	0.080	0.017
3	0.001	0.024	0.357	0.231	0.254	0.103
4	--	--	0.040	0.402	0.157	0.238
5	--	--	--	0.054	0.433	0.110

$A^2\Pi - X^2\Sigma^+$

v_A \ v_X	0	1	2	3	4	5
0	0.942	0.054	0.003	--	--	--
1	0.057	0.830	0.104	0.008	0.001	--
2	0.001	0.113	0.719	0.149	0.016	0.002
3	--	0.003	0.168	0.612	0.187	0.026
4	--	--	0.006	0.220	0.510	0.217
5	--	--	--	0.010	0.269	0.415

$B^2\Sigma^+ - A^2\Pi$

v_B \ v_A	0	1	2	3	4	5
0	0.957	0.041	0.002	--	--	--
1	0.043	0.888	0.064	0.005	--	--
2	--	0.071	0.847	0.075	0.007	--
3	--	--	0.086	0.828	0.076	0.010
4	--	--	--	0.092	0.827	0.070
5	--	--	--	--	0.089	0.838

Only values ≥ 0.0005 have been included.

frustrated by extreme sequence congestion and spectral overlap, as evidenced by the head of heads shown in Table I. The (0, 1) band was found to be relatively free of overlap and was analyzed first to obtain preliminary constants for the X and B states. These constants were then used to guide the analysis of the remainder of the bands in the $B-X$ system. The $B-X$ data were fitted using standard $^2\Sigma^+$ energy level expressions (*6*, p. 249), but γ' and γ'' were strongly correlated.

The X-state constants were then used to assign the $\Delta v = 0$ bands in the $A-X$ system. Analysis of the $A-X$ system and a combined fit of the $A-X$ bands with selected $B-X$ bands provided well determined values for γ''. The $B-X$ bands were then refit with γ'' fixed.

The standard $^2\Pi-^2\Sigma^+$ Hamiltonian uses Λ doubling and spin–rotation parameters derived using the Van Vleck transformation (*8*). In CaI, the $^2\Pi \sim {}^2\Sigma^+$ interaction is so strong that second-order perturbation theory cannot adequately explain the Λ doubling of the $A\,^2\Pi$ state. In order to fit the $A-X$ transition, the $^2\Pi \sim {}^2\Sigma^+$ interaction parameters η and ξ (*14*) were explicitly used in combined $A-X$ and $B-X$ fits. These fits also provided estimates of the "true" mechanical B and ω constants, uncontaminated by magnetic contributions introduced by Born–Oppenheimer breakdown (*8*).

TABLE III

$B^2\Sigma^+ - X^2\Sigma^+$ Observed Transitions (cm^{-1})

Band	N	P_{1ee}	$\Delta\nu^a$	P_{2ff}	$\Delta\nu$	R_{1ee}	$\Delta\nu$	R_{2ff}	$\Delta\nu$
(1,1)	18					16 193.243	1		
	19	16 188.274	-2	-		16 193.494	0		
	20	16 188.151	-2	-		16 193.854	0		
	21	16 188.034	-2	-		16 194.016	-1		
	22	16 187.919	-2	-		16 194.187	3		
	23	16 187.806	-2	-		16 194.359	3		
	24	16 187.702	0	-		-			
	25	16 187.599	0	-		-			
	26	16 187.498	0	-		-			
	27	16 187.400	0	-		-			
	28	16 187.310	2	-		-			
	29	16 187.220	2	-		-			
	30	16 187.131	0	-		-			
	31	16 187.050	1	-		-			
	32	16 186.967	1	-		-			
	33			-		-			
	34			-		-			
	35	16 186.742	-98	-		-			
	36	16 186.684	16	16 190.203	2	-			
	37	16 186.624	-28	16 190.234	1	-			
	38	16 186.567	2	16 190.268	4	-			
	39	16 186.516	0	16 190.307	0	-			
	40	16 186.464	0	16 190.346	0	-			
	41	16 186.417	0	16 190.393	0	-			
	42	16 186.374	0	16 190.441	0*	-			
	43	16 186.334	0	16 190.492	19	-			
	44	16 186.299	1	16 190.544	19	-			
	45	16 186.267	1	16 190.605	2	-			
	46	16 186.238	2	16 190.661	1	-			
	47	16 186.209	0	16 190.725	0	-			
	48			16 190.789	2	-			
	49			16 190.861	0	-			
	50			16 190.933	0	-			
	51			16 191.008	0	-			
	52			16 191.084	1	-			
	53			16 191.165	1	-			
	54			16 191.246	1	-			
	55			16 191.330	3	-			
	56			16 191.410	3	-			
(2,2)	15							16 191.104	4
	16					16 191.727	3		
	17					16 191.928	1	16 191.590	2
	18					16 192.082	-9	16 193.016	4
	19					16 192.248	4	16 194.084	4
	20					16 192.459	-6	16 194.231	0
	21					16 192.678	5		
	22					16 192.748	-4		
	23					16 192.976	1		
	24	16 186.713	0			16 193.106	1		
	25	16 186.599	1					16 195.244	1
	26	16 186.095	0						
	27	16 186.003	0			16 193.658	0	16 196.176	1
	28	16 185.913	0			16 193.849	1	16 196.451	1
	29	16 185.828	1			16 194.241	1	16 196.746	1
	30	16 185.743	0			16 194.711	3	16 197.098	6
	31	16 185.663	0			16 194.442	5	16 197.194	6
	32	16 185.588	1			16 194.650	4		
	33	16 185.515	2			16 194.854	0		
	34	16 185.443	0			16 195.068	1		
	35	16 185.380	1			16 195.278	1		
	36	16 185.318	2			16 195.493	5		
	37					16 195.711	4		
	38					16 195.939	-6		
	39					-			
	40					-			
	41								
	42					16 196.889	3		
	43					16 197.126	1		
	44					16 197.375	5		
	45					16 197.617	-1		
	46					16 197.869	-3		
	47					16 198.124	-3		
	48								
	49								
	50								
	51								
	52								
	53								
	54								
	55					16 200.298	0*		
	56					16 200.588	3		
	57					16 200.864	-9		
	58					16 201.174	7		
	59					16 201.456	-4		
	60								
	61					16 202.060	-1		
	62					16 202.373	0		
(0,0)	2			15 716.477	-94				
	3			15 716.242	-88				
	4			15 716.013	79				
	5	15 715.818	4	15 716.469	59				
	6	15 715.428	1	15 716.457	-54				
	7	15 715.443	-1	15 716.395	-14				
	8	15 715.244	-1	15 716.362	-18	15 717.561	0		
	9	15 715.093	-2	15 716.337	0*	15 717.477	-1		
	10	15 714.934	5	-		15 717.800	0		
	11	15 714.775	5	-		15 717.923	0		
	12	15 714.614	6	-		15 718.050	1		
	13	15 714.458	0	-		15 718.188	0	15 720.488	1
	14	15 714.310	0	-		15 718.327	1	15 720.633	4
	15	15 714.167	0	-		15 718.467	3	15 720.846	1
	16	15 714.025	-4	-		15 718.617	-1	15 721.150	0
	17	15 713.898	0	-		15 718.772	0	15 721.450	1
	18	15 713.748	-2	-		15 718.933	1	15 721.750	1
	19	15 713.650	1	15 716.135	2	15 719.099	1	15 722.054	1
	20	15 713.535	4	15 716.159	0	15 719.265	0	15 722.369	1
	21	15 713.421	2	15 716.191	1	15 719.439	0	15 722.683	0
	22	15 713.322	1	15 716.226	2	15 719.619	0	15 723.000	0
	23	15 713.208	0	15 716.267	1	15 719.803	0	15 723.331	0*
	24	15 713.109	-1	15 716.312	1	15 719.990	0	15 723.663	18
	25	15 713.017	-18	15 716.360	0	15 720.186	0	15 723.999	18
	26	15 712.931	0*	15 716.413	2	15 720.385	0	15 724.337	-28
	27	15 712.850	18	15 716.470	0	15 720.591	0	15 724.677	0
	28	15 712.771	0*	15 716.534	0	15 720.797	0	15 725.026	-18
	29	15 712.697	-18	15 716.601	0	15 721.011	0	15 725.380	0
	30	15 712.631	0*	15 716.673	0	15 721.231	0	15 725.735	1
	31	15 712.567	18	15 716.748	0	15 721.457	0	15 726.096	1
	32	15 712.510	0*	15 716.831	0	15 721.677	4	15 726.464	4
	33	15 712.456	18	15 716.918	0	15 721.917	4	15 726.837	1
	34	15 712.410	0*	15 717.007	0	15 722.163	4	15 727.215	0
	35	15 712.368	-1	15 717.101	0	15 722.393	4	15 727.595	0
	36	15 712.331	0	-		15 722.642	4	15 727.979	1
	37	15 712.297	-24	-		15 722.894	4	15 728.365	1
	38	15 712.269	-38	-		15 723.159	0	15 728.757	1
	39			-		15 723.431	0	15 729.158	1
	40			-		15 723.692	0		
	41			-		15 723.956	0		
	42			-		15 724.234	-7		
	43			-		15 724.524	-7	15 730.821	0*
	44			-		15 724.816	0	15 731.241	0*
	45								
	46			-		15 725.468	0	15 732.080	1
	47			-		15 725.811	-1	15 732.519	12
	48	15 712.273	-28	-		15 726.021	1		
	49	15 712.301	-29	-		15 726.353	0		
	50	15 712.335	-19	-		15 726.691	1		
	51	15 712.373	-18	-		15 726.927	0		
	52	15 712.417	1	-		15 727.280	1		
	53	15 712.465	-1	-		15 727.634	0		
	54	15 712.518	-1	-		15 727.976	0		
	55	15 712.577	0	-		15 728.331	2		
	56	15 712.640	0	-		15 728.688	1		
	57	15 712.709	0	-		15 729.031	0		
	58	15 712.782	0	-		15 729.376	1		
	59	15 712.860	0	-		15 729.740	0		
	60	15 712.942	1	-		15 730.110	0		
	61	15 713.032	0	-		15 730.482	0		
	62	15 713.127	1	-		15 730.858	-1		
	63	15 713.224	3						
	64	15 713.330	4						
	65	15 713.437	2						
	66	15 713.556	2						
	67	15 713.668	2						
	68	15 713.793	98						
	69	15 713.919	29						
	70	15 714.052	-58						
	71	15 714.184	-38						
	72	15 714.327	-34						
	73	15 714.474	-2						
	74	15 714.626	4						
	75	15 714.786	1						
	76	15 714.951	0						
	77	15 715.131	2						
	78	15 715.294	3						
	79	15 715.466	-28						
(1,0)	4	15 478.514	-1			15 479.443	-1		
	5	15 478.332	-2	-		15 479.481	1		
	6	15 478.152	-1			15 479.521	4		
	7	15 477.988	-4			15 480.087	-1	15 481.443	1
	8	15 477.822	-4			15 480.206	0	15 481.745	1
	9	15 477.666	1			15 480.479	-4	15 481.999	0
	10	15 477.508	0			15 480.641	0		
	11	15 477.359	1			15 480.989	0		
	12	15 477.214	1	-		15 480.740	0	15 482.844	4
	13	15 477.075	3			15 480.881	0	15 483.111	5
	14	15 476.749	1			15 481.059	0	15 483.435	1
	15	15 476.611	1			15 481.197	0	15 483.712	6
	16	15 476.487	1			15 481.341	1	15 484.016	-9
	17	15 476.368	0			15 481.526	0	15 484.350	4
	18	15 476.252	0	15 478.914	0	15 481.707	0		
	19	15 476.150	1	15 478.975	0	15 481.881	1	15 484.963	1
	20	15 476.049	2	15 479.017	0	15 482.068	1	15 485.314	1
	21	15 475.953	3	15 479.048	0	15 482.260	1	15 485.664	1
	22	15 475.862	1	15 479.114	1	15 482.458	1	15 486.024	1
	23	15 475.776	0	15 479.147	1	15 482.658	1	15 486.386	1
	24	15 475.696	0	15 479.217	2	15 482.866	1	15 486.756	1
	25	15 475.622	0	15 479.301	19	15 483.078	1	15 487.131	58
	26	15 475.550	0	15 479.387	2	15 483.297	0	15 487.508	1
	27	15 475.490	1	15 479.481	1	15 483.513	0	15 487.888	0

N	P_{1ee}	$\Delta\nu$	P_{2ff}	$\Delta\nu$	R_{1ee}	$\Delta\nu$	R_{2ff}	$\Delta\nu$
29	15 475.436	1	15 479.534	1	15 483.750	0	15 488.114	1
30	15 475.386	38	15 479.627	0	15 483.987	0	15 488.489	0
31	15 475.344	2	15 479.714	-1	15 484.222	1	15 488.869	1
32	15 475.304	10*	15 479.813	-2	15 484.470	1	15 489.253	1
33	15 475.269	88	15 479.917	-2	15 484.717	0	15 489.641	0
34	15 475.238	68	15 480.025	-2	15 484.974	0	15 490.036	1
35	15 475.210	28	15 480.138	3	15 485.236	0	15 490.425	1
36	15 475.185	48	15 480.256	3	15 485.500	4	15 490.828	0
37	-		15 480.386	14	15 485.775	0	15 491.238	1
38	-		15 480.514	18	15 486.053	1	15 491.640	0
39	15 475.173	58	15 480.648	1	15 486.339	1	15 492.059	0
40	-		15 480.787	1	15 486.628	1	15 492.480	1
41	-		15 480.929	0	15 486.924	1	15 492.878	1
42	-		15 481.079	0	15 487.226	0	15 493.347	1
43	-		15 481.234	1	15 487.530	0	15 493.804	0
44	-		15 481.384	-4	15 487.847	1		
45	-		15 481.552	-2	15 488.161	0		
46	15 475.303	-78	15 481.720	-3	15 488.485	0		
47	15 475.350	38	15 481.895	-1	15 488.813	0		
48	15 475.401	0	15 482.068	-7	15 489.145	0		
49	15 475.454	0	-		15 489.481	0		
50	15 475.514	1	-		15 489.829	0		
51	15 475.581	1	-		15 490.182	0		
52	15 475.651	0	-		15 490.537	0		
53	15 475.727	0	-		15 490.899	0		
54	15 475.809	1	-					
55	15 475.897	2	-		15 491.637	0		
56	15 475.991	3	-		15 491.016	3		
57	15 476.087	1	-					
58	15 476.192	2	-		-			
59	15 476.300	1	-		15 493.176	0		
60	15 476.414	1	-		15 493.574	-2		
61	15 476.534	-2	-		15 493.981	0		
62	15 476.661	2	-		15 494.395	1		
63	15 476.792	1	-		-			
64	15 476.929	1	-		15 495.232	1		
65	15 477.072	3	-		15 495.659	1		
66	15 477.219	1	-		15 496.086	-1		
67	15 477.371	0	-		15 496.524	0		
68	15 477.529	0	-		15 496.944	1		
69	15 477.692	2	-		15 497.363	3		
70	15 477.860	-3	-		15 497.811	0		
71	15 478.037	-2	-		15 498.230	0		
72	15 478.219	0	-		15 498.795	0		
73	15 478.403	-2	-		15 499.267	2		
74	15 478.597	0						
75	15 478.793	-1						
76	15 478.994	-1						
(1,1)	2	-	15 481.499	38				
3	-		15 481.426	18				
4	-		15 481.385	78				
5	-		15 481.328	28				
6	-		15 481.284	58				
7	-		15 481.231	48				
8	-		15 481.208	48				
9	-		15 481.175	48	15 482.459	0		
10	-				15 482.790	0		
11	-				15 482.972	1		
12	15 479.625	1	-		15 483.069	1		
13	15 479.498	1	-		15 483.269	1	15 488.047	1
14	15 479.384	2	-		15 483.369	1	15 488.345	-5
15	15 479.279	2	-		15 483.527	1	15 488.632	-3
16	15 479.188	4	-		15 483.692	4	15 488.925	0
17	15 479.097	0	-		15 483.859	2	15 489.219	0
18	15 478.974	-1	-		15 484.036	59	15 489.523	0
19	15 478.749	0	15 481.146	0	15 484.212	2	15 489.831	4
20	15 478.648	-1	15 481.137	4	15 484.399	4	15 490.139	1
21	15 478.573	0	15 481.126	4			15 490.449	-1
22	15 478.484	0	15 481.141	3	15 484.761	1	15 490.774	0
23	15 478.397	-2	15 481.184	1	15 484.983	2	15 491.097	0
24	15 478.318	-2	15 481.310	5	15 485.187	0	15 491.431	1
25	15 478.244	0	15 481.382	1	15 485.394	0	15 491.766	0
26	15 478.177	-1	15 481.437	3	15 485.614	0	15 492.105	0
27	15 478.113	-1	15 481.498	3	15 485.837	0	15 492.452	0
28	15 478.054	-1	15 481.564	3	15 486.064	0	15 492.801	1
29	15 478.002	-2	15 481.630	-1	15 486.295	0	15 493.156	2
30	15 477.955	-3	15 481.707	-1			15 493.520	0
31	15 477.914	-3	15 481.788	-2	15 486.760	1	15 493.887	1
32	15 477.878	-3	15 481.875	-1	15 487.031	3	15 493.256	1
33	15 477.847	-3	15 481.962	-1	15 487.305	0	15 494.625	0
34	15 477.820	-3	15 482.062	-1	15 487.583	0	15 495.000	0
35	-		15 482.164	-1	15 487.860	0	15 495.381	0
36	-		15 482.270	1	15 488.147	0	15 495.766	1
37	-		15 482.377	1	15 488.437	0	15 496.156	1
38	-		15 482.487	-2	15 488.727	0	15 496.581	0
39	-				15 489.022	0	15 496.988	1
40	15 477.793	49	15 482.747	0	15 489.315	1	15 497.394	1
41	-		15 482.877	0	15 489.614	2	15 497.809	1
42	15 477.817	-3	15 483.011	0	15 489.916	2		
43	15 477.842	-3	15 483.154	0	15 490.125			
44	15 477.872	-3	15 483.300	0	15 490.528	1		
45	15 477.907	0	15 483.450	0	15 490.758	1		
46	15 477.948	1	-		15 491.084	1		
47	15 477.994	1	15 483.765	0	15 491.414			
48	15 478.042	0	15 483.931	0	15 491.749	0		
49	15 478.098	0	15 484.101	0	15 492.085	1		
50	15 478.160	0	15 484.274	38	15 492.430	1		
51	15 478.227	-1	15 484.451	2	15 492.781	0		
52	15 478.300	0	-		15 493.138	0		
53	15 478.378	0	-		15 493.498	0		
54	15 478.463	1	-		15 493.865	0		
55	15 478.554	3	-		15 494.244	-4		
56	15 478.651	1	-		15 494.629	99		
57	15 478.747	3	-		15 494.999	0		
58	15 478.853	4	-		15 495.387	0		
59	15 478.963	4	-		-			
60	15 479.078	1	-		15 496.175	4		
61			-		15 496.580	-4		
62			-		15 496.983	0		
63			-		15 497.406	-1		
64			-		15 497.826	0		
65			-		15 498.254	0		
66			-		15 498.686	0*		
67			-		15 499.121	1		
(2,3)	10				15 485.190	3		
11	-				15 485.325	4		
12	-				15 485.482	0	15 487.022	84
13	-				15 485.627	1	15 487.295	4
14	-				15 485.790	1	15 487.588	1
15	-				15 485.954	1	15 487.862	1
16	-				15 486.122	0	15 488.156	18
17	15 481.440	2			15 486.295	0	15 488.450	1
18	15 481.333	1			15 486.475	1	15 488.679	19
19	15 481.231	0			15 486.654	1	15 488.975	0
20	15 481.134	0			15 486.844	3	15 489.279	4
21	15 481.045	-1			15 487.044	2	15 489.587	1
22	15 480.966	-1			15 487.241	-2	15 489.897	1
23	15 480.880	-2			15 487.442	0	15 490.202	-2
24	15 480.808	0	15 483.473	1	15 487.655	1	15 490.547	48
25	15 480.738	1	15 483.614	0	15 487.869	1	15 490.848	0
26	15 480.674	-1	15 483.540	1	15 488.097	0	15 491.183	49
27	15 480.614	-1	15 483.610	0	15 488.317	0	15 491.511	0
28	15 480.565	0	15 483.667	0	15 488.547	0	15 491.853	0
29	15 480.514	0	15 483.726	1	15 488.781	0	15 492.197	0
30	15 480.474	0	15 483.794	0	15 489.027	0	15 492.546	1
31	15 480.434	-1	15 483.866	1	15 489.270	0	15 492.900	0
32	15 480.404	-1	15 483.936	1	15 489.521	0	15 493.260	2
33	15 480.380	1	15 484.013	2	15 489.775	0		
34			15 484.101	-1	15 490.038	0		
35			15 484.192	-4	15 490.298	1		
36	-		15 484.287	4	15 490.561	1		
37	-		15 484.385	1	15 490.829	1		
38	-		15 484.493	1	15 491.145	1		
39	-		15 484.598	1	15 491.424	1		
40	-		15 484.710	0	15 491.724	4		
41	-		15 484.841	0	15 492.025	1		
42	15 480.477	-3	15 484.965	0				
43	15 480.402	-3	15 485.091	0	15 492.634	0		
44	15 480.434	0	15 485.224	0	15 492.950	1		
45	15 480.472	-1	15 485.359	0	15 493.271	1		
46	15 480.514	-1	15 485.504	0	15 493.594	0		
47	15 480.561	-1	15 485.654	0	15 493.924	0		
48	15 480.615	0	15 485.804	0	15 494.257	0		
49	15 480.674	0	15 485.964	1	15 494.594	18		
50	15 480.738	1	15 486.124	1	15 494.948	1		
51	15 480.804	1	15 486.291	1	15 495.298	1		
52	15 480.885	0			15 495.654	1		
53	15 480.961	1			15 496.014	1		
54	15 481.047	1			15 496.378	-5		
55	15 481.139	2			15 496.744	1		
56	15 481.232	1			15 497.117	0		
57	15 481.331	1			15 497.501	1		
58	15 481.440	1			15 497.900	0		
59	15 481.557	4			15 498.279	1		
60	15 481.663	0			15 498.687	18		
61	15 481.788	4			15 499.097	0		
62	15 481.907	1						
63	15 482.044	1						
64	15 482.182	2						
(3,4)	15				15 488.318	1		
16					15 488.488	0		
17					15 488.679	1		
18					15 488.878	0		
19					15 489.078	1		
20	-				15 489.283	0		
21	-				15 489.437	0		
22	-				15 489.692	1		
23	-				15 489.842	2		
24	-				15 490.075	2		
25	-				15 490.264	1		
26	-				15 490.457	18		
27	-				15 490.319	0		
28	-				15 490.952	0		
29	-				15 491.183	98		
30	-				15 491.438	0		
31	-				15 491.683	0		
32	-				15 491.939	1		
33	-				15 492.197	1		
34	-				15 492.460	1		
35	-				15 492.728	1		
36	-				15 493.000	1		
37	-				15 493.274	1		
38	-				15 493.560	1		

[a] Observed minus calculated in 10^{-3} cm^{-1}

Lines marked with an asterisk are blended.

TABLE IV

$B^2\Sigma^+$–$X^2\Sigma^+$ Rotational Constants (cm^{-1})

v_B =	0	1	2	3	4
$B_v \times 10^2$	7.16292(19)	7.13135(34)	7.09543(35)	7.065704(66)	7.03562(36)
$D_v \times 10^8$	3.099(12)	3.069(27)	3.079(31)	3.100[b]	3.100[b]
γ_v	-0.140017(26)	-0.123334(40)	-0.108778(38)	-0.095699(83)	-0.084701(58)
$\gamma_{Dv} \times 10^6$	2.306(17)	2.250(25)	2.274(22)	1.981(41)	2.004(60)
v_X =	0	1	2	3	4
$B_v \times 10^2$	6.91928(19)	6.89300(19)	6.86814(33)	6.83842(33)	6.81461(19)
$D_v \times 10^8$ [c]	2.34	2.34	2.34	2.34	2.34
$\gamma_v \times 10^4$ [d]	56.01	55.70	55.39	55.08	54.77

Numbers in parentheses are 1σ uncertainties.

[a]The $B^2\Sigma^+$ constants are not deperturbed and must not be used for generation of potential energy curves.

[b]Fixed at the value for v' = 0 .

[c]Values calculated using program DHL (13).

[d]Values obtained from A-X fits for v''=0 and 1 and extrapolated for v''=2,3,4 using α_γ = -0.00031.

The B–X bands were also fit alone, since the simple $^2\Sigma$–$^2\Sigma$ energy level expressions adequately reproduce the spectra. However, the B-state constants are to be treated as effective parameters because of the strong $^2\Pi$ ~ $^2\Sigma^+$ interaction. These constants must never be used to derive RKR potentials.

A. $B^2\Sigma^+$–$X^2\Sigma^+$ *Analysis*

The most recent vibrational bandhead analysis was performed by Rao *et al.* (*3*), but they made several vibrational band misassignments. In addition, the parity assignment of the P_1 and P_2 bandheads was reversed.[2] Extreme spectral congestion rendered it virtually impossible to disentangle a head of heads that occurs in the $\Delta v = 1$ sequence. Also, small Franck–Condon factors (see Table II) for the (2, 0) and (3, 1) bands prevented their observation by nonlaser methods, and led to an incorrect absolute numbering of the bands in the $\Delta v = 2$ sequence. A list of measured bandheads appears in Table I.

Even in our initial laser excitation survey of bandheads, detecting total fluorescence, the heads belonging to the (2, 0) and (3, 1) bands were overlooked. The rapid decrease in Franck–Condon factors (Table II) with decreasing v'' level outweighs the increase in population. The weak (2, 0) and (3, 1) bands were buried

[2] Proper assignment of *e*/*f* parity (*15*) should have been possible on the basis of the known ordering of the A and B states in CaI. The presence of a $B^2\Sigma^+$ state to higher energy than the $A\,^2\Pi$ state suggests a negative value of the spin–rotation constant (γ). This information is sufficient to determine the correct parity assignments of the P_1 and P_2 heads using the standard energy level expressions (*6*, p. 222).

TABLE V

$B^2\Sigma^+$–$X^2\Sigma^+$ Band Origins (cm^{-1})[a]

(4,2)	16 189.694(2)	(1,2)	15 481.635(1)
(3,1)	16 191.213(1)	(2,3)	15 483.975(1)
(0,0)	15 716.750(1)	(3,4)	15 486.263(2)
(0,1)	15 479.257(1)		

Numbers in parentheses represent 1σ uncertainties.

[a]To be used only with the constants of Table IV.

under the stronger lines of other bands in the sequence. Our preliminary vibrational analysis suggested their presence. The bandheads were then located using excitation spectroscopy with narrow-bandpass detection of fluorescence, which eliminated most of the lines from the stronger bands of the sequence.

Rotational assignments were established by the standard method of combination differences between transitions from a common N' level. Measured line positions for the $\Delta v = 2$ [(4, 2), (3, 1)], 0 (0, 0) and −1 [(3, 4), (2, 3), (1, 2), (0, 1)] bands appear in Table III. Blended lines are marked with an asterisk. In most cases, blended lines arise from accidental overlap between transitions of similar N values in the same branch but belonging to different vibrational bands of the same sequence. The CaI bands were so severely overlapped that it was seldom possible to isolate a single branch.

A useful preliminary estimate of $\gamma' \sim -0.17$ cm^{-1} was supplied by the pure-precession relationship (*16*) with $l = 1$. The magnitude of γ' was thus expected to be 2 to 3 times larger than the rotational constant, B'. The very large γ' explained the sizable P_1, P_2 bandhead separations of Table I.

The B–X system was successfully fitted by the direct approach of Zare *et al.* (*8*), using standard $^2\Sigma^+$ matrix elements (*17*). However, in the initial fits, γ' and γ'' were badly correlated. In order to break this correlation, values for γ''_0 and γ''_1 were obtained from A–X fits (see Section IIIB). Values for γ''_v for $v = 2$ through $v = 4$ of the X state were then extrapolated and fixed in the fits of the B–X system. The B–X (0, 0) and (0, 1) bands were fitted together as were the (4, 2), (1, 2) and (3, 1), (3, 4) pairs of bands. The (2, 3) band was fitted alone. The rotational constants determined from the fits appear in Table IV. Seven band origins were determined from the B–X fits and appear in Table V. In the final fits the D'' values were fixed to the values computed using the program DHL of Albritton *et al.* (*18*). This program was found to give accurate values for the $X^2\Sigma^+$ state of CaBr (*11*).

Values of the rotational constants, B' and B'', as well as γ', were fitted by weighted least squares to the usual polynomials in $(v + 1/2)$ (*6*, p. 106) with

$$\gamma_v = \gamma_e + \alpha_\gamma(v + 1/2) + \gamma_\gamma(v + 1/2)^2. \quad (1)$$

The band origins of Table V were also fitted to the usual polynomial expression (*6*, p. 151). The results of these fits comprise a table of effective equilibrium mo-

TABLE VI

Equilibrium Molecular Constants for $B^2\Sigma^+$ and $X^2\Sigma^+$ States

	$X^2\Sigma^+$	$B^2\Sigma^+$
T_e	0.0	15 716.1713(30)
ω_e	238.7496(33)	239.9183(37)
$\omega_e x_e$	0.62789(64)	0.64985(79)
$B_e \times 10^2$	6.93254(84)	7.17916(116)
$\alpha_e \times 10^4$	2.640(35)	3.255(66)
$D_0 \times 10^8$	2.34[b]	3.099(12)
$\gamma_e^c \times 10^4$	56.17(9)[d]	-1 490.65(22)
$\alpha_\gamma^c \times 10^4$	-0.31(11)[d]	185.74(31)
$\gamma_\gamma^c \times 10^4$	--	-9.492(65)
R_e (Å)	2.8286	--

[a]B state values are effective constants that reproduce line positions. These constants must not be used to generate potential energy curves for the $B^2\Sigma^+$ state.

[b]Value calculated using program DHL (13).

[c]Spin-rotation expansion constants obtained from expression

$$\gamma_v = \gamma_e + \alpha_\gamma(v + \tfrac{1}{2}) + \gamma_\gamma(v + \tfrac{1}{2})^2 \quad .$$

[d]Value obtained from A-X fits for v'' = 0 and 1.

lecular constants (Table VI), in the sense that the A- and B-state interaction has destroyed the simple mechanical meaning of the B-state rotational and vibrational constants. The $B-X$ fits were made without consideration of contributions from electronic perturbation parameters, and hence do not remove these electronic contributions from the molecular constants. This problem will be discussed in the next section on the $A-X$ system. Note that the X-state constants of Table VI are free of perturbation effects and can be considered as mechanical constants.

The large vibrational dependence of γ' results from the increasing size of the nondiagonal Franck–Condon factors as v increases (Table II). This allows the interaction of vibrational levels of the $A\,^2\Pi$ state lying above a given v level of the B state to partially cancel the effects of the $A\,^2\Pi$ vibrational levels lying below this v.

B. $A\,^2\Pi-X\,^2\Sigma^+$ Analysis

The appearance of the $A-X$ band system of CaI is characteristic of a transition between a Hund's case (a) $^2\Pi$ state and a $^2\Sigma^+$ state. The Q_{2ef}, P_{21ee}, P_{2ff} and Q_{12ef}, P_{1ee}, P_{12ff} branches belonging to the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ subbands, respectively, all form bandheads shaded to the violet. Laser-induced fluorescence was observed in the (0, 0) and (1, 1) bands of the $\Delta v = 0$ sequence. The bandheads are listed in

TABLE VII

$A\,^2\Sigma$–$X\,^2\Sigma^+$ Bandheads (cm^{-1})

band	P_{12ff}	Q_{12ef} + P_{1ee} [a]	P_{2ff}	P_{21ee}	Q_{2ef}
(0,0)	15 572.87	15 588.53	15 637.66	15 647.12	15 647.35
(1,1)	15 578.16	15 592.71	15 640.59	15 650.01	15 650.22

Accuracy ±0.01 cm^{-1}.

[a] Q_{12ef} and P_{1ee} heads are overlapped.

Table VII. The large $^2\Pi \sim {}^2\Sigma^+$ interaction causes the Q_{12ef} and P_{1ee} heads to occur at very low J and hence prevents their resolution. Rotational assignments in the A–X system were made in the same fashion as in the B–X system, with the added advantage that good X-state constants were available. The measured line positions for the (0, 0) and (1, 1) bands appear in Table VIII.

Attempts were made to fit the A–X transitions using the standard $^2\Pi$ Hamiltonian with Λ-doubling parameters derived using the Van Vleck transformation (*17*). This approach was not successful because the $A\,^2\Pi_{3/2}$–$A\,^2\Pi_{1/2}$ separation of ~60 cm^{-1} is about the same size as the ~90-cm^{-1} $A\,^2\Pi$–$B\,^2\Sigma^+$ separation. The two spin components of the A state thus have significantly different separations from the $B\,^2\Sigma^+$ state. The usual definition of a single set of o, p, and q parameters for both spin components of the $A\,^2\Pi$ state is clearly not appropriate in the case of CaI. In addition, the $^2\Pi \sim {}^2\Sigma^+$ interaction is so large that $|p| \sim 2B$, thus an approach based on second-order perturbation theory will neither have the correct functional form nor provide physically meaningful parameters.

The Λ doubling was fitted by explicit introduction of perturbation matrix elements, η and ξ, that connect the $A\,^1\Pi$ and $B\,^2\Sigma^+$ states (*14*):

$$\eta_{vv'} = (1/2)\langle n^2\Pi v' | B(R) l_+ | n^2\Sigma^+ v\rangle, \tag{2a}$$

$$\xi_{vv'} = (1/2)\langle n^2\Pi v' | A(R) l_+ | n^2\Sigma^+ v\rangle. \tag{2b}$$

The interaction matrix elements are

$$\begin{aligned} H(^2\Pi_{1/2}, {}^2\Sigma^+) &= \xi - \eta(J - 1/2) \qquad (e) \\ &= \xi + \eta(J + 3/2) \qquad (f), \end{aligned} \tag{3}$$

$$H(^2\Pi_{3/2}, {}^2\Sigma^+) = -\eta[J^2 + J - 3/4]^{1/2}. \tag{4}$$

Since the A- and B-state potential curves are similar, the interaction is approximately diagonal in v for $v = 0$ and 1. Thus the major portion of the Λ doubling of $v = 0$ of the A state results from $v = 0$ of the B state, so the (0, 0) A–X and B–X bands were fitted together. Similarly, the (1, 1) A–X and (1, 2) B–X bands [the (1, 1) B–X band was not analyzed] were fitted together.

It was found that ξ was badly correlated with T_Σ, T_Π (band origins), A, and η and so could not be independently determined. Equations (2) suggest that

TABLE VIIIa

Observed Transitions in $A\,^2\Pi_{1/2}-X\,^2\Sigma^+$ (0, 0) Subband (cm^{-1})

J	R_{1ee}	$\Delta\nu$[a]	R_{12ff}	$\Delta\nu$	Q_{1fe}	$\Delta\nu$	P_{12ff}	$\Delta\nu$
6.5	-		-				15 586.764	-8
7.5	-		-				15 586.500	-7
8.5	-		-		-		15 586.239	-5
9.5	-		-		-		15 585.979	-4
10.5	-		-		-		15 585.720	-4
11.5	-		-		-		15 585.466	-3
12.5	15 592.595	-4	-		-		15 585.216	0
13.5	15 592.912	-3	-		-		15 584.963	-2
14.5	15 593.231	-4*	-		-		15 584.711	-6
15.5	15 593.558	2	-		-		15 584.463	-8
16.5	15 593.881	1	-		-		15 584.221	-7
17.5	15 594.206	0	-		-		-	
18.5	15 594.529	-5	-		-		-	
19.5	15 594.862	-3	-		-		-	
20.5	15 595.196	-2	-		-		-	
21.5	15 595.532	-2	-		-		15 583.045	-4*
22.5	15 595.870	-2	15 589.147	4	-		15 582.819	-2
23.5	15 596.212	0	15 589.203	4	-		15 582.593	-2
24.5	-		15 589.257	1	15 589.063	1	15 582.369	-3
25.5	-		15 589.318	1	15 589.113	-1	15 582.149	-2
26.5	15 597.245	0	15 589.382	1	15 589.168	-1	15 581.931	-2
27.5	15 597.595	0	15 589.443	-4	15 589.226	-1	15 581.715	-3
28.5	15 597.946	-1	15 589.513	-2	15 589.287	0	15 581.502	-2
29.5	15 598.299	-1	15 589.585	-1	15 589.348	-2	15 581.288	-6
30.5	15 598.656	-1	15 589.658	-1	15 589.418	-3	15 581.082	-4
31.5	15 599.015	0	15 589.736	1	15 589.483	0	15 580.877	-3
32.5	15 599.378	2	15 589.814	0	15 589.555	2	15 580.676	-2
33.5	-		15 589.895	0	15 589.624	-2	15 580.476	-2
34.5	15 600.105	1	15 589.977	0	15 589.700	-1	15 580.279	-1
35.5	15 600.475	3	15 590.066	2	15 589.779	0	-	
36.5	15 600.843	1	15 590.152	0	15 589.858	-2	-	
37.5			15 590.243	-1	15 589.942	-1	-	
38.5	15 601.593	5	15 590.339	2	15 590.028	1	-	
39.5	15 601.965	0	15 590.434	1	15 590.113	-2	-	
40.5	15 602.344	0	15 590.534	3	15 590.208	2	-	
41.5	15 602.725	0	15 590.635	2	15 590.305	6	-	
42.5	15 603.109	1	15 590.739	3	15 590.393	-1	15 578.788	-3*
43.5	15 603.497	4*	15 590.844	2	15 590.492	0	15 578.613	-3*
44.5	-		15 590.951	0	15 590.592	-1	15 578.441	-3*
45.5	-		15 591.063	1	15 590.693	-3	15 578.272	-2*
46.5	-		15 591.177	1	15 590.800	-2	15 578.105	-2
47.5	-		15 591.295	3	15 590.910	0	15 577.941	-2
48.5	-		15 591.413	1	15 591.022	1	15 577.782	0
49.5	-		15 591.534	1	15 591.136	2	15 577.624	2
50.5	-		15 591.658	1	15 591.250	0	15 577.468	2
51.5	-		15 591.784	1	15 591.369	1	15 577.314	2
52.5	-		15 591.914	2	15 591.490	11	15 577.164	3
53.5	-		15 592.043	-1	15 591.613	0	15 577.016	4
54.5	-		15 592.176	-1	15 591.739	1	15 576.872	5
55.5	-		15 592.311	-3	15 591.868	1	-	
56.5	-		15 592.451	-2	15 591.995	-3	15 576.588	6
57.5			15 592.594	-1	15 592.128	-4	15 576.449	5
58.5	-		15 592.739	-1	15 592.265	-3	15 576.314	6
59.5	-		15 592.885	-1	15 592.401	-5	15 576.180	5
60.5			15 593.036	0	15 592.545	-2	15 576.050	5
61.5	-		15 593.186	-2	15 592.689	-3	15 575.921	5
62.5	-		15 593.341	-2	15 592.836	-2	15 575.798	6
63.5	-		15 593.497	-2	15 592.986	-1	15 575.672	3
64.5	-		15 593.657	-2	15 593.137	1	15 575.553	5
65.5	-		-		15 593.289	-3	15 575.436	4
66.5	-		-		15 593.447	-2	15 575.324	7
67.5			-		15 593.605	-3	15 575.211	6
68.5	-		15 594.320	-2			15 575.104	8
69.5	-		15 594.492	-3	-		15 574.999	10
70.5	-		15 594.668	-2	-		15 574.894	9
71.5	-		15 594.844	-3	15 594.765	-4	-	
72.5	-		15 595.027	0	15 594.438	-3	-	
73.5	-		15 595.215	5	15 594.613	-3	-	
74.5	-		15 595.401	6	15 594.790	-2	-	
75.5	-		15 595.585	2	15 594.971	-1	-	
76.5	-		15 595.781	8	15 595.156	2	-	
77.5	-		15 595.972	7	15 595.344	5		
78.5	-		-		15 595.533	8	15 574.142	4
79.5			-		15 595.723	8	15 574.039	5
80.5	-		-		15 595.915	8	15 573.982	-5
81.5	-		-		15 596.110	8	15 573.909	-2
82.5	-		-				15 573.833	-6
83.5					-		15 573.765	4
84.5	-		-				15 573.698	-4
85.5	-		15 597.603	5	-		15 573.633	-4
86.5	-		15 597.817	3			15 573.569	6
87.5	-		15 598.037	5			15 573.510	4
88.5	-		15 598.256	3	15 597.542	5	15 573.454	4
89.5	-		15 598.478	2	15 597.757	6	15 573.402	-2
90.5	-		15 598.703	2	15 597.974	5	15 573.455	2
91.5	-		15 598.931	1	15 598.192	3	15 573.305	1
92.5	-		15 599.161	0	15 598.414	4	15 573.258	0
93.5			15 599.393	-1	15 598.639	2	15 573.214	0
94.5			15 599.629	-1	15 598.867	2	15 573.174	1
95.5	-		15 599.867	-1	15 599.095	0	15 573.135	0
96.5	-		-		15 599.329	0	15 573.098	-2
97.5	-		15 600.350	-2	15 599.563	0	15 573.066	0
98.5	-		15 600.595	4	15 599.801	0	15 573.034	-2
99.5			15 600.844	3	-		15 573.005	3
100.5	-		15 601.101	3	15 600.281	-3		
101.5	-		15 601.353	1	15 600.529	-1	-	
102.5	-		15 601.610	2	15 600.776	-2	-	
103.5	-		15 601.867	1	15 601.033	4	-	
104.5	-		15 602.125	3	15 601.286	4	-	
105.5			15 602.386	-5	15 601.540	3		
106.5			15 602.655	-3	15 601.799	3	-	
107.5			15 602.922	-5	15 602.056	0	-	
108.5			15 603.191	-7	15 602.318	-1	-	
109.5	-		15 603.465	-7	15 602.586	1	-	
110.5			-		15 602.851	-1		
111.5			-		15 603.124	-1		
112.5	-		-		15 603.394	-3	-	

[a] Observed minus calculated in 10^{-3} cm^{-1}.

Lines marked with an asterisk are blended.

TABLE VIIIb

Observed Transitions in $A^2\Pi_{3/2}-X^2\Sigma^+$ (0, 0) Subband (cm^{-1})

J	R_{21ee}	$\Delta\nu$[a]	R_{2ff}	$\Delta\nu$	Q_{21fe}	$\Delta\nu$	P_{2ff}	$\Delta\nu$
2.5	-		15 648.929	8	-		-	
3.5	-		15 649.007	7	15 648.906	5	-	
4.5	-		15 649.092	10	15 648.980	4	-	
5.5	15 649.963	1	15 649.172	7	15 649.055	3	-	
6.5	15 650.180	1	15 649.259	8	15 649.135	5	15 647.295	7
7.5	15 650.403	4	15 649.343	6	15 649.211	2	-	
8.5	15 650.622	1	15 649.433	6	15 649.296	6	15 646.909	5
9.5	15 650.844	1	15 649.525	8	15 649.378	5	15 646.718	4
10.5	15 651.070	2	15 649.618	9	15 649.461	3	-	
11.5	15 651.296	2	15 649.713	9*	15 649.548	4	-	
12.5	15 651.526	3	15 649.812	13*	15 649.636	2	15 646.158	7
13.5	15 651.753	1	15 649.908	11*	15 649.728	4*	15 645.973	-1
14.5	15 651.985	1	15 650.004	7*	15 649.813	-3*	15 645.792	-1
15.5	15 652.218	1	15 650.100	2*	15 649.909	-1*	15 645.613	-1
16.5	15 652.452	0	15 650.203	2*	15 650.004	-1*	15 645.437	0
17.5	15 652.689	0	15 650.305	-1*	15 650.102	-1*	15 645.262	1
18.5	-		15 650.404	-6*	15 650.204	2*	15 645.088	0
19.5	15 653.163	-4	15 650.514	-7*	15 650.305	2*	15 644.917	0
20.5	15 653.406	-4	-		15 650.406	0*	15 644.747	0
21.5	15 653.649	-3	15 650.747	3	15 650.514	3*	15 644.578	1
22.5	15 653.893	-5	15 650.864	6	15 650.626	7*	15 644.413	0
23.5	15 654.144	-1	15 650.978	4	15 650.731	4*	15 644.247	-2
24.5	15 654.391	-3	15 651.096	4	15 650.841	4	15 644.084	-2
25.5	15 654.645	1	15 651.214	3	15 650.951	2	15 643.923	-3
26.5	15 654.897	1	15 651.336	3	15 651.064	1	15 643.765	-2
27.5	15 655.147	-3	15 651.459	2	15 651.179	0	15 643.608	-3
28.5	15 655.395	-10	15 651.583	1	15 651.298	1	15 643.455	-2
29.5	15 655.653	-10	15 651.712	3	15 651.416	-1	15 643.305	2
30.5	15 655.912	-9	15 651.840	3	15 651.534	-4	15 643.152	0
31.5	15 656.175	-7	15 651.974	6	15 651.663	2	15 643.002	-2
32.5	15 656.435	-10	15 652.104	3	15 651.789	3	15 642.855	-1
33.5	15 656.701	-7	15 652.239	3	15 651.915	2	15 642.710	-1
34.5	-		15 652.374	1	15 652.043	0	15 642.567	0
35.5	-		15 652.513	2	15 652.173	-1	15 642.425	-1
36.5	-		15 652.652	1	15 652.309	3	15 642.285	-1
37.5	-		15 652.795	2	15 652.441	-1	15 642.147	-2
38.5	-		15 652.939	1	15 652.576	-1	15 642.008	-5
39.5	-		15 653.084	0	15 652.715	-1	15 641.875	-5
40.5	-		15 653.232	0	15 652.856	-1	15 641.744	-4
41.5	-		15 653.380	-1	15 652.998	-2	15 641.613	-5
42.5	-		15 653.532	-2	15 653.142	-2	15 641.487	-4
43.5	-		15 653.687	0	15 653.287	-3	15 641.362	-3
44.5	-		15 653.844	0	15 653.436	-2	-	
45.5	-		15 654.002	1	15 653.585	-3	15 641.114	-5
46.5			15 654.162	2	15 653.738	-3	15 640.994	-6
47.5	-		15 654.323	1	15 653.893	-1	15 640.877	-5
48.5	-		15 654.487	1	15 654.050	-1	15 640.761	-5
49.5	-		15 654.652	0	15 654.209	0	15 640.648	-5
50.5	-		15 654.818	-1	15 654.367	-2	15 640.536	-4
51.5			15 654.989	1	15 654.530	-1	15 640.426	-5
52.5	-		15 655.159	-1	15 654.693	-1	15 640.319	-5
53.5	-		15 655.332	2	15 654.858	-2	15 640.214	4
54.5	-		15 655.508	-1	15 655.026	-2	15 640.111	-4
55.5	-		15 655.684	-3	15 655.195	-3	15 640.010	3
56.5	-		15 655.863	-3	15 655.365	-5	15 639.909	-5
57.5	-		15 656.048	0	15 655.539	5	15 639.812	3
58.5	-		15 656.233	2	15 655.715	-5	15 639.717	-3
59.5	-		15 656.419	2	15 655.894	-4	15 639.622	5
60.5	-		15 656.604	0	15 656.077	-1	15 639.533	-3
61.5			15 656.795	1	15 656.258	-2	15 639.442	-5
62.5	-		-		15 656.441	-2	15 639.354	-6
63.5			-		15 656.627	-3	15 639.270	5
64.5	-		-		-		15 639.189	-3
65.5	-		-		-		15 639.109	-3
66.5			-		15 657.202	2*	15 639.028	-5
67.5					15 657.398	3*	15 638.953	-4
68.5	-		-		15 657.591	1*	15 638.878	-4
69.5			-		15 657.790	1*	15 638.806	4
70.5	-		-		15 657.990	1*	15 638.737	-3
71.5					15 658.193	1*	15 638.669	3
72.5			-		15 658.398	2*	15 638.606	0
73.5			-		15 658.603	0*	15 638.544	1
74.5					-		15 638.483	2
75.5	-		-				15 638.425	4
76.5	-		-		-		15 638.366	2
77.5	-				-		15 638.314	4
78.5	-		-		-		15 638.258	1
79.5	-		-		-		15 638.211	5
80.5			-		-		15 638.161	4
81.5	-		-				15 638.115	4
82.5	-		-		-		15 638.070	3
83.5	-		-		-		15 638.030	5
84.5			-		-		15 637.991	6
85.5	-		-				15 637.955	7
86.5	-		-				15 637.919	6
87.5	-		-				15 637.888	7
88.5					-		15 637.856	6
89.5	-		-		-		15 637.826	5
90.5	-				-		15 637.802	7
91.5			-				15 637.779	8

[a] Observed minus calculated in 10^{-3} cm^{-1}.

Lines marked with an asterisk are blended.

TABLE VIIIc

Observed Transitions in $A^2\Pi_{1/2}-X^2\Sigma^+$ (1, 1) Subband (cm^{-1})

J	R_{1ee}	$\Delta\nu$[a]	Q_{1fe}	$\Delta\nu$	R_{12ff}	$\Delta\nu$	P_{12ff}	$\Delta\nu$
15.5	15 597.516	-4	-		-		15 588.757	0*
16.5	15 597.825	-7	-		-		15 588.526	2*
17.5	15 598.144	-4	-		-		15 588.289	-3
18.5	15 598.462	-4	15 593.246	-12*	-		-	
19.5	15 598.781	-4	15 593.299	-14*	-		-	
20.5	15 599.104	-4	15 593.356	-14*	-		15 587.609	-5
21.5	15 599.430	-3	15 593.416	-13*	15 593.246	-4*	15 587.389	-4
22.5	-		15 593.477	-13*	15 593.299	-5*	15 587.171	-4
23.5	15 600.091	3*	15 593.544	-11*	15 593.356	-4*	15 586.954	-5
24.5	15 600.422	3	15 593.613	-9*	15 593.416	-2*	15 586.742	-3
25.5	15 600.755	2	15 593.682	-9*	15 593.477	-3*	15 586.531	-3
26.5	15 601.092	3	15 593.759	-5*	15 593.544	0*	15 586.324	-1
27.5	15 601.429	2	15 593.832	-5*	15 593.613	3*	15 586.120	0
28.5	15 601.770	2	15 593.910	-5*	15 593.682	3*	15 585.918	2
29.5	15 602.116	6*	15 593.991	-4*	15 593.759	8*	15 585.716	0
30.5	15 602.460	5	-		15 593.832	8*	15 585.519	1
31.5	15 602.807	5	15 594.150	-11*	15 593.910	9*	15 585.325	3
32.5	15 603.156	6	15 594.238	-10*	15 593.991	10*	15 585.130	1
33.5	15 603.506	4	15 594.325	-12*	-		15 584.941	3
34.5	-		15 594.426	-4*	15 594.150	4*	15 584.756	6
35.5	-		15 594.522	-3*	15 594.238	6*	-	
36.5	-		15 594.619	-3*	15 594.325	4*	15 584.381	-2
37.5	-		15 594.719	-3*	15 594.416	3*	15 584.199	-3
38.5	-		15 594.824	-1*	15 594.509	2*	15 584.024	-1
39.5	-		15 594.928	-1	15 594.608	4*	15 583.848	-2
40.5	-		15 595.035	-1	15 594.707	3*	-	
41.5	-		15 595.146	-1	15 594.807	1*	-	
42.5	-		15 595.256	-3	15 594.913	4	-	
43.5	-		15 595.372	-3	15 595.021	4	15 583.174	-2
44.5	-		15 595.490	-2	15 595.129	3	15 583.014	0
45.5	-		15 595.612	0	15 595.240	2	15 582.856	2
46.5	-		15 595.735	-1	15 595.355	2	15 582.698	1
47.5	-		15 595.861	0	15 595.471	0	15 582.544	1
48.5	-		15 595.987	-2	15 595.592	2	15 582.394	2*
49.5	-		15 596.118	-1	15 595.713	0	15 582.245	2
50.5	-		15 596.252	0	15 595.836	-2	15 582.100	4
51.5	-		15 596.386	-2	15 595.963	-2	15 581.957	4*
52.5	-		15 596.525	-1	15 596.096	0	15 581.817	5
53.5	-		-		15 596.228	0	15 581.677	4
54.5	-		-		15 596.363	0	15 581.542	4
55.5	-		-		15 596.501	0	15 581.410	5
56.5	-		-		-		15 581.290	16*
57.5	-		-		-		15 581.153	6
58.5	-		15 597.413	2	-		15 581.026	5
59.5	-		15 597.568	1	-		15 580.897	-17*
60.5	-		15 597.728	2	-		15 580.783	4
61.5	-		15 597.890	3	-		15 580.666	4*
62.5	-		15 598.053	2	15 597.540	1	15 580.551	4
63.5	-		15 598.222	3	15 597.698	0	-	
64.5	-		15 598.389	2	15 597.860	1	15 580.331	5
65.5	-		15 598.559	0	15 598.024	1	15 580.223	4
66.5	-		15 598.734	0	15 598.191	2	-	
67.5	-		15 598.914	2	15 598.358	0	-	
68.5	-		15 599.094	3	15 598.529	0	-	
69.5	-		15 599.276	3	15 598.704	0	-	
70.5	-		15 599.459	0	15 598.881	0	-	
71.5	-		-		15 599.062	1	-	
72.5	-		-		15 599.241	-1	-	
73.5	-		-		15 599.428	1	-	
74.5	-		-		15 599.615	1	-	
75.5	-		15 600.425	3	-		-	
76.5	-		15 600.625	2	-		-	
77.5	-		15 600.827	1	-		-	
78.5	-		15 601.033	2	15 600.390	1	-	
79.5	-		15 601.239	-1	15 600.590	1	-	
80.5	-		15 601.451	0	15 600.792	1	-	
81.5	-		15 601.663	-2	15 600.998	1	-	
82.5	-		15 601.879	-1	15 601.205	0	-	
83.5	-		15 602.098	-2	15 601.414	-2	-	
84.5	-		15 602.318	-3	15 601.626	-2	-	
85.5	-		15 602.543	-2	15 601.843	-1	-	
86.5	-		15 602.769	-2	15 602.061	-1	-	
87.5	-		15 602.997	-3	15 602.281	-2	-	
88.5	-		15 603.228	-4	15 602.505	-2	-	
89.5	-		15 603.461	-5	15 602.730	-3	-	
90.5	-		-		15 602.960	-2	-	
91.5	-		-		15 603.190	-3	-	
92.5	-		-		15 603.424	-3	-	

[a] Observed minus calculated in 10^{-3} cm^{-1}.

Lines marked with an asterisk are blended.

TABLE VIIId

Observed Transitions in $A^2\Pi_{3/2}-X^2\Sigma^+$ (1, 1) Subband (cm^{-1})

J	R_{21ee}	$\Delta\nu^a$	R_{2ff}	$\Delta\nu$	Q_{21fe}	$\Delta\nu$	P_{2ff}	$\Delta\nu$
9.5	15 653.674	4	-		-		-	
10.5	15 653.898	3	-		-		-	
11.5	15 654.125	5	-		-		-	
12.5	15 654.346	-2	-		-		-	
13.5	15 654.578	1	-		-		-	
14.5	15 654.810	1	-		-		-	
15.5	15 655.043	2	-		-		-	
16.5	15 655.277	1	-		-		-	
17.5	15 655.513	1	-		-		-	
18.5	15 655.750	-1	-		-		-	
19.5	15 655.990	-1	-		-		-	
20.5	15 656.232	0	-		-		-	
21.5	15 656.475	0	-		-		-	
22.5	15 656.720	-1	-		-		15 647.270	2
23.5	-		-		-		-	
24.5	15 657.216	0	15 653.929	6	-		15 646.947	3
25.5	15 657.466	0	15 654.049	6	-		15 646.786	2
26.5	15 657.716	-2	15 654.169	4	15 653.899	4	15 646.629	3
27.5	15 657.970	-3	15 654.292	5	15 654.014	3	15 646.470	-1
28.5	-		15 654.417	5	15 654.132	4	15 646.315	-2
29.5	-		15 654.544	4	15 654.251	3	15 646.164	-2
30.5	-		15 654.672	3	15 654.372	2	15 646.015	-1
31.5	-		15 654.804	4	15 654.494	1	15 645.865	-2
32.5	-		15 654.936	4	15 654.622	4	15 645.721	-1
33.5	-		15 655.071	3	15 654.747	1	-	
34.5	-		15 655.206	2	15 654.877	2	-	
35.5	-		15 655.341	-1	15 655.010	4	15 645.294	0
36.5	-		15 655.481	-1	15 655.141	2	15 645.155	-1
37.5	-		15 655.624	-1	15 655.271	-3	15 645.019	-1
38.5	-		15 655.769	0	15 655.408	-3	15 644.884	-1
39.5	-		15 655.914	-2	15 655.546	-3	15 644.752	-1
40.5	-		15 656.065	2	15 655.688	-2	15 644.619	-3
41.5	-		15 656.217	3	15 655.831	-2	15 644.490	-4
42.5	-		15 656.363	-2	15 655.977	0	15 644.362	-5
43.5	-		15 656.521	2	15 656.124	1	15 644.237	-6
44.5	-		15 656.678	3	15 656.272	1	15 644.114	-6
45.5	-		-		15 656.423	1	15 643.994	-5
46.5	-		-		15 656.574	1	15 643.876	-4
47.5	-		-		15 656.728	1	15 643.762	-2
48.5	-		15 657.320	3	-		15 643.646	-3
49.5	-		15 657.484	1	-		15 643.533	-3
50.5	-		15 657.650	1	15 657.202	0	15 643.422	-3
51.5	-		15 657.820	0	15 657.364	0	15 643.308	-9
52.5	-		15 657.993	1	15 657.528	0	15 643.209	-1
53.5	-		15 658.165	0	15 657.693	0	15 643.102	-4
54.5	-		15 658.339	-2	15 657.861	0	15 643.001	-2
55.5	-		15 658.515	-3	15 658.031	0	15 642.900	-2
56.5	-		15 658.695	-2	15 658.200	-3	15 642.802	-2
57.5	-		-		15 658.374	-3	15 642.707	0
58.5	-		-		15 658.550	-3	15 642.610	-3
59.5	-		-		15 658.728	-3	15 642.517	-3
60.5	-		-		-		15 642.429	2
61.5	-		-		-		15 642.341	-1
62.5	-		-		-		15 642.255	-1
63.5	-		-		-		15 642.170	-2
64.5	-		-		-		15 642.085	-5
65.5	-		-		-		15 642.007	-4
66.5	-		-		-		15 641.929	-3
67.5	-		-		-		15 641.852	-5
68.5	-		-		-		15 641.781	-2
69.5	-		-		-		15 641.708	-3
70.5	-		-		-		15 641.639	-3
71.5	-		-		-		15 641.575	0
72.5	-		-		-		15 641.508	-1
73.5	-		-		-		15 641.445	-2
74.5	-		-		-		15 641.385	-1
75.5	-		-		-		15 641.327	0
76.5	-		-		-		15 641.269	-1
77.5	-		-		-		15 641.215	-1
78.5	-		-		-		15 641.163	-1
79.5	-		-				15 641.113	-1
80.5	-		-		-		15 641.066	1
81.5	-		-		-		15 641.019	0
82.5	-		-		-		15 640.977	1
83.5			-		-		15 640.937	3
84.5	-		-		-		15 640.895	1
85.5	-		-		-		15 640.862	5
86.5	-		-		-		15 640.827	5
87.5	-		-		-		15 640.794	5
88.5	-		-				15 640.764	6
89.5	-		-		-		15 640.737	7
90.5	-		-		-		15 640.713	10

[a] Observed minus calculated in 10^{-3} cm^{-1}.

Lines marked with an asterisk are blended.

TABLE IX

Deperturbed A–X, B–X Constants (cm^{-1})

	v=	0	1	2
$B^2\Sigma^+$	$B_v \times 10^2$	7.13747(93)	7.09797(176)	--
	$D_v \times 10^8$	2.344(24)	2.054(35)	--
Interaction Matrix Elements	$\eta_v \times 10^2$	6.2311(10)	5.7758(12)	--
	$\eta_{Dv} \times 10^7$	-1.72(23)	-9.32(49)	--
	ξ_v^a	40.4828	37.8377	--
	$\xi_{Dv} \times 10^4$	0.39(11)	2.03(24)	--
$A^2\Pi$	$B_v \times 10^2$	7.03523(45)	7.01369(93)	--
	$D_v \times 10^8$	2.401(11)	2.604(15)	--
	A_v	45.7075(29)	46.0860(32)	--
	$A_{Dv} \times 10^5$	-1.18(43)	-8.72(87)	--
	$p \times 10^2$	-1.3674(38)	-1.1475(56)	--
$X^2\Sigma^+$	$B_v \times 10^2$	6.91827(17)	6.89192(25)	6.86926(33)
	$D_v \times 10^8$	2.34[b]	2.34[b]	2.34[b]
	$\gamma_v \times 10^4$	56.007(69)	55.698(81)	55.35[c]

Numbers in parentheses refer to 1σ uncertainties.

[a]Determined by the approximate expression $\xi = \frac{1}{2}\langle A\ell_+\rangle \sim A\eta/B_\Pi$.

[b]Fixed at values determined by program DHL (13) .

[c]Fixed at a value linearly extrapolated from v'' = 0 and 1 levels.

$$\xi_v \approx A_v \frac{\langle v(^2\Pi)\,|\,v(^2\Sigma^+)\rangle}{\langle v(^2\Pi)\,|B\,|\,v(^2\Sigma^+)\rangle}\,\eta_v, \tag{5}$$

where A is the $A^2\Pi$ spin–orbit constant. The $\langle v(^2\Pi)\,|B\,|\,v(^2\Sigma)\rangle/\langle v(^2\Pi)\,|\,v(^2\Sigma)\rangle$ ratio of vibrational integrals was computed from the vibrational wavefunctions. The ratio was found to be within 1% of B_Π, so

$$\xi_v \approx \frac{A_v}{B_{v\Pi}}\,\eta_v. \tag{6}$$

In subsequent fits, the parameter ξ was fixed at the value determined from Eq. (6). This procedure removed the correlation between ξ and the origins as well as between ξ and η. While η and ξ account for most of the interaction between the A and B states, there still exists a nonnegligible interaction with other ($\Delta v \neq 0$) vibrational levels. This is especially true for $v > 0$, because the Franck–Condon factors become increasingly nondiagonal as v increases.

TABLE X

Deperturbed Band Origins (cm^{-1})

(v',v'')	$A^2\Pi - X^2\Sigma^+$	$B^2\Sigma^+ - X^2\Sigma^+$
(0,0)	15 625.905(2)	15 702.326(3)
(1,1)	15 628.549(2)	15 705.124(3)

Numbers in parentheses are 1σ uncertainties.

Residual p and γ parameters must be inserted into the Hamiltonian to account for the remaining interactions with $\Delta v \neq 0$. However, strong correlation between p and γ prevents their simultaneous variation. This correlation was artificially broken by setting γ(residual) to zero. Consequently, η, ξ, and p(residual) are effective parameters that have accomodated the small interaction parametrized by γ(residual). The results of this direct interaction fit are the deperturbed constants of Table IX.

It was found necessary to include distortion terms in the interaction parameters:

$$\eta_v(\text{eff}) = \eta_v + \eta_{Dv}J(J + 1), \tag{7a}$$

$$\xi_v(\text{eff}) = \xi_v + \xi_{Dv}J(J + 1). \tag{7b}$$

Band origins determined from the rotational fits are presented in Table X. The difference between the deperturbed (0, 0) band origin and the effective band origin in the B–X transition would correspond to the value of the parameter o^Σ (*8*), had a second-order perturbation theory approach been possible.

The values of B_0 and B_1 in the A and B states, determined from the combined A–X, B–X fits, allowed determination of "true" mechanical constants, free of electronic perturbation. The results are shown in Table XI. The rotational constant α_e was determined from B_0 and B_1, and used to determine the vibrational constant $\omega_e x_e$ from the Pekeris relationship (*6*). The ground-state constants (ω''_e and $\omega''_e x''_e$) and the (0, 0) and (1, 1) band origins determined from the combined fits allowed determination of values for $\Delta G'_{1/2}$ and then ω'_e using $\omega'_e x'_e$ (Pekeris). T_e values were then obtained from the standard expression containing T_0, ω_e, and $\omega_e x_e$:

$$T_0 = T_e + \frac{\omega'_e}{2} - \frac{\omega'_e x'_e}{4} - \frac{\omega''_e}{2} + \frac{\omega''_e x''_e}{4}. \tag{8}$$

The deperturbation of the A and B states can account for a puzzling feature of the Λ doubling of the $A^2\Pi$ state. For CaI, the e Λ component is higher in energy than the f component of the $^2\Pi_{1/2}$ spin component, as expected, but f is higher than e in the $^2\Pi_{3/2}$ component. For CaF and CaBr (*10, 11*), e is higher than f in both $A\,^2\Pi_{1/2}$ and $A\,^2\Pi_{3/2}$ spin components. When o, p, and q are used to try to fit the Λ doubling of CaI $A\,^2\Pi$, p is negative but q is positive. This is disconcerting, because examination of the summation definitions of p and q, derived using the Van Vleck transformation, indicate that p and q must have the same sign (*8*). The direct perturbation approach accounts for the unusual Λ-doubling pattern with physically reasonable values of η and ξ.

TABLE XI

Deperturbed Equilibrium Molecular Constants for $A\,^2\Pi$ and $B\,^2\Sigma^+$ States

	$A^2\Pi$	$B^2\Sigma^+$
T_e [a]	15 624.67(5)	15 700.52(12)
ω_e [a]	241.19(7)	242.63(17)
$\omega_e x_e$ (Pekeris)	0.53(5)	1.17(12)
$B_e \times 10^2$	7.0460(14)	7.1572(22)
$\alpha_e \times 10^4$	2.15(10)	3.95(20)
$D_0 \times 10^8$	2.40(1)	2.34(2)
R_e (Å)	2.8057(3)	2.7839(4)

Deperturbed constants for $X^2\Sigma^+$ are in Table VI. Numbers in parentheses are 1σ uncertainties.

[a]Determined using $\omega_e' x_e'$ (Pekeris) which was assumed to have an uncertainty of 10%.

The deperturbation of the $A-X$ and $B-X$ transitions is not entirely satisfactory. The obs. − calc. column of Table VIII is not completely random, although the variance of the fits indicate that lines are fitted to within their estimated experimental error. In addition, the vibrational variation of several parameters, η, η_D, ξ, and ξ_D, in particular, seems unrealistically large (Table IX). These problems result from inclusion of only a single pair of $^2\Pi$, $^2\Sigma^+$ vibrational levels in the effective Hamiltonian matrix. The magnitudes of the perturbation parameters, however, seem reasonable in the sense that $\eta/\eta_D \approx B/D$ and $|\xi/\xi_D| \approx A/A_D$.

C. CaI Orbital Character

The interaction matrix elements η and ξ provide some insight into the orbital composition of the $A\,^2\Pi$ and $B\,^2\Sigma^+$ states. It is possible to define a nonintegral l_{eff}

$$\frac{2\eta}{B_\Pi} = (l_{\text{eff}}(l_{\text{eff}} + 1))^{1/2} \tag{9}$$

that characterizes the $^2\Pi \sim {}^2\Sigma^+$ interaction. If the molecular orbitals are M_L components of pure atomic orbitals, then l_{eff} will have integer values and the states are said to be in pure precession. Note that the converse of this statement is not necessarily true (*20*).

For CaI, $l_{\text{eff}} = 1.35$, indicating some d character in the A and B states. This value of l_{eff} can be combined with the ratio of the $A-X$ and $B-X$ transition dipole moments (*19*) to estimate the excited-state molecular orbital composition (*20*). The results are that the $A\,^2\Pi$ state is 70% $4p\pi$ (Ca^+) and 30% $3d\pi$ (Ca^+) while the $B\,^2\Sigma^+$ state is 57% $4p\sigma$ (Ca^+) and 43% $3d\sigma$ (Ca^+). The A- and B-state mixing coefficients can be used to estimate a more accurate value of ξ, the off-diagonal $^2\Pi-{}^2\Sigma^+$ spin–

orbit matrix element. The A- and B-state wavefunctions are written as

$$\psi(B^2\Sigma^+) = e\,|4p\sigma\,(\mathrm{Ca}^+)\rangle - (1 - e^2)^{1/2}\,|3d\sigma\,(\mathrm{Ca}^+)\rangle,$$
$$\psi(A^2\Pi) = f\,|4p\pi\,(\mathrm{Ca}^+)\rangle - (1 - f^2)^{1/2}\,|3d\pi\,(\mathrm{Ca}^+)\rangle. \tag{10}$$

The diagonal spin–orbit interaction is given by

$$A = f^2\zeta_{4p} + (1 - f^2)\zeta_{3d}. \tag{11}$$

With $\zeta_{4p}/\zeta_{3d} = 6.1$, determined from the Ca^+ atom, $A = 45.7\ \mathrm{cm}^{-1}$ for CaI, and mixing fractions 0.70 ($4p$) and 0.30 ($3d$), then $\zeta_{4p} = 61$ and $\zeta_{3d} = 10\ \mathrm{cm}^{-1}$. The $\mathbf{AL}\cdot\mathbf{S}$ operator acting between the $A^2\Pi$ and $B^2\Sigma^+$ states gives

$$\xi = \frac{1}{2}\langle Al_+\rangle = \frac{2^{1/2}}{2}ef\zeta_{4p} + \frac{6^{1/2}}{2}(1 - e^2)^{1/2}(1 - f^2)^{1/2}\zeta_{3d}. \tag{12}$$

This leads to $\xi = 31\ \mathrm{cm}^{-1}$, which is 22% smaller than the value of 40 cm^{-1} provided by Eq. (6).

The value of ξ calculated using Eq. (12) is different from that obtained from Eq. (6) because the A and B states are not pure p or d states. Experimentally, the two values cannot be distinguished because the variance of the fit is insensitive to the magnitude of ξ. For instance, changing ξ to 36 cm^{-1} changes the variance by less than 10%.

The values of p(res) and γ(res), due to interaction with $\Delta v \neq 0$, can be estimated from the values of η and ξ ($v = 0$), $\langle v'(^2\Sigma)|\,v'(^2\Pi)\rangle$, and $B_{\Sigma\Pi}$. In particular, retaining only the $\Delta v = 1$ term:

$$p_0(\mathrm{res}) \approx \frac{8\eta_{10}\xi_{10}}{\nu_{0,^2\Pi_{1/2}} - \nu_{1,^2\Sigma^+}} \approx \frac{8\eta_{00}\xi_{00}}{\Delta\nu_{1,0}}\left(\frac{\langle 1(^2\Sigma)|\,0(^2\Pi)\rangle}{\langle 0(^2\Sigma)|\,0(^2\Pi)\rangle}\right)\left(\frac{B_{1,0}}{B_{0,0}}\right), \tag{13}$$

$$\gamma_0(\mathrm{res}) \approx \frac{8\eta_{01}\xi_{01}}{\nu_{1,^2\Pi_{1/2}} - \nu_{0,^2\Sigma^+}} \approx \frac{8\eta_{00}\xi_{00}}{\Delta\nu_{0,1}}\left(\frac{\langle 0(^2\Sigma)|\,1(^2\Pi)\rangle}{\langle 0(^2\Sigma)|\,0(^2\Pi)\rangle}\right)\left(\frac{B_{0,1}}{B_{0,0}}\right). \tag{14}$$

The results are $p_0(\mathrm{res}) = -0.0021\ \mathrm{cm}^{-1}$ and $\gamma_0(\mathrm{res}) = +0.0084\ \mathrm{cm}^{-1}$. Since only the difference between γ_0(res) and p_0(res) could be determined and γ_0(res) was set equal to zero in the fit, p(res, eff) $= -0.011\ \mathrm{cm}^{-1}$. This compares favorably with the observed value of $-0.014\ \mathrm{cm}^{-1}$.

IV. CONCLUSION

CaI is suited neither to classical experimental techniques nor to classical techniques of spectroscopic analysis. Extreme spectral congestion makes single-mode laser excitation spectroscopy and narrow-band fluorescence detection a necessity. The small energy separation between the $A^2\Pi$ and $B^2\Sigma^+$ states requires the use of deperturbation techniques on a system that would not normally be considered to be perturbed because of the absence of level crossings. This deperturbation is necessary to fit the A–X data and derive estimates of true molecular constants (*8*) for the A and B states. In particular, this allows calculation of Franck–Condon factors, quantities of value in the determination of product distributions of chemical

reactions. Of perhaps even greater value is the insight obtained into the orbital composition of the electronic states.

ACKNOWLEDGMENTS

We thank Bernard Pinchemel and Claude Dufour for communicating their preliminary CaI $A^2\Pi-X^2\Sigma^+$ fluorescence results. P.F.B. was supported, in part, by a Natural Sciences and Engineering Research Council of Canada postgraduate fellowship. Support for this research was provided by Grants AFOSR-76-3056, NSF CHE-78-18427, and CHE-78-10178.

RECEIVED: December 30, 1980

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