PERTURBATIONS IN THE SPECTRA OF CO ISOTOPIC MOLECULES I. PARTIAL ANALYSIS OF $e^3\Sigma^- - A^1\Pi$ PERTURBATIONS

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For the purpose of obtaining some of the $e^3\Sigma^-$ state constants of CO isotopic molecules two perturbations in the $v = 0$ and $v = 2$ levels of the $A^1\Pi$ state are analysed.

In this paper analyses of two perturbations in the lowest levels of the $A^1\Pi$ state of $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{12}C^{18}O$ molecules caused by the $e^3\Sigma^-$ state are reported. These perturbations appear in the $v = 0$, $v = 2$ and $v = 5$ vibrational levels of the A state and they are caused by the $v = 1$, $v = 4$ and $v = 8$ levels, respectively, of the e state. The perturbation is greatest for $v = 0$, smaller for $v = 2$, and unperceptible in practice for $v = 5$, which is why the latter case is not analysed here. The perturbation in the $v = 2$ level of the $^{12}C^{18}O$ molecule could not be analysed also because of incomplete experimental data. The analysis is made with the aid of Kovács' $f_x(J)$ and $g_x(J)$ functions [1]. The analysed bands and the sources of data are listed in the 2nd, 3rd and 4th columns of Table II.

TABLE I

B_v values of the $e^3\Sigma^-$ state (in cm^{-1})

Molecule	v	B_v value	
		After Simmons and Tilford [2]	Actually obtained
$^{12}C^{16}O$	1	1.2582	1.2582 ± 0.0003
	4	1.2048	1.2039
$^{13}C^{16}O$	1	—	1.2032 ± 0.0005
	4	—	1.1515
$^{12}C^{18}O$	1	—	1.1955 ± 0.0006

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The analysis by means of the $f_x(J)$ function gives five B_v values for the e state (Table I). From these values the rotational constants are evaluated by the leastsquares method for the ordinary CO molecule; they are $B_e = (1.2845 \pm 0.0010)$ cm^{-1} and $\alpha_e = (0.0180 \pm 0.0003)$

TABLE II

Term combinations obtained for the $e^3\Sigma^-$ state (in cm^{-1})

Molecule	System	Band analyzed	Source of data	Term combination	Value obtained
$^{12}C^{16}O$	$A-X$	0—0, 0—1	[3]	σ_{10}^{eX}	64802.82 ± 0.01
	$B-A$	0—0	[8]	σ_{01}^{Be}	22113.34 ± 0.01
	$B-A$	1—0	[8]	σ_{11}^{Be}	24195.43 ± 0.09
	$B-A$	0—2	[8]	σ_{04}^{Be}	18944.76
$^{13}C^{16}O$	$B-A$	0—0	[9]	σ_{01}^{Be}	22125.51 ± 0.36[a]
	$B-A$	1—0	[9]	σ_{11}^{Be}	24162.82 ± 0.23[b]
	$C-A$	0—0	[10]	σ_{01}^{Ce}	27127.97 ± 0.35[c]
	$B-A$	0—2	[9]	σ_{04}^{Be}	19024.82
$^{12}C^{18}O$	$C-A$	0—0	[11]	σ_{01}^{Ce}	27128.87 ± 0.15[d]

[a, b, c, d] Deperturbed values largest with 0.79, 0,70, 0.64 and 0.68, respectively.

cm^{-1} (the values quoted by Simmons and Tilford [2]) are $B_e = (1.2836 \pm 0.0024)$ cm^{-1} and $\alpha_e = (0.0174 \pm 0.0005)$ cm^{-1}.

Subsequently the analysis by $g_x(J)$ function is made, however some formulas and results are presented by some what different means the original ones [1]. They are expressed by the term combinations

$$\sigma_{v'v''}^{AB} = T_e^A - T_e^B + G^A(v') - G^B(v'') + F_v'^A(0) - F_v''^B(0),$$

which can have meaning of the band origins, if the transitions are possible.

For the purpose of obtaining the equations for the considered $^3\Sigma^- - ^1\Pi$ perturbation the following simplified formulas for the respectives components of the $^3\Sigma^-$ state were adopted:

$$F_{J-1}(J) = B_v^p J(J-1) - \lambda,$$

$$F_J(J) = B_v^p J(J+1),$$

$$F_{J+1}(J) = B_v^p (J+1)(J+2) - \lambda.$$

If the lower state is perturbed, the following formulas for the $J-1$, J and $J+1$ components result (n means the unperturbed state participating in the transition):

$$g_{\overline{PR}}(J) + g_{\overline{PR}}^*(J) = \sigma_{v'v''}^{nA} + \sigma_{v'v''}^{ne} + 2B_v^n + B_v^e(J-1) + \lambda,$$

$$g_Q(J) + g_Q^*(J) = \sigma_{v'v''}^{nA} + \sigma_{v'v''}^{ne},$$

$$g_{\overline{PR}}(J) + g_{\overline{PR}}^*(J) = \sigma_{v'v''}^{nA} + \sigma_{v'v''}^{ne} + 2B_v^n - B_v^e(J+1) - \lambda.$$

Using these formulas and the analogous ones for the case of perturbations in the upper state (for the analysis of the IV positive system bands) yields the results given in Table II. The errors are standard ones.

The 0–1 band of the $A-X$ transition [3] was reduced by using the constants of Rank, St. Pierre and Wiggins [4] to the 0–0 band, thereby letting both bands to be analyzed together. This analysis showed that the σ_{00}^{AX} value given by Simmons, Bass and Tilford [3] disagrees by 4 cm^{-1} with the experimental value [2]. Therefore, the value used is $\sigma_{00}^{AX} = 64744.82$ cm^{-1} evaluated from data of Rytel [5], which agrees fairly well with the result of our analysis of 0–0 band wave numbers given in the work of Simmons, Bass and Tilford [3].

The well confirmed value $\lambda = 0.84$ cm^{-1} used for the case of the $^{12}C^{16}O$ molecule is that of Herzberg and Hugo [6]. From the analysis of the 0–0 and 0–1 bands of the Ångström system and 0–0 band of the Herzberg system in the $^{13}C^{16}O$ molecule the λ-value for this molecule is obtained; it is $\lambda = (0.94 \pm 0.19)$ cm^{-1}.

Using the σ_{00}^{BX} and σ_{00}^{CX} values of Tilford and Vanderslice [7] for the $^{12}C^{16}O$ and $^{13}C^{16}O$ molecules together with the $\Delta G_{\frac{1}{2}}$ values of Kępa and Rytel [8] and Rytel [9], it was also

TABLE III

Band origins of e—X transition (in cm^{-1})

Molecule	$v'-v''$	Band origin	
		Measured [2]	Actually obtained
$^{12}C^{16}O$	1–0	64802.74	64802.82
	4–0	64970.84	67971.40
$^{13}C^{16}O$	1–0	—	64791[a]
	4–0	—	67892.00

[a] Deperturbed value is 64790.53.

possible to evaluate some deperturbed values $\sigma_{v'0}^{eX}$. These values are compared in Table III with those for ^{12}C ^{16}O from experimental observations of Simmons and Tilford [2].

From our deperturbed values $\sigma_{v'0}^{eX}$ the vibrational constants of state were estimated (for the $^{12}C^{16}O$ molecule). They are $\omega_e = 1110.08$ cm^{-1} and $\omega_e x_e = 8.98$ cm^{-1}. The resulting electronic terms are $T_e = 64230.59$ cm^{-1} (for $^{12}C^{16}O$ molecule) and $T_e = 64239.40$ cm^{-1} (for the $^{13}C^{16}O$ molecule).

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