

Analysis of the Multiple Perturbation Arising in the $b^3\Sigma^+(v = 0)$ State of the CO Molecule

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The (0, 1) band of the Third Positive system of the CO molecule ($b^3\Sigma^+ - a^3\Pi$ transition) and the associated (31, 1) band of the induced $a'^3\Sigma^+ - a^3\Pi$ transition have been photographed in the ninth order of a grating spectrograph. As the b state is strongly perturbed by the succession of vibrational levels of the a' state, an effective Hamiltonian matrix has been constructed, which describes this multiple perturbation. A least-squares fit was carried out and as a result the pre-1940 interpretation of band lines was improved and expanded. The calculation has also provided the first precise set of molecular constants of both interacting states. © 1991 Academic Press, Inc.

INTRODUCTION

The Third Positive system in the spectrum of the CO molecule has been the subject of many spectroscopic studies for the past 50 years (1). Since that time, the experimental methods, methods of treating perturbations, and the calculating methods have markedly improved. This paper is a further study of this system.

The Third Positive group of bands of the CO molecule is due to the electronic transition between two triplet states $b^3\Sigma^+ - a^3\Pi$. Two levels $v = 0$ and $v = 1$ of the upper state of this system are massively perturbed, owing to the interaction with a number of vibrational levels of the $a'^3\Sigma^+$ state which are close to the dissociation limit. The distances between the perturbing vibrational levels are very short and decrease rapidly as they approach the dissociation limit (Fig. 1). These are vibrational levels $v = 31$ to $v = 42$ of the $a'^3\Sigma^+$ state.

Associated with the Third Positive system are two bands (31, 1) and (35, 0) resulting from $a'^3\Sigma^+ - a^3\Pi$ transition found by Gerö (2). These bands are weak and their appearance results from the interaction and mixing of wavefunctions: the (31, 1) band is associated with the (0, 1) band of the Third Positive system, and the (35, 0) band is associated with the (1, 0) band.

EXPERIMENTAL DETAILS

The photographs of the Third Positive system bands and bands associated with them have been taken with the help of the PGS2 spectrograph (C. Zeiss, Jena) in the ninth order of a grating with a reciprocal dispersion of 0.4 Å/mm. An ordinary Geissler tube filled with carbon dioxide was used as the light source. The exposure times of the main system ranged from 5 min to 3 hr and for induced bands up to 5 hr.

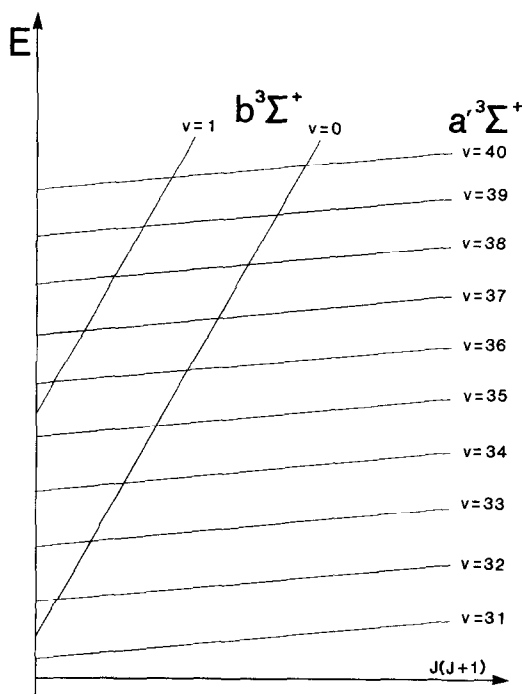


FIG. 1. Schematic diagram of $b^3\Sigma^+$ and $a'^3\Sigma^+$ states.

Plates were calibrated by the Th spectrum (3) obtained from a hollow-cathode type lamp. The measurements were made with great precision using an automatic comparator built in our laboratory. In this comparator, the plate position (controlled interferometrically) and line profiles (measured photoelectrically point by point) were loaded onto floppy-disks. Later, these records were processed with the help of a microcomputer, which makes it possible to obtain accurate wavenumbers not only for simple lines but also for blended ones.

With the aim of increasing the extent of the band analyzed, every band was exposed in intervals changing the gas pressure in the lamp and the exposure time. The (0, 1) and (31, 1) bands, which are investigated in this work, are composed from five plates.

THEORETICAL MODEL

In a parity symmetrized basis functions set, the matrix of a $^3\Sigma^+$ state splits into two independent matrices. Detailed element forms are taken according to Table I. There the indices s must be substituted properly for different $^3\Sigma^+$ states:

$s \rightarrow b$ for the $b^3\Sigma^+$ state,

$s \rightarrow i$ for the i th vibrational level of the $a'^3\Sigma^+$ state (the assumption

$i = v - 31$ was made).

TABLE I
Hamiltonian Matrix Elements for $^3\Sigma^+$ States

$$\begin{aligned}
 H_{11}^{ee} &= T_e + \varepsilon_e - \gamma_e + B_e x - D_e x^2 + H_e x^3 \\
 H_{00}^{ef} &= T_e - 2\varepsilon_e - 2\gamma_e + B_e (x + 2) - D_e (x^2 + 8x + 4) \\
 &\quad + H_e (x^3 + 18x^2 + 28x + 8) \\
 H_{11}^{ef} &= T_e + \varepsilon_e - \gamma_e + B_e x - D_e x (x + 4) \\
 &\quad + H_e x [x^2 + 4(3x + 2)] \\
 H_{01}^{ef} &= -\sqrt{x} [2B_e - \gamma_e - 4D_e (x + 1) \\
 &\quad + H_e (6x^2 + 20x + 8)]
 \end{aligned}$$

The elements of interaction between two $^3\Sigma$ states were taken with the form represented in Table II. This is the simplified form of Kovács' model (4).

The constants of subsequent vibrational levels of the a' state were presented with the help of polynomials containing different powers of the index i (Table III).

The final form of the Hamiltonian for the upper state used in the calculation has been given in Table IV. There are two matrices for e and f components. They describe the system of all interacting states: the b state and subsequent vibrational levels of the a' state. In the computer program the Hamiltonian has been constructed dynamically, so its size can be changed depending on the specified number of perturbing levels.

The $a^3\Pi$ lower state matrix has a standard form with standard notation (5).

CALCULATIONS AND RESULTS

In this work, calculations have been done on the basis of measurements of the (0, 1) band of the Third Positive system and associated with the latter (31, 1) band of the $a'-a$ transition.

TABLE II
Hamiltonian Representing Interaction of Two $^3\Sigma^+$ States

e matrix:		f matrix:			
H_{00}^{ie}	x_i	H_{00}^{if}	H_{01}^{if}	x_i	
	H_{00}^{be}		H_{11}^{if}		x_i
				H_{00}^{bf}	H_{01}^{bf}
					H_{11}^{bf}

TABLE III
Parameters of the $a'^3\Sigma^+$ State in Polynomial Form

$$\begin{aligned}
 T_i &= t_0 + it_1 + i^2 t_2 + i^3 t_3 + \dots \\
 B_i &= b_0 + ib_1 + i^2 b_2 + \dots \\
 -D_i &= d_0 + id_1 + \dots \\
 \epsilon_i &= e_0 + ie_1 + \dots \\
 \gamma_i &= g_0 + ig_1 + \dots \\
 X_i &= x_0 + ix_1 + i^2 x_2 + \dots
 \end{aligned}$$

TABLE IV
General Form of Hamiltonian Matrix Used

e component:

H_{11}^{0e}	X_0				
	H_{11}^{1e}	X_1	X_2	X_3	X_4
		H_{11}^{2e}			
			H_{11}^{3e}		
				H_{11}^{4e}	

f component:

H_{00}^{0f}	H_{01}^{0f}	X_0					
	H_{11}^{0f}		X_0				
		H_{00}^{1f}	H_{01}^{1f}	X_1		X_2	
			H_{11}^{1f}		X_1		X_2
				H_{00}^{2f}	H_{01}^{2f}		
					H_{11}^{2f}		
						H_{00}^{3f}	H_{01}^{3f}
							H_{11}^{3f}

TABLE V
 Constants of the $b^3\Sigma^+ (v=0)$ State (in cm^{-1})*

Constant	After Gerö and Schmid (6,7)	After Stepanov (8)	After Dabrowski <i>et al.</i> (9)	This work
T_b	83828 ^b	83816 ^b	-8243.848(8) ^c	33634.587(14) ^a
B_b	2.058	1.965	1.7975(10)	1.950561(77)
$-D_b \cdot 10^7$	-	-60	8040(190)	-8.6(12)
$H_b \cdot 10^9$	-	-	-2470(130)	-1.951(50)
$\epsilon_b \cdot 10^2$	-	-	-	1.78(14)
$\gamma_b \cdot 10^3$	-	-	-	4.01(15)

*Uncertainties in parentheses are one standard deviation in units of the last digit quoted.

^aEnergy above the $a(v=1)$ level. For the energy above the $X(v=0)$ level we obtain the value 83822.53 cm^{-1} (if we take after Field *et al.* (10) the value $\sigma_{10}^{ax} = 50187.941 \text{ cm}^{-1}$).

^bEnergy above the $X(v=0)$ level.

^cEnergy above the $c(v=0)$ level. For the energy above the $X(v=0)$ level we obtain the value 83833.1 cm^{-1} (if we take after Tilford (11) the value $\sigma_{00}^{cx} = 92076.9 \text{ cm}^{-1}$).

Both of these two bands have common lower states and were fitted simultaneously by a damped least-squares method. Calculations have been done using data up to different values of J_{max} . It was shown that the Hamiltonian given in Table IV describes well the entire (31, 1) band and part of the (0, 1) band up to $J = 40$, i.e., up to the point of the perturbation caused by the $v = 34$ level of the a' state. For the vibrational levels above this point the influence of the $v = 1$ level of the b state was significant.

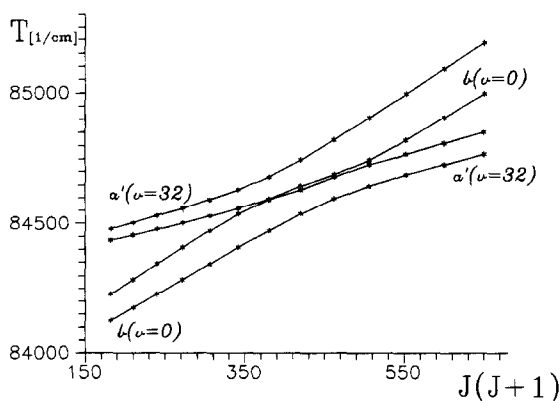


FIG. 2. An example of terms crossing (calculated): $a' (v = 32)$ and $b (v = 0)$ levels (f components).

So the final calculation was done including only up to $J = 40$. As a result, we could obtain, with remarkable precision, for the first time the constants for the $b^3\Sigma^+ (v = 0)$ state (Table V) and for four vibrational levels of the $a'^3\Sigma^+$ state which perturbs it (Table VI).

The T_b constant given in the last column of Table V and the T_i constants given in Table VI represent the values of energy measured above the level $v = 1$ of the $a^3\Pi$ state. If we add to them the value $\sigma_{10}^{aX} = 50\,187.941\text{ cm}^{-1}$, given by Field *et al.* (10), we can obtain their energies above the $v = 0$ level of the $X^1\Sigma^+$ state. For the most precisely found $v = 31$ level we obtain the value $\sigma_{31,0}^{aX} = 83\,715.93\text{ cm}^{-1}$. We can compare this value with the value $83\,726\text{ cm}^{-1}$ predicted by Simmons and Tilford (14). We observe in Table V the significant discrepancy for constants obtained by Dabrowski *et al.* from the $c^3\Pi-b^3\Sigma^+$ transition (9). However, they have not taken

TABLE VI
Constants of the $a'^3\Sigma^+$ State (in cm^{-1})*

a) Parameters of polynomial forms ^a				
Parameter	i=0	i=1	i=2	i=3
t_i	33527.989(13)	601.343(32)	-11.564(94)	-1.24(17)
b_i	0.80996(12)	$-2.286(29) \times 10^{-2}$	$2.79(69) \times 10^{-3}$	$-4.00(79) \times 10^{-6}$
d_i	$-5.11(42) \times 10^{-6}$	$-7.7(7.9) \times 10^{-7}$	-	-
h_i	$-4.33(58) \times 10^{-9}$	-	-	-
e_i	-0.6238(12)	-	-	-
g_i	$-6.76(15) \times 10^{-3}$	$-3.0(2.2) \times 10^{-4}$	-	-
x_i	45.788(15)	-3.734(31)	0.203(21)	$-1.33(42) \times 10^{-2}$

^aAll parameters are examined by application of the F-test and accepted as significant (12).

b) Constants resulting for levels $v=31$ to $v=34$				
Constant	i=0 (v=31)	i=1 (v=32)	i=2 (v=33)	i=3 (v=34)
T_i	33527.989(13)	34116.52(20)	34674.5(1.4)	35194.3(4.6)
B_i	0.80996(12)	0.78989(75)	0.7754(28)	0.7664(62)
$-D_i \times 10^6$	-5.11(42)	-5.88(90)	-6.6(1.7)	-7.4(2.4)
$H_i \times 10^9$	-4.33(58)	-4.33(58)	-4.33(58)	-4.33(58)
ϵ_i	-0.6238(12)	-0.6238(12)	-0.6238(12)	-0.6238(12)
$\gamma_i \times 10^3$	-6.76(15)	-7.06(26)	-7.36(46)	-7.66(67)
X_i	45.788(15)	42.245(41)	39.03(11)	36.06(24)

*Uncertainties in parentheses are one standard deviation in units of the last digit quoted.

TABLE VII
Line Wavenumbers in the (31, 1) Band

J	P_{11ff}	Q_{2100}	Q_{11f0}	$R_{Q_{210f}}$	R_{11ff}	$S_{Q_{31f0}}$
0					33548.974	
1			33547.657 ^a		547.975	33554.108 ^a
2			543.541	33544.989 ^a	545.708	553.477
3	33532.688		538.205	541.522	542.196	551.607
4	524.282	33530.868	531.554	536.682	537.384	548.411
5	514.567 ^a	522.813 ^a	523.565	530.464	531.209	543.830
6	503.624 ^a	513.476	514.223	522.813	523.565	537.733
7	33491.158	502.648	503.379	513.630	514.404	530.096
8	477.253	33490.282	33490.978	502.867	503.624	
9	461.705	476.286	477.027	33490.485	33491.305	
10	444.628	460.751 ^a	461.434	476.504	477.253	
11	425.882	443.461 ^a	444.177	460.751 ^a	461.705 ^a	
12	405.482	424.473	425.248	443.461	444.177 ^a	
13	33383.392	403.886	404.650	424.473 ^a	425.248 ^a	
14	359.582	33381.564	33382.320	403.695	404.467	
15	334.084	357.561 ^a	358.299	33381.248	33382.019 ^a	
16	306.846		332.567 ^a		357.857	
17	33277.893		305.121		332.034 ^a	
18	247.237		33275.961		304.409	
19	214.864		245.099		33275.135	
20	33180.768		212.518		244.112	
21	144.949		33178.235		211.425	
22			142.234			

J	$S_{R_{2100}}$	$O_{P_{12ff}}$	$P_{P_{2200}}$	$P_{Q_{12f0}}$	$Q_{P_{32ff}}$	$Q_{Q_{220f}}$
1	33552.901			33504.928 ^a		
2	552.402	33498.430		500.558	33504.835 ^a	33503.624 ^a
3	550.558	490.656		33494.588	500.558	33499.502
4	547.409	481.364	33486.454	487.147	33494.817	493.768
5	542.826	470.586	477.490	478.185	487.473	486.454
6	536.682	458.297	466.837 ^a	467.608	478.500	477.490
7	529.053	444.348	454.694	455.407	467.856	466.837
8	519.802	428.721	440.717	441.463	455.407	454.413
9	508.919	411.395	425.022	425.882 ^a	441.248	440.203
10	33496.390	33392.343	407.530	408.309	425.248 ^a	424.212
11	482.106 ^a	371.503	33388.277	33389.048	407.530 ^a	406.437
12	466.370 ^a	348.873	367.223	367.984	33387.932 ^a	33386.861
13	448.818 ^a	324.434	344.325	345.123	366.539 ^a	365.490
14		33298.214	319.679	320.441	343.385 ^a	342.324
15		270.185	33293.225	33293.995		317.375
16		240.372	264.979	265.763		33290.639
17		208.827	234.968	235.752		262.135
18			203.179	203.924		231.869
19			33169.621			33199.825
20			134.297			166.057

^aLines not used in the calculations.

TABLE VII—Continued

J	${}^{\alpha}R_{12ff}$	${}^RQ_{32fe}$	${}^RR_{22ee}$	${}^SR_{32ff}$	${}^NP_{13ff}$	${}^OP_{23ee}$
1	33507.030	33511.488		33517.040 ^a		
2	504.362	510.463		517.793	33463.311 ^a	33464.785 ^a
3	500.181	507.978 ^a	33507.030 ^a	517.040	454.413 ^a	457.668
4	33494.438 ^a	504.033	503.040 ^a	514.715 ^a	443.815	448.818
5	487.147 ^a	33498.430	33497.391 ^a	510.707	431.418	438.161
6	478.185 ^a	491.158 ^a	490.108	504.928	417.277	425.685
7	467.608	482.106	481.083	33497.391	401.300	411.395
8	455.155	471.288	470.259	488.076	33383.392 ^a	33395.215
9	440.977	458.689	457.668 ^a	477.027 ^a	363.883	377.155
10	425.022	444.348 ^a	443.239	463.943 ^a	342.324 ^a	357.200
11	407.213	428.088	427.042	449.308	319.062 ^a	335.376
12	33387.640	410.192 ^a	408.991	432.834		311.671
13	366.246 ^a	33390.288	33389.237	414.482 ^a		33286.079
14		368.735 ^a	367.635			258.663
15		345.337	344.325 ^a			229.385 ^a
16		320.154	319.062			
17			33292.147			
18			263.435 ^a			
19			232.981 ^a			

J	${}^OQ_{13fe}$	${}^PP_{33ff}$	${}^RQ_{23ef}$	${}^OQ_{33fe}$	${}^OR_{23ee}$	${}^RR_{33ff}$
2	33465.346		33468.578	33475.284	33474.220	33482.667
3	458.297	33464.390	463.311	471.757	470.779 ^a	480.861
4	449.492	457.263	456.219	466.370	465.346	477.253 ^a
5	438.828 ^a	448.314	447.288	459.112	458.108	471.536
6	426.411	437.503	436.484	449.925	448.818 ^a	463.943
7	412.125	424.803	423.788	438.828	437.808	454.413 ^a
8	33395.969	410.192	409.176	425.685 ^a	424.803 ^a	442.856
9		33393.697	33392.652	410.821	409.802	429.423
10		375.266	374.249	33393.960	33392.933	414.061
11		354.981	353.935	375.121 ^a	374.116	33396.811
12		332.800	331.747	354.547	353.450	377.698
13		308.750	307.689 ^a	332.034		356.705
14		33282.827	33281.785	307.689 ^a		333.886
15		255.099	254.036 ^a	33281.507		309.209
16		225.554		253.497		33282.827 ^a
17		33194.173		223.698		254.475
18		161.021		33192.088		224.414
19		126.070		158.695		33192.528
20				123.513		

into account the strong perturbations occurring for $J = 0$ levels in both lower and upper states (6, 7, 15–17).

Gerö's interpretation of the (31, 1) band (2) has been largely changed and improved. Since the (31, 1) band is entirely interpreted, we are able to give its wavenumbers in Table VII. Since the (0, 1) band has been interpreted only up to $J = 40$, we intend to publish the wavenumbers for it in a subsequent paper, when the interpretation has been completed.

In Fig. 2 we have an example of terms crossing as calculated from the Hamiltonian.

In Table VIII the obtained constants of the $a^3\Pi$ state have been collected. Their values are in accordance with those previously given (5, 10, 13).

TABLE VIII
 Constants of the $a^3\Pi$ ($v = 1$) State (in cm^{-1})*

Constant	After Effantin <i>et al.</i> (5)	After Field <i>et al.</i> (13)	This work
A_P	41.2818 (9)	41.266 (4) ^a	41.2826 (14)
B_P	1.66257 (1)	1.66267 (1) ^a	1.662357 (63)
$-D_P^* 10^6$	- 6.407 (2)	-	- 6.01 (10)
$H_P^* 10^{10}$	-	-	- 1.73 (42)
α_P	- 0.8536 (8)	- 0.8682 (23)	- 0.8498 (14)
$e_P^* 10^2$	2.18 (7)	1.39 (13)	1.923 (89)
$A_{DP}^* 10^4$	- 3.57 (5)	- 3.98 (16) ^b	- 3.86 (15)
$p_P^* 10^2$	1.071 (6)	1.000 (18) ^b	1.053 (18)
$q_P^* 10^4$	1.127 (2)	1.216 (40) ^b	1.070 (80)

*Uncertainties in parentheses are one standard deviation in units of the last digit quoted.

^aField *et al.* (10).

^bEvaluated using constants interrelations.

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