High-resolution Fourier transform spectroscopy of the CaO $A^1\Sigma^+ - X^1\Sigma^+$ transition: New insights into perturbations by the $a^3\Pi_{0^+}$ and $A^1\Pi$ states ☆

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Abstract

The emission spectrum of the $A^1\Sigma^+ - X^1\Sigma^+$ transition of CaO has been recorded at a resolution of 0.03 cm^{-1} using a Fourier transform spectrometer in the 10 000–15 000 cm^{-1} spectral range. New information has been collected for the low-J term values of several vibrational levels of the $A^1\Sigma^+$ state and also for the perturbing states. For example, about 40 term values of $a^3\Pi_{0^+}(v = 6)$ level [which perturbs the $A^1\Sigma^+(v = 0)$ level] have been identified for the first time. A least squares procedure has been used to determine the vibrational and rotational constants of these states. In each case an empirical 2×2 matrix has been used with an off-diagonal term linking the two electronic states to account for the interaction. Our study is limited to perturbations for which extensive experimental information is available for both interacting states. The derived constants, especially the off-diagonal coupling constants, are in agreement with those published by R.W. Field [J. Chem. Phys. 60 (1974) 2400–2413].
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1. Introduction

The $A^1\Sigma^+ - X^1\Sigma^+$ transition of CaO has been recorded using a Fourier transform spectrometer (FTS) in the 10 000–15 000 cm^{-1} spectral range along with the $A'^1\Pi - X^1\Sigma^+$ transition lying in the 4000–10 000 cm^{-1} region. This $A'^1\Pi - X^1\Sigma^+$ transition has been studied by us previously and the results published in [1] along with an extensive bibliography that will not be repeated in this paper. Let us note, however, the two major contributions to the study of the $A^1\Sigma^+ - X^1\Sigma^+$ transition of CaO: first the pioneering work by Hultin and Lagerqvist [2] published in

1950, which can be considered as a milestone in the understanding and experimental study of perturbations in the pre-computer era. Second, the identification in 1974 by Field [3] of the symmetries of the main perturbing states ($a^3\Pi_i$ and $A'^1\Pi$) interacting with the $A^1\Sigma^+$ state and the vibrational assignment of the levels involved in the perturbations. Field's work is also a classic that shows the power of modern spectroscopic analysis in untangling and fitting perturbations. In the following years Field's group carried out laser experiments on the electronic transitions of CaO to build up a comprehensive energy level diagram of the electronic states. However, no new attempts were made to record high resolution spectra over a wide spectral range until 1999 when a measurement campaign was completed at the University of Waterloo on CaO [1], SrO [4,5], and BaO [6].

The study of the $A'^1\Pi - X^1\Sigma^+$ transition of CaO [1] included 19 bands in which the ground state was covered

from $v'' = 1$ to $v'' = 7$. Optical data were merged with milli-meter-wave ($v'' = 0$ and 1) [7] and infrared ($v'' = 0$–3) [8] data to determine an accurate set of Dunham parameters for the $X^1\Sigma^+$ state. In the upper $A'^1\Pi$ state, the presence of perturbations limited the analysis to the $v' = 0$ and $v' = 1$ vibrational levels although term values were derived for $v' = 2$ and 3.

The aim of present work was to collect as many experimental data as possible on the $A^1\Sigma^+ - X^1\Sigma^+$ transition, including new bands too far to the red to be photographically recorded by Hultin and Lagerqvist. These bands have been recorded at low resolution by Brewer and Hauge [9]. From the new equilibrium constants determined for the ground state [1], we could calculate the average rotational term values (see Section 2 for details) in each vibrational level of the $A^1\Sigma^+$ state using all available experimental data. The second stage of our analysis was the determination of the vibrational and rotational constants of the interacting states. For this purpose we focused our attention on well defined local perturbations for which information about the two interacting states was extensive enough to allow us to obtain a fit. Our fits used a least squares procedure in which the states were represented by the diagonal elements of an empirical matrix that included off-diagonal terms to account for the perturbation interaction between two nearby states. The main purpose of our paper was to make available our new $A^1\Sigma^+ - X^1\Sigma^+$ data as a prelude to a complete global analysis of the interacting $A^1\Sigma^+$, $b^3\Sigma^+$, $A'^1\Pi$, and $a^3\Pi$ set of states.

2. Description of the bands

The only difference in the experimental procedure as compared to the work presented in [1] is the use of a silicon photodiode detector, which is more sensitive in the near infrared than the InSb detector used for the $A'^1\Pi - X^1\Sigma^+$ transition.

Hultin and Lagerqvist [2] observed 16 vibrational bands belonging to five sequences of the $A^1\Sigma^+ - X^1\Sigma^+$ transition of CaO. In our work, we recorded 42 bands at high resolution from six sequences ($\Delta v = -3$ to $\Delta v = +2$). The relative intensities of the sequences are different from what was observed by Hultin and Lagerqvist because of the use of different emission sources [1,2]. For example, we did not see the $\Delta v = +3$ sequence and the $\Delta v = +2$ sequence is weak in our spectra. The extraction of information for perturbed transitions is rather tedious and in most cases we started our analysis using Hultin and Lagerqvist's work [2]. They determined the exact numbering of the rotational lines of the P and R branches of each band. As mentioned in the introduction we built up the list of the term values of a given vibrational level of the upper $A^1\Sigma^+$ state by adding the term values calculated [1] for the $X^1\Sigma^+$ state to the wavenumbers of the P and R lines. Comparison of the $A^1\Sigma^+$ term values derived from different bands allowed us to check the identification of the rotational lines.

The quality of the information on the experimental lines depends on the intensity of the studied bands and on the possible overlapping of bands, which induces blending of lines, particularly for weak lines. In most cases two to five bands provided information about a given vibrational level of the $A^1\Sigma^+$ state leading 4 to 10 numerical values for each term value when both P and R lines were observed. We discarded the outliers (typically 0.05 cm^{-1} away from the mean value) and we averaged the remaining data to build up a single set of excited state term values. For sake of clarity we will study first the interaction between the $A^1\Sigma^+$ and $a^3\Pi_{0^+}$ states and then the perturbations between the $A^1\Sigma^+$ and $A'^1\Pi$ states.

3. The $A^1\Sigma^+$ state perturbed by the $a^3\Pi_{0^+}$ state

3.1. Interaction between the $A^1\Sigma^+$ ($v = 0$) and the $a^3\Pi_{0^+}$ ($v = 6$) vibrational levels

For their analysis, Hultin and Lagerqvist [2] used the graphical method suggested by Gerö [10], which is very convenient for visualizing the perturbations. In [2], Figs. 7–9 show that, in some cases [the $A^1\Sigma^+$ ($v = 2$) state perturbed by the $a^3\Pi_{0^+}$ ($v = 9$) state, for example], the interaction may involve a large number of rotational levels of the $A^1\Sigma^+$ state. The mixing of the electronic wavefunctions makes possible the observation of extra emission lines arising from the transition between the perturbing state and the ground state. Even if such a transition is forbidden, it is enhanced by mixing of the interacting states. This is the case for the very first lines of the $A^1\Sigma^+$ ($v = 0$) $- X^1\Sigma^+$ ($v = 0$) transition although Hultin and Lagerqvist did not see any rotational lines arising from the forbidden transition between the perturbing state [identified by Field [3] as $a^3\Pi_{0^+}$ ($v = 6$)] and the $X^1\Sigma^+$ ($v = 0$) ground state. It was tempting to look for lines of this transition, taking advantage of the high quality of the experimental recording of the 0–0 band of the $A^1\Sigma^+ - X^1\Sigma^+$ transition (Fig. 1). It has been possible to assign the extra lines of the P and R branches of the $a^3\Pi_{0^+}$ ($v = 6$) $- X^1\Sigma^+$ ($v = 0$) transition leading to the determination of the $J = 2$ to $J = 40$ term values of the $a^3\Pi_{0^+}$ ($v = 6$) state. (Note that there are extensive global and local perturbations in the four low-lying excited electronic states of CaO, but for the sake of convenience in this paper we identify them by their dominant character.) In addition, accurate term values for the $A^1\Sigma^+$ ($v = 0$) level were calculated using data collected in the 0–0, 0–1, 0–2, and 0–3 bands of the $A^1\Sigma^+ - X^1\Sigma^+$ transition. About 40 term values (Table 1) were used to account for each of the two $A^1\Sigma^+$ ($v = 0$) and $a^3\Pi_{0^+}$ ($v = 6$) states. The empirical 2×2 matrix used to describe the interaction between the two states is very simple in this homogeneous perturbation [11]: the two diagonal elements are: $T_v + B_v J(J+1) - D_v J^2(J+1)^2$ and the off-diagonal term is a constant H. The energies are referred to the origin ($v = 0$, $J = 0$) of the ground state. The crossing of the states occurs at a "negative" value of J. The result of the fit is excellent if we consider the differences between the observed and calculated term values (Table 1) and a fit of the two sets of data in absence of the off-diagonal matrix element is not
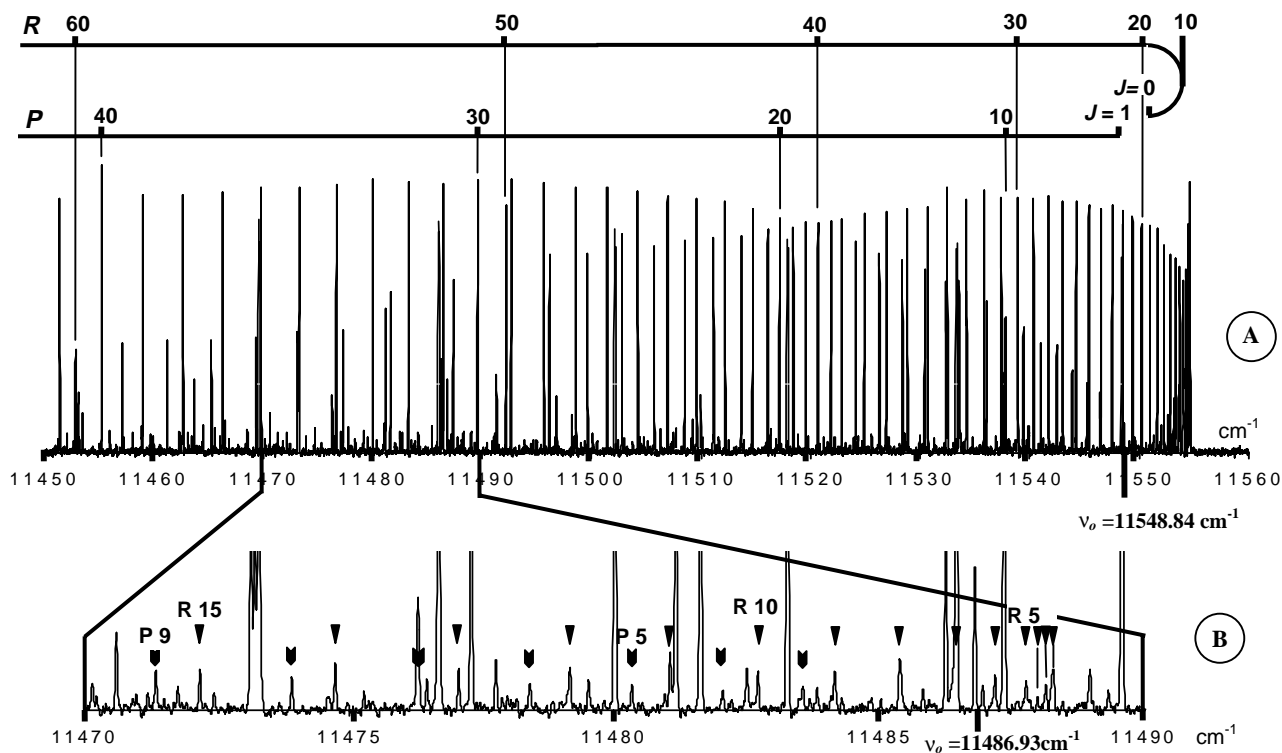
Fig. 1. An expanded portion of the $A^1\Sigma^+(v=0) - X^1\Sigma^+(v=0)$ [Trace A] emission spectrum of CaO displaying the weak $a^3\Pi_{0^+}(v=6) - X^1\Sigma^+(v=0)$ lines [Trace B]. (The origins of the bands are effective values.)

good at all. The derived constants are listed in Table 2. When Norman et al. [12] studied the $C^3\Sigma^+(v=0) - a^3\Pi_i(v=0)$ transition of CaO, they observed a large and fairly constant Λ-doubling in the $a^3\Pi_0(v=0)$ state. As the e-parity levels of the $A^1\Sigma^+(v=0)$ state do not mix with the f-parity levels of the $a^3\Pi_0(v=6)$ state, we do not observe any Q_{fe} lines of the $a^3\Pi_0(v=6) - X^1\Sigma^+(v=0)$ transition. Norman et al. found that at $J=0$ the e and f term values of the $a^3\Pi_0(v=0)$ state are separated by 2.42 cm^{-1} with the e level located above the f one. This means that the exact value of T_6 for the $a^3\Pi_0(v=6)$ state is about 1–2 cm^{-1} lower than our calculated value if we ignore the v dependence of the Λ-doubling. The value of the rotational constant $B_0 = 0.40795(1)$ cm^{-1} for $A^1\Sigma^+(v=0)$ is larger than the value given by Hultin and Lagerqvist [2] ($B_0 = 0.4056$ cm^{-1}) and by Norman et al. ($B_0 = 0.4052$ cm^{-1}).

For the $a^3\Pi_0(v=0)$ state, an important piece of information for the present work is the effective value $B_0 = 0.34425$ cm^{-1} derived from a fit of the term values $J=0$ to $J=69$ published by Norman et al. However, their value of α_e from the expression $B_v = B_e - \alpha_e(v+0.5)$ [13] will be slightly modified. An extrapolation of the term values of the $a^3\Pi_{0^+}(v=6)$ state did not allow us to identify new P and R lines of the $a^3\Pi_{0^+}(v=6) - X^1\Sigma^+(v=0)$ transition for $J>40$. This is not surprising if we realize that the interacting energy levels of the $a^3\Pi_{0^+}(v=6)$ and the $A^1\Sigma^+(v=0)$ states with the same J value are more distant from each other as J

increases. As a consequence, the effect of the interaction, which is inversely proportional to the energy gap between the interacting levels, is decreasing as J increases. This mixing is responsible for the observation of the forbidden $a^3\Pi_{0^+}(v=6) - X^1\Sigma^+(v=0)$ transition, and thus rotational lines are absent for $J>40$.

3.2. Interaction between the $A^1\Sigma^+$ ($v=2$) and the $a^3\Pi_{0^+}(v=9)$ states

This homogeneous perturbation occurs between the same two electronic states as in the previous section. Hultin and Lagerqvist [2] observed two sets of P and R branches in the vicinity of the perturbation located at $J=18$ for 14 common J values ($J=9$–22) for the 2–0, 2–1, and 2–3 bands. In our experiments we collected lines in the 2–0, 2–1, 2–3, 2–4, and 2–5 bands leading to the determination of term values of the two interacting states for common J values between $J=1$ and $J=39$ (Table 1). The derived constants are collected in Table 2. In Table 3 we present the value of the off-diagonal constant H and the value of the (noninteger) constant J_0 which is the effective value of J at which the states would cross in the absence of interaction. In addition, we estimated H using the method of Field [3], in which we also introduced a contribution from centrifugal distortion because of the presence of term values with high J values, and obtained $H = 16.79$ cm^{-1} [14] in excellent agreement with our observations (Table 3).

Table 1
Term values (in cm^{-1}) for the $v = 0$ to $v = 5$ vibrational levels of the $A^1\Sigma^+$ state and of the associated perturbing levels of the $a^3\Pi_{0^+}$ and $A'^1\Pi$ perturbing states

J	$A^1\Sigma\,(v=0)$ level Obs − calc		$a^3\Pi_0\,(v=6)$ level Obs − calc	
1	11551.330	−9		
2	11552.932	−4	11488.931	1
3	11555.325	−5	11490.961	−2
4	11558.520	−5	11493.672	1
5	11562.523	4	11497.060	4
6	11567.315	0	11501.114	−1
7	11572.915	2	11505.844	−3
8	11579.315	1	11511.250	0
9	11586.522	4	11517.321	−2
10	11594.531	2	11524.063	−1
11	11603.353	6	11531.471	−3
12	11612.973	1	11539.546	−2
13	11623.413	5	11548.285	0
14	11634.656	4	11557.683	−2
15	11646.714	6	11567.746	0
16	11659.580	4	11578.465	−1
17	11673.259	4	11589.844	0
18	11687.750	1	11601.880	2
19	11703.057	2	11614.568	1
20	11719.177	0	11627.911	1
21	11736.109	−2	11641.914	6
22	11753.859	−1	11656.560	3
23	11772.419	−3	11671.859	1
24	11791.795	−4	11687.812	1
25	11811.984	−5	11704.413	1
26	11832.987	−5	11721.665	−1
27	11854.801	−7	11739.567	1
28	11877.431	−4	11758.118	2
29	11900.871	−4	11777.313	0
30	11925.122	−3	11797.153	−5
31	11950.185	−1	11817.649	0
32	11976.056	0	11838.785	−2
33	12002.736	3	11860.569	−1
34	12030.221	3	11882.995	−5
35	12058.520	8	11906.073	−1
36	12087.617	8	11929.792	−1
37	12117.518	7	11954.151	−4
38	12148.222	4	11979.162	0
39	12179.726	−1	12004.814	3
40	12212.026	−13	12031.107	5

J	$A^1\Sigma\,(v=1)$ level Obs − calc		$A'^1\Pi\,(v=7)$ level Obs − calc	
3	12262.620	16		
4	12265.829	7		
5	12269.852	7		
6	12274.678	8		
7	12280.297	1		
8	12286.718	−3		
9	12293.939	−2		
10	12301.955	−1		
11	12310.752	−6		
12	12320.328	−9		
13	12330.667	−15		
14	12341.763	−6		
15	12353.553	−10	12365.343	−14
16	12365.992	−5	12376.270	0
17	12378.956	−5	12388.108	−1
18	12392.302	−2	12401.024	1
19	12405.909	4	12415.136	1
20	12419.780	13	12430.436	−6

Table 1 (*continued*)

J	$A^1\Sigma\,(v=1)$ level Obs − calc		$A'^1\Pi\,(v=7)$ level Obs − calc	
21	12433.993	5	12446.836	−6
22			12464.225	−5
23			12482.530	−7
24			12501.711	−4
25			12521.745	1
26			12542.605	1
27			12564.296	9
28			12586.801	13
29			12610.113	13
30			12634.231	13
31			12659.150	7
32			12684.866	−2
33			12711.371	−27

J	$A^1\Sigma\,(v=2)$ level Obs − calc		$a^3\Pi_0\,(v=9)$ level Obs − calc	
1	13003.845	−15	12960.572	−16
2	13005.193	−16	12962.130	−12
3	13007.233	1	12964.467	−7
4	13009.919	−15	12967.573	−6
5	13013.315	1	12971.453	−4
6	13017.371	−8	12976.103	0
7	13022.129	−1	12981.500	−11
8	13027.564	−9	12987.678	−1
9	13033.713	−2	12994.600	0
10	13040.558	−5	13002.268	4
11	13048.131	4	13010.663	−2
12	13056.422	5	13019.795	7
13	13065.457	8	13029.627	7
14	13075.249	12	13040.153	9
15	13085.811	11	13051.348	4
16	13097.169	11	13063.206	9
17	13109.346	13	13075.693	11
18	13122.359	11	13088.787	12
19	13136.233	10	13102.471	16
20	13150.991	11	13116.711	11
21	13166.640	7	13131.503	6
22	13183.201	7	13146.844	12
23	13200.674	7	13162.708	7
24	13219.050	0	13179.104	0
25	13238.341	1	13196.048	3
26	13258.528	−2	13213.531	0
27	13279.605	−4	13231.571	1
28	13301.564	−6	13250.165	−6
29	13324.394	−7	13269.330	−14
30	13348.085	−10	13289.077	−18
31	13372.630	−9	13309.421	−16
32	13398.021	−10	13330.343	−28
33	13424.252	−9	13351.894	−12
34	13451.316	−8	13374.036	−10
35	13479.209	−6	13396.793	−5
36	13507.925	−3	13420.179	16
37	13537.457	−5	13444.155	11
38	13567.812	0	13468.747	2
39	13598.976	3	13493.976	9
40	13630.947	2		
41	13663.731	9		
42	13697.318	11		
43	13731.706	12		
44	13766.895	14		
45	13802.879	11		
46	13839.654	2		
47	13877.228	−4		
48	13915.589	−17		

Table 1 (*continued*)

J	$A^1\Sigma(v=3)$ Obs − calc	
2	13677.465	11
3	13679.869	2
4	13683.088	6
5	13687.114	12
6	13691.928	4
7	13697.556	4
8	13703.983	1
9	13711.216	1
10	13719.248	−4
11	13728.090	−1
12	13737.732	−1
13	13748.173	−5
14	13759.419	−5
15	13771.464	−8
16	13784.316	−6
17	13797.958	−15
18	13812.409	−16
19	13827.665	−12
20	13843.718	−10
21	13860.577	−3
22	13878.230	−1
23	13896.676	−5
24	13915.937	8
25	13935.981	7
26	13956.830	14
27	13978.472	16
28	14000.912	21
29	14024.139	17
30	14048.161	14
31	14072.962	−6
32	14098.540	−40

J	$A^1\Sigma\ (v=4)$ level Obs − calc		$a^3\Pi_0\ (v=12)$ level Obs − calc	
1	14379.178	13		
2	14380.757	−9		
3	14383.172	4		
4	14386.371	−1		
5	14390.381	5		
6	14395.182	2		
7	14400.790	4		
8	14407.196	6		
9	14414.400	3		
10	14422.402	0		
11	14431.212	4		
12	14440.813	0		
13	14451.216	−1		
14	14462.423	0		
15	14474.427	2		
16	14487.226	−1		
17	14500.826	−1		
18	14515.219	−7		
19	14530.421	1		
20	14546.409	−1		
21	14563.194	−4		
22	14580.768	−7		
23	14599.138	−5		
24	14618.293	−2		
25	14638.205	−10		
26	14658.851	−11		
27	14680.044	−5	14685.422	−6
28	14700.759	34	14704.751	21

Table 1 (*continued*)

J	$A^1\Sigma\ (v=4)$ level Obs − calc		$a^3\Pi_0\ (v=12)$ level Obs − calc	
29	14719.846	−13	14726.984	−10
30	14738.926	−25	14750.667	−54
31	14758.541	15	14775.426	43
32	14778.691	12	14800.903	16
33			14827.207	3
34			14854.327	1
35			14882.246	−2
36			14910.964	−4
37			14940.478	−3
38			14970.788	−1
39			15001.889	0
40			15033.779	1
41			15066.456	−6
42			15099.933	−1
43			15134.194	−2
44			15169.248	1
45			15205.084	−2
46			15241.707	−6
47			15279.121	−5
48			15317.325	0
49			15356.312	3
50			15396.079	−1
51			15436.639	6
52			15477.970	−1
53			15520.091	0
54			15563.011	18
55			15606.677	2
56			15651.147	8
57			15696.381	−1
58			15742.405	0
59			15789.194	−11
60			15836.779	−5

J	$A^1\Sigma\ (v=5)$ level Obs − calc		$A'^1\Pi\ (v=13)$ level Obs − calc	
4	15085.483	7		
5	15089.475	13		
6	15094.258	14		
7	15099.838	15		
8	15106.203	4		
9	15113.379	7		
10	15121.350	8		
11	15130.114	6		
12	15139.668	−2		
13	15150.029	1		
14	15161.185	2		
15	15173.138	6		
16	15185.876	−2		
17	15199.418	0		
18	15213.740	−14		
19	15228.882	−2		
20	15244.805	−5		
21	15261.526	−4		
22	15279.035	−8		
23	15297.350	−1		
24	15316.445	−6		
25	15336.337	−7		
26	15357.020	−10		
27	15378.494	−14		
28	15400.770	−8		
29	15423.830	−7		
30	15447.683	−6		

(*continued on next page*)

Table 1 (*continued*)

J	$A^1\Sigma$ ($v = 5$) level Obs − calc		$A'^1\Pi$ ($v = 13$) level Obs − calc	
31	15472.327	−2		
32	15497.759	0		
33	15523.973	−4		
34	15550.981	0		
35	15578.770	−1		
36	15607.347	6		
37	15636.696	7		
38	15666.816	9		
39	15697.692	12		
40	15729.289	20		
41	15761.454	12		
42	15793.533	−37	15800.974	−1
43	15823.327	21	15831.561	−17
44				
45			15900.942	−2
46			15937.260	−4
47			15974.428	1
48			16012.406	2
49			16051.182	4
50			16090.745	0
51			16131.108	10
52			16172.244	8
53			16214.157	−1
54			16256.852	−8
55			16300.325	−17

Note that a perturbation causes the appearance of extra lines in a second column and the high J lines after the perturbation continue in this second column.

Table 2
Effective constants (in cm^{-1}) for the studied vibrational levels of the $A^1\Sigma^+$, $a^3\Pi_{0^+}$ and $A'^1\Pi$ states

v	T_v (exp)	B_v	D_v ($\times 10^7$)
$A^1\Sigma$			
0	11543.267 (12)	0.407951 (11)	9.53 (15)
1	12257.774 (13)	0.404502 (20)	9.82 (45)
2	12967.763 (12)	0.404015 (13)	7.42 (14)
3	13675.043 (10)	0.402001 (25)	8.74 (75)
4	14378.419 (10)	0.400490 (10)	5.56 (10)
5	15077.505 (10)	0.398619 (12)	5.35 (12)
$a^3\Pi$			
0[a]	8352.0392 (25)	0.3442522 (50)	6.361 (10)
1[b]	8889.840	0.3418	
6	11494.171 (10)	0.330023 (12)	7.48 (15)
9	12995.232 (10)	0.321847 (10)	2.45 (15)
12	14446.69[c]	0.315091 (25)	5.24 (22)
$A'^1\Pi$			
0[d]	8608.4386 (10)	0.341743 (1)	5.403 (7)
1[d]	9148.7173 (10)	0.339471 (1)	5.657 (6)
7	12285.956 (60)	0.32577 (14)	3.6 (3)
13	15245.014 (45)	0.308307 (24)	9.0 (fixed)

[a] Ref. [12].
[b] Ref. [15].
[c] Fixed value.
[d] Ref. [1].

3.3. Interaction between the $A^1\Sigma^+$ ($v = 4$) and the $a^3\Pi_{0^+}$ ($v = 12$) states

The experimental information is obtained from the 4-2, 4-5, 4-6, and 4-7 vibrational bands. The data set is improved because the term values for $J = 0$ to $J = 12$ have been determined for the first time. The difference between the rotational B_v parameters for the interacting $A^1\Sigma^+$ and $a^3\Pi_{0^+}$ states increases as v increases. As a consequence the range of J values where the two states interact is smaller and the term values identified as being from the forbidden $a^3\Pi_{0^+}$ ($v = 12$) − $A^1\Sigma^+$ ($v = 0$) transition are limited to six (Table 1). The absence of any other perturbation up to $J = 60$ allowed us to include high J values in the fit that provides the constants listed in Table 2, which are in good agreement with those previously calculated. The off-diagonal constant H and the value of J_0 are listed in Table 3.

3.4. Interaction between the $A^1\Sigma^+$ ($v = 6$) and the $a^3\Pi_{0^+}$ ($v = 15$) states

The only workable band involving the $A^1\Sigma^+$ ($v = 6$) level is the weak $A^1\Sigma^+$ ($v = 6$) − $X^1\Sigma^+$ ($v = 8$) band although Hultin and Lagerqvist [2] studied the 6–3 band. We do not observe good agreement between the two sets of term values derived from these bands particularly for the perturbed levels. In the absence of any other band which could provide extra information, a direct determination of the constants of these states was not good enough for them to be used in the determination of equilibrium constants.

3.5. Conclusion

In the study of the perturbations described in this section, we took advantage of new experimental data. In the first three cases, we observed lines at very low J values, allowing us to determine more accurate constants, especially the T_v values. In addition, the identification of term values for both interacting states for numerous J-values made possible a fitting procedure in which the experimental term values were accurately modeled. We note that the values of the off-diagonal matrix elements agree with those previously determined by Field [3] confirming his analysis.

4. The $A^1\Sigma^+$ state perturbed by the $A'^1\Pi$ state

The $A'^1\Pi$ electronic state has been studied in [1]. Molecular constants have been determined for the $v = 0$ and $v = 1$ vibrational levels, but the $v = 2$ and $v = 3$ levels were represented by term values because of a strong interaction with the $b^3\Sigma^+$ state and no transition involving vibrational levels for $v \geqslant 4$ of the upper state has been observed in the $A'^1\Pi − X^1\Sigma^+$ transition. In the absence of equilibrium constants for the $A'^1\Pi$ state, only rough extrapolations for the T_v and B_v constants can be made for the $v \geqslant 6$ levels of the $A'^1\Pi$ state that interact with the $A^1\Sigma^+$ state. However,

Table 3
Off-diagonal matrix element H, and value of J, denoted as J_0, at the virtual crossing point of the interacting states in absence of perturbation

Interacting states	H (cm^{-1})		J_0	
	This work	Field [Ref. [3]]	This work	Field [Ref. [3]]
$A^1\Sigma^+$ $(v=0)$ and $a^3\Pi_0$ $(v=6)$	20.249 (11)			
$A^1\Sigma^+$ $(v=1)$ and $A'^1\Pi(v=7)$	4.301 (10)	4.37 (10)	18.46	18.2
$A^1\Sigma^+$ $(v=2)$ and $a^3\Pi_0$ $(v=9)$	16.7839 (22)	16.81 (5)	17.81	18.0
$A^1\Sigma^+$ $(v=4)$ and $a^3\Pi_0$ $(v=12)$	1.9340 (95)	1.74 (20)	27.78	27.6
$A^1\Sigma^+$ $(v=5)$ and $A'^1\Pi$ $(v=13)$	3.328 (10)	3.06 (20)	42.41	41.9

these values will be used as initial estimates in our fits of the rovibrational levels of the $A'^1\Pi$ state.

4.1. Interaction between the $A^1\Sigma^+$ $(v=5)$ and the $A'^1\Pi$ $(v=13)$ states

Despite the fact that only the 5–7 band of the $A^1\Sigma^+ - X^1\Sigma^+$ has been studied, the quality of our experimental spectrum provided data starting at $J=4$. Note that Hultin and Lagerqvist [2] did not observe lines for J values lower than 21. The heterogeneous perturbation [11] occurring between the $A^1\Sigma^+$ $(v=5)$ and the $A'^1\Pi(v=13)$ states culminates at $J \approx 42$, and the next perturbation is far enough away ($J \approx 60$) to allow us to fit 55 term values. The empirical off-diagonal matrix element is now equal to $\beta\sqrt{J(J+1)}$, and comparison with the parameter H given by Field [3] for this heterogeneous perturbation gives $H = \beta\sqrt{J_0(J_0+1)}$ in which J_0 is, as already noted, the value of J where the interacting states would cross in absence of interaction. As stated previously, the diagonal elements are always: $T_v + B_v J(J+1) - D_v J^2(J+1)^2$. It is obvious that the term values which are not affected by the local perturbation will provide information about the $A^1\Sigma^+$ $(v=5)$ state while the constants of the $A'^1\Pi(v=13)$ state will be determined by only a limited number of experimental data. For example, the value of T_v for this state is not accurate because the perturbation is located far away from the origin of this vibrational level, and we made some tests which showed that the quality of the fit was not sensitive to the value of T_{13} used in the fit. For the same reason the centrifugal distortion constant D of the $A'^1\Pi(v=13)$ state has been kept fixed. However, the constant B_{13} appears to be determined reliably. The crossing point of the two states occurs at $J_0 = 42.41$ and the derived value of H is 3.33 cm^{-1}; Field [3] found, respectively, $J_0 = 41.9$ and $H = 3.06$ cm^{-1} (Table 3). The constants calculated for the $A^1\Sigma^+$ $(v=5)$ level agree with the set of constants determined in Section 3 as it will be seen in the next section. A search for extra lines in the 5–7 band was not successful despite the fact that the $A'^1\Pi - X^1\Sigma^+$ transition is allowed.

4.2. The $A^1\Sigma^+$ $(v=3)$ level

The $A^1\Sigma^+$ $(v=3)$ level interacts with the $A'^1\Pi(v=10)$ state at $J \approx 36$, and no local perturbation is observed for lower J values. Hultin and Lagerqvist [2] noted the presence of three other perturbations occurring around $J \approx 42$ [$a^3\Pi_2(v=11)$], $J \approx 50$ [$a^3\Pi_1(v=11)$] and $J \approx 58$ [$a^3\Pi_0(v=11)$]. As a consequence it is not possible to separate the first interaction from the others as we have done for all the other perturbations in this study. Spectra of the 3–1, 3–4, 3–5, and 3–6 bands provided term values for the $A^1\Sigma^+(v=3)$ upper state starting at $J=2$, while the data collected by Hultin and Lagerqvist [2] started at $J=10$. We fitted the term values from $J=2$ to $J=30$ to determine the effective constants of the $A^1\Sigma^+(v=3)$ state, which are presented in Table 2.

4.3. Interaction between the $A^1\Sigma^+$ $(v=1)$ and the $A'^1\Pi$ $(v=7)$ states

The term values for the $A^1\Sigma^+(v=1)$ and $A'^1\Pi(v=7)$ levels have been obtained from the study of the 1–0, 1–1, 1–2, 1–3, and 1–4 bands. The perturbation between the two levels occurs at $J \approx 18$ and the next perturbation [$a^3\Pi_2(v=8)$] is located at $J \approx 37$. This makes it possible to handle the first perturbation with the effective 2×2 matrix used in Section 4.1. It has been possible to identify the term values of the two interacting states in the range $J=15$ to $J=21$. The first term value is $J=3$, which is comparable to the value $J=5$ observed by Hultin and Lagerqvist [2] and the last one introduced in the fit is $J=33$ to avoid the local perturbation by the $a^3\Pi_2(v=8)$ level. The off-diagonal constant β is equal to 0.233 cm^{-1} and the value of J_0 at the crossing of the two unperturbed term values is $J_0 = 18.46$ cm^{-1}, the derived value of $H = \beta\sqrt{J_0(J_0+1)} = 4.30$ cm^{-1} in good agreement with the value $H = 4.37$ cm^{-1} given by Field [3] (see Table 3). The value of T_1 for the $A^1\Sigma^+(v=1)$ level agrees with estimates made using the other vibrational levels. However despite the goodness of the fit, the rotational constant $B_1 = 0.4045$ cm^{-1}, which lies between the values $B_0 = 0.4079$ cm^{-1} and $B_2 = 0.4041$ cm^{-1}, is about 0.0015 cm^{-1} smaller than expected presumably due the interaction with other states not included in our fit.

5. The equilibrium constants of the $A^1\Sigma^+$, $a^3\Pi_0$, and $A'^1\Pi$ states

5.1. The $A^1\Sigma^+$ state

In this work, a significant improvement has been achieved in the identification of the low-J term values of the levels with $v=0$ to $v=5$ of the $A^1\Sigma^+$ state. If we con-

Table 4
Equilibrium constants (in cm^{-1}) for the $A^1\Sigma^+$ and $a^3\Pi_{0^+}$ states

	$A^1\Sigma^+$		$a^3\Pi_{0^+}$	
	This work	Ref. [12]	This work	Ref. [12]
T_0	11543.267 (12)	11548.8		
T_e	11184.77 (40)		8082.23 (91)	
ω_e	717.96 (30)	718.9	541.87 (59)	544.1
$\omega_e x_e$	1.85 (5)	2.11	2.60 (6)	3.15
B_e	0.40899 (18)	0.4059	0.34520 (21)	
α_e	0.00211 (5)	0.0014	0.00211 (14)	
γ_e	0.000042 (22)		0.000036 (14)	

sider the vibrational constants one observes that the very first few term values of the $v = 1$ to $v = 5$ levels do not suffer from local perturbations. In the case of the $v = 0$ level, a discrepancy exists between our value [$T_0 = 11543.267$ cm^{-1}] and the value published by Field [$T_0 = 11548.8$ cm^{-1}] [3,12]. This difference originates from the fact that we could identify about 40 term values of the perturbing $a^3\Pi_{0^+}(v = 6)$ state that allowed us to carry out a quantitative deperturbation of the first term values of the $A^1\Sigma^+(v = 0)$ state. Hultin and Lagerqvist [2] just localized qualitatively this perturbation on the basis of Gerö's graphical method [10]. With these new data, one can expect that the derived equilibrium vibrational constants, T_v, ω_e, and $\omega_e x_e$, listed in Table 4, are more accurate than those published previously [3,12]. The values of the equilibrium rotational constants B_e, α_e, and γ_e [13] are determined in a similar way. It is not surprising to see that our value of $B_0 = 0.40795$ cm^{-1} is different from the values published by Hultin and Lagerqvist [2] and Field [3] [see Section 3.1]. As noted previously our fit includes the interaction with the $a^3\Pi_{0^+}(v = 6)$ state with a large number of new experimental data. The experimental B_v values for $v = 2$–5 display a nearly linear dependence on v, but the value of $B_1 = 0.4045$ cm^{-1} does not have the expected value $B_1 \approx 0.4060$ cm^{-1}. If we compare the data for the various vibrational levels, it appears that the $A^1\Sigma^+(v = 1)$ level is the one for which the experimental data are the least numerous. As a consequence, we excluded B_1 from the fit carried out to determine the equilibrium constants listed in Table 4. The presence of a $\gamma_e(v + 1/2)^2$ term significantly improves the fit (although its mechanical significance is dubious), and γ_e is two orders of magnitude smaller than α_e, as observed for the ground state [1]. Attempts to fit the term values of the $A^1\Sigma^+(v = 1)$ level with a value of B_1 fixed to the value derived from the equilibrium constants were unsuccessful. The centrifugal distortion parameters do not show a smooth variation with v due to interactions with other states, but their order of magnitude agrees with expected values as compared to similar constants in the ground state.

5.2. The $a^3\Pi_{0^+}$ state

The low-J term values of the $v = 0$ [12], 6 and 9 levels are determined and will be used to derive vibrational constants.

Unfortunately, the data are only for the e-parity levels of the $\Omega = 0^+$ spin-orbit component of the $a^3\Pi_i$ state. Consequently, the derived constants will be effective constants for the $a^3\Pi_{0^+}$ spin-orbit component. The origin T_{12} of the $v = 12$ level cannot be used because of the lack of experimental information on the low-J term values for this level. It turns out that in the fit Section 3.3 the retrieved value of T_{12} is very close to the initial value, which could be changed by ± 10 cm^{-1} without a significant change in the variance of the fit. Marks et al. [15] studied two electronic transitions involving the $a^3\Pi_i$ state as a lower state, and they collected information on the $v = 1$ vibrational level. If one assumes that the vibrational constants are the same for the three spin-orbit components of this state, it is possible to estimate the value of T_1 for the $a^3\Pi_0(v = 1)$ level. Marks et al. found the value of $T_1 - T_0$ to be 538 cm^{-1} and we added this vibrational interval to the value of T_0 [12] to obtain a value for T_1 (Table 3). The equilibrium vibrational constants derived from the data in Table 3 are listed in Table 4. In the same way one can collect information about the value of the B_1 rotational constant of the $a^3\Pi_0(v = 1)$ state. Marks et al. [15] published the experimental lines of the $d^3\Delta_1(v = 1) - a^3\Pi_0(v = 1)$ transition of CaO. We calculated the mean values of the R_{ee} and R_{ff} branches and of the Q_{ef} and Q_{fe} ones and the usual combination differences [13] provided a value of $B_1 = 0.3418$ cm^{-1} on the basis of the rotational lines from $J = 4$ to $J = 17$. The difference $B_0 - B_1 = 0.0024$ cm^{-1} is an estimate for α_e and it agrees with the value $\alpha_e = 0.0026$ cm^{-1} of [12]. This value of B_1 has been included in the fit carried out to determine the equilibrium rotational constants. We did not include the value of B_{12} because the experimental information on the term values of the $a^3\Pi_{0^+}(v = 12)$ state is considerably less extensive than for the other levels, and one observes (Table 1) that the quality of the fit in the vicinity of the perturbation is not as good as for the other bands.

5.3. The $A'^1\Pi$ state

In the case of the $A'^1\Pi$ state, equilibrium constants are not calculated. The new experimental information is too modest to trust in a fit that includes the very accurate data published on the $v = 0$ and $v = 1$ levels [1] with the data collected in this paper for the $v = 7$ and $v = 13$ levels. What is needed to obtain improved equilibrium constants is, for example, a deperturbation of the $v = 2$ and $v = 3$ levels of the $A'^1\Pi$ state.

6. Conclusion

In this paper new experimental information has been collected on the $A^1\Sigma^+ - X^1\Sigma^+$ transition of CaO. The FTS technique allowed us to improve considerably the accuracy of the experimental data and the spectroscopic analysis. Several local perturbations have been studied using a direct approach in which the interacting electronic states are included in a effective 2×2 matrix with an off-di-

agonal term to account for the coupling between the two states. In two cases, the $A^1\Sigma^+(v=0)$ and $A^1\Sigma^+(v=2)$ levels, the new data allowed us to fit a set of data in which the perturbed and perturbing states are equally represented. The quality of the fits gives us confidence in the derived constants for the $A^1\Sigma^+$ state. We were able to identify low-J term values, which were not measured previously by Hultin and Lagerqvist [2]. In addition we observe good agreement for the coupling parameters, H, that we derive for both homogeneous and heterogeneous perturbations, and those published by Field [3]. Apart from the case of the $A^1\Sigma^+(v=0)$ and $A^1\Sigma^+(v=2)$ levels, attempts made in other levels to identify more than a few new extra rotational lines linking the perturbing states and the ground states were not successful, despite the fact that the experimental spectra have been carefully examined. In such cases our work only provides limited information about the vibrational levels of the perturbing states. The derived equilibrium constants for the $A^1\Sigma^+$ state are improved over the previous work because information concerning the first five vibrational levels has been collected. In the case of the $a^3\Pi_{0^+}$ state, the values of the equilibrium vibrational constants are also reasonable and we used data collected previously by Marks et al. [15] for the $v=0$ and the $v=1$ levels. The effective equilibrium rotational constants are less reliable because the information about the $a^3\Pi_0$ state concerns only the e-parity levels. Nevertheless reasonable agreement is found with the results previously published by Norman et al. [12].

Improved constants are now available to study other perturbations of the $A^1\Sigma^+$ state of CaO. In a perturbation analysis there is often not enough data to determine all of the parameters, such as for the $A^1\Sigma(v=5)$ state perturbed by the $A'^1\Pi(v=13)$ state. In such cases some of the constants need to be fixed, and the results of the present work will be useful for this purpose. The goal of the present work is not a complete perturbation analysis but presentation of our new $A^1\Sigma^+ - X^1\Sigma^+$ data and the derivation a set of improved constants that will facilitate further studies on the $A^1\Sigma^+$ state of CaO.

Acknowledgments

References

[1] C. Focsa, A. Poclet, B. Pinchemel, R.J. Le Roy, P.F. Bernath, J. Mol. Spectrosc. 203 (2000) 330–338.
[2] M. Hultin, A. Lagerqvist, Arkiv Fysik 2 (1950) 471–507.
[3] R.W. Field, J. Chem. Phys. 60 (1974) 2400–2413.
[4] H. Li, R.H. Skelton, C. Focsa, B. Pinchemel, P.F. Bernath, J. Mol. Spectrosc. 203 (2000) 188–195.
[5] R.H. Skelton, H. Li, C.D. Boone, R.J. Le Roy, P.F. Bernath, C. Focsa, B. Pinchemel, J. Mol. Spectrosc. 219 (2003) 1–12.
[6] H. Li, C. Focsa, B. Pinchemel, R.J. Le Roy, P.F. Bernath, J. Chem. Phys. 113 (2000) 3026–3033.
[7] W.H. Hocking, E.F. Pearson, R.A. Creswell, G. Winnewisser, J. Chem. Phys. 68 (1978) 1128–1134.
[8] H.G. Hedderich, C.E. Blom, J. Chem. Phys. 90 (1989) 4660–4663.
[9] L. Brewer, R. Hauge, J. Mol. Spectrosc. 25 (1968) 330–339.
[10] L. Gerö, Z. Physik. 93 (1935) 669.
[11] H. Lefebvre-Brion, R.W. Field, Perturbations in the Spectra of Diatomic Molecules, Academic Press, New York, 1986, and The Spectra and Dynamics of Diatomic Molecules, Elsevier, San Diego, 2004.
[12] J.B. Norman, K.J. Cross, H.S. Schweda, M. Polak, R.W. Field, Mol. Phys. 66 (1989) 235–268.
[13] G. Herzberg, "Spectra of Diatomic Molecules", second ed., Van Nostrand Reinhold, New York, 1950.
[14] M. Tudorie, DEA Dissertation, Lille (2004).
[15] R.F. Marks, R.A. Gottscho, R.W. Field, Phys. Scr. 25 (1982) 312–328.