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5.80 Small-Molecule Spectroscopy and Dynamics  
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# Lecture # 18 Supplement

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## A. A Model for the Perturbations and Fine Structure of the $\Pi$ States of CO

This paper reports the results of an analysis of the numerous perturbations of the CO  $a^3\Pi$  and  $A^1\Pi$  states, which belong to the  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p)^4 (\sigma 2p) (\pi^* 2p)$  electronic configuration (abbreviated  $\sigma\pi^*$ ), by the  $a'^3\Sigma^+$ ,  $e^3\Sigma^-$ ,  $d^3\Delta_i$ ,  $I^1\Sigma^-$  and  $D^1\Delta$  states, which belong to the  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p)^3 (\sigma 2p)^2 (\pi^* 2p)$  configuration (abbreviated  $\pi^3\pi^*$ ). As many data as possible from the absorption, emission, and radio frequency spectra involving these states were combined in a uniform and systematic analysis. In several cases it was possible to use earlier data from the work of Gerö and Szabo[3] to augment the modern studies.

The vibronic levels fitted are listed in Table I. The letters adjacent to each level indicate the sources of the data. The 47 horizontal rows contain the combinations of vibronic levels treated by degenerate perturbation theory. The choice of which levels to include in each of the groups was usually determined by selecting all of the nearest and strongest perturbers of a given  $a^3\Pi$  or  $A^1\Pi$  level. (The vibronic levels of the A and a states conveniently never occur at the same energy.) Therefore, the fitted  $a^3\Pi$  and  $A^1\Pi$  constants reported here should be regarded as fully deperturbed with respect to all of the nearest interacting levels.

Extensive use was made of a nonlinear least squares fitting procedure which has been described earlier. The elements of the effective Hamiltonian matrix are given by Wicke *et al.*[2]

The analysis of perturbations of the CO  $a^3\Pi$  and  $A^1\Pi$  states has led to two important conclusions.

- (i) For perturbations between vibronic levels belonging to a given pair of electronic states the perturbation matrix element is the product of a vibrational factor with a constant electronic factor.
- (ii) Simple, single-configuration arguments successfully predict the sign and relative magnitude of each of the electronic factors for perturbations between levels of each pair of electronic states. Thus all of the perturbations considered here can be related to two constants which are joint properties of the electronic configurations. It is now possible to calculate the interaction energy between any rovibronic level of one electronic configuration with those of the other configuration whenever the vibrational wave-functions are known.

## B. Factorization of Perturbation Parameters

All perturbation parameters are listed in Table II. The electronic part of each perturbation parameter was obtained by dividing the spin-orbit parameter,  $A$  or  $\alpha$ , by the vibrational overlap  $\langle v|v'\rangle$ , or by dividing the rotation-electronic parameter,  $\beta$ , by  $\frac{h}{8\pi^2c\mu} \langle v|r^{-2}|v'\rangle \equiv \langle v|B|v'\rangle = B_{vv'}$ . For extremely weak perturbations, the beta parameters, denoted with an asterisk, were calculated by multiplying an average value of the assumed constant electronic factor by the proper vibrational factor. Also included in Table II are the r-centroids,  $\langle v|r|v'\rangle/\langle v|v'\rangle$  which indicate the internuclear distance of maximum vibrational overlap (stationary phase point). For perturbations between any pair of electronic states, the r-centroid is nearly constant. For a given perturbing state the r-centroids are approximately 0.3 Å greater for perturbations of  $a^3\Pi$  than of  $A^1\Pi$ . This indicates that the overlap is greater at a larger internuclear distance for perturbations of the  $a^3\Pi$  state than for the  $A^1\Pi$  state. This result can be rationalized by examining the potential energy curves for CO. The inner wall of the  $A^1\Pi$  state runs close to and parallel to the inner walls of the perturbing  $a'$ ,  $e$ ,  $d$ ,  $D$ , and  $I$  states, whereas the curves of the perturbing states cross the  $a^3\Pi$  state on the outer wall.

For the pairs of states for which multiple determinations of the electronic part of the perturbation parameters were possible, the independence of this constant electronic factor with respect to  $v$ ,  $v'$  is demonstrated in Table II. Thus, it is possible to partially evaluate second order effects by summations over all known vibrational levels of a particular electronic symmetry. Second-order constants for the  $a^3\Pi$  state are calculated and discussed by Wicke *et al.*[2]

## C. The Electronic Perturbation Parameters

The relative signs and magnitudes of the electronic perturbation parameters have been derived considering only two electronic configurations:

$$\begin{array}{l} \sigma\pi^* \quad (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2 \quad | \quad (\pi 2p)^4(\sigma 2p)(\pi^* 2p) \quad \text{a}^3\Pi, \text{A}^1\Pi \\ \pi^3\pi^* \quad (\sigma 1s)(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2 \quad | \quad (\pi 2p)^3(\sigma 2p)^2(\pi^* 2p) \quad \text{a}^3\Sigma^+, \text{e}^3\Sigma^-, \text{d}^3\Delta_i, \text{D}^1\Delta, \text{I}^1\Sigma^-, \text{}^1\Sigma^+. \end{array}$$

The treatment which follows considers the six 2p electrons to the right of the line and neglects those to the left as core. The general procedures used to obtain wavefunctions in a Hund's case a basis set and to calculate matrix elements are analogous to those given by Condon and Shortley,[4] Chapter 6. The Hamiltonian operators and symmetry operator,  $\sigma_v$ , used here are those given by Hougen[5] and are consistent with the phase convention of Condon and Shortley.[4]

The complete wavefunctions of definite overall parity contain electronic, rotational, and vibrational parts. Consider first the electronic part. In order to maintain a consistent arbitrary phase throughout the calculation, a standard order for the complete set of individual spin-orbital quantum numbers must be defined. The standard order for the 2p orbitals chosen here was  $(1^+1^- - 1^+ - 1^-0^+0^-1^{*-}1^{*-} - 1^{*+} - 1^{*-})$  where the numerals denote the values of  $m_\ell$ ,  $\pm$  denotes  $m_s = \pm\frac{1}{2}$ , and the asterisk denotes the  $(\pi^*2p)$  orbital. All possible six-electron functions were formed for each electronic configuration. There are eight such functions for the  $\sigma\pi^*$  configuration and sixteen for the  $\pi^3\pi^*$  configuration. Each function could immediately be characterized by  $|\Lambda\Sigma\rangle$ . Functions characterized by  $|\Lambda S\Sigma\rangle$  were then generated. Those with  $\Lambda = \pm 1$  or  $\pm 2$  and  $\Sigma = 1$  could be identified as triplets by inspection. The corresponding  $|\Lambda 10\rangle$  and  $|\Lambda 1 - 1\rangle$  functions were obtained by successively applying the ladder operator  $\mathbf{S}_- = \sum_{i=1}^6 \mathbf{s}_{i-}$  (see Condon and Shortley, Chapter 8, §5 [4]). The functions with  $\Lambda = 0$  were generated in the same way except, since there were initially two functions with  $\Lambda = 0$ ,  $\Sigma = 1$ , the sum and difference functions were used. The singlet functions  $|\Lambda 00\rangle$  were formed by taking linear combinations of the original functions which were orthogonal to the triplet functions  $|\Lambda 10\rangle$ .

The transformation properties of the  $\Sigma$  state functions and those with  $\Omega = 0$  under the symmetry operation  $\sigma_v$  (see Hougen §2.3 [5]) are denoted by + if they transform into themselves and by - if they transform into their negatives. It should be noted that the  ${}^3\Pi_0$  functions,  $|-111\rangle$  and  $|11 - 1\rangle$  generated by the above procedure did not transform properly, therefore the sum and difference functions which do transform properly were used for the  ${}^3\Pi_0\pm$  states. The resulting functions were then anti-symmetrized with the operator  $\mathbf{A}$  (see Condon and Shortley page 164 [4]) and are shown in Table III. The rotating-molecule wave functions were formed by multiplying the electronic part by the appropriate rotational part  $|\Omega JM\rangle$ , and, for  $\Omega \neq 0$ , taking sums and differences of

functions with equal  $|\Omega|$  for a given electronic state. The parity of the rotating-molecule functions was determined with the operator  $\sigma_v$ , used here are those given by Hougen [5] and are consistent with the phase convention of Condon and Shortley. [4]

The complete wavefunctions of definite overall parity contain electronic, rotational, and vibrational parts. Consider first the electronic part. In order to maintain a consistent arbitrary phase throughout the calculation, a standard order for the complete set of individual spin-orbital quantum numbers must be defined. The standard order for the  $2p$  orbitals chosen here was

$$(1^+1^- - 1^+ - 1^-0^+0^-1^{*+}1^{*-} - 1^{*+} - 1^{*-}), \quad (1)$$

where the numerals denote the values of  $m_\ell$ ,  $\pm$  denotes  $m_s = \pm 1/2$ , and the asterisk denotes the ( $\pi^*2p$ ) orbital. All possible six-electron functions were formed for each electronic configuration. There are eight such functions for the  $\sigma\pi^*$  configuration and sixteen for the  $\pi^3\pi^*$  configuration. Each function could immediately be characterized by  $|\Lambda\Sigma\rangle$ . Functions characterized by  $|\Lambda S\Sigma\rangle$  were then generated. Those with  $\Lambda = \pm 1$  or  $\pm 2$  and  $\Sigma = 1$  could be identified as triplets by inspection. The corresponding  $|\Lambda 10\rangle$  and  $|\Lambda 1 - 1\rangle$  functions were obtained by successively applying the ladder operator  $\mathbf{S}_- = \sum_{i=1}^6 \mathbf{s}_{i-}$  [See Condon and Shortley (18, Ch. 8 Section 5) [4]]. The functions with  $\Lambda = 0$  were generated in the same way except, since there were initially two functions with  $\Lambda = 0$ ,  $\Sigma = 1$ , the sum and difference functions were used. The singlet functions  $|\Lambda 00\rangle$  were formed by taking linear combinations of the original functions which were orthogonal to the triplet functions  $|\Lambda 10\rangle$ .

The transformation properties of the  $\Sigma$  state functions and those with  $\Omega = 0$  under the symmetry operation  $\sigma_v$  [see Hougen (Section 2.3) [4]] are denoted by  $+$  if they transform into themselves and by  $-$  if they transform into their negatives. It should be noted that the  ${}^3\Pi_0$  functions,  $|-111\rangle$  and  $|11 - 1\rangle$  generated by the above procedure did not transform properly, therefore the sum and difference functions which do transform properly were used for the  ${}^3\Pi_0\pm$  states. The resulting functions were then antisymmetrized with the operator  $A$  [see Condon and Shortley (p. 164) [4]] and are shown in Table III. The rotating molecule wavefunctions were formed by multiplying the electronic part by the appropriate rotational part  $|\Omega JM\rangle$ , and for  $\Omega \neq 0$ , taking sums and differences of functions with equal  $|\Omega|$  for a given electronic state. The parity of the rotating-molecule functions was determined with the operator  $\sigma_v$ .

For the six-electron system the spin-orbit operator can be written

$$\mathbf{H}_{\text{SO}} = \sum_{i=1}^6 a_i \boldsymbol{\ell}_i \cdot \mathbf{s}_i \quad (2)$$

where

$$\boldsymbol{\ell} \cdot \mathbf{s} = \ell_z s_z + \frac{1}{2} \ell_+ s_- + \frac{1}{2} \ell_- s_+ \quad (3)$$

$$a \equiv \langle \pm 1 | a \ell_{\pm} | 0 \rangle = \langle 0 | a \ell_{\mp} | \pm 1 \rangle. \quad (4)$$

The matrix elements of  $\mathbf{H}_{\text{SO}}$  were evaluated according to the procedure given by Condon and Shortley, Chapter 6 §6.[4]

The six-electron operator corresponding to  $\text{BL}_{\pm} \mathbf{S}_{\mp}$ :

$$\text{BL}_{\pm} \mathbf{S}_{\mp} = B \left( \sum_{i=1}^6 \ell_{i\pm} \right) \left( \sum_{j=1}^6 \mathbf{s}_{j\mp} \right) = B \left[ \sum_{i=1}^6 \ell_{i\pm} \mathbf{s}_{i\mp} + \sum_{i>j=1}^6 (\ell_{i\pm} \mathbf{s}_{j\mp} + \ell_{j\pm} \mathbf{s}_{i\mp}) \right] \quad (5)$$

$$b \equiv \langle \pm 1 | \ell_{\pm} | 0 \rangle = \langle 0 | \ell_{\mp} | \pm 1 \rangle. \quad (6)$$

The matrix elements of the 2<sup>nd</sup> sum of the  $\text{BL}_{\pm} \mathbf{S}_{\mp}$  operator were evaluated by the procedure given by Condon and Shortley Chapter 6 §7. [4]

The six-electron operator for  $-\text{BJ}_{\pm} \mathbf{L}_{\mp}$  is simply  $-\text{BJ}_{\pm} \sum_{i=1}^6 \ell_{i\mp}$ . The matrix elements of  $\mathbf{J}_{\pm}$  were taken from Hougen page 9. [5]

The perturbation matrix elements written in terms of the parameters  $a$  and  $b$  are summarized in Table IV. The relationships of the perturbation parameters defined by Wicke *et al.* [1] to the parameters  $a$  and  $b$  are given in Table V. Also included in the last column of Table V are the experimental values for  $a$  and  $b$  determined from perturbations between various pairs of electronic states. The close agreement among the experimentally determined values of  $a$  and  $b$  is striking.

Table I: A<sup>1</sup>Π Perturbation Parameters

A <sup>1</sup> Π ( <i>v</i> )	Perturber ( <i>v'</i> )	A (cm <sup>-1</sup> )	A/⟨ <i>v v'</i> ⟩ (cm <sup>-1</sup> )	<i>r</i> -centroid (Å)
0	a'(9)	1.41*		1.1231
1	a'(10)	2.890(29)	-21.54(22)	1.1297
2	a'(11)	3.93*		1.1363
3	a'(13)	-4.058(37)	-20.89(19)	1.1295
4	a'(14)	-4.21*		1.1362
5	a'(16)	4.15*		1.1300
6	a'(17)	3.996(10)	-20.87(5)	1.1367
7	a'(19)	-3.64*		1.1310
8	a'(20)	-3.082(18)	-20.62(12)	1.1381
10	a'(23)	2.058(35)	-20.04(34)	1.1401
12	a'(26)	-1.25*		1.1422
0	e(1)	8.708(6)	-24.73(2)	1.2890
1	e(3)	2.07*		1.2602
2	e(4)	7.416(32)	-24.92(11)	1.2815
3	e(5)	5.51*		1.2947
4	e(7)	-4.41*		1.2855
5	e(8)	-0.469(31)	-17.1(11)	1.3504
6	e(10)	0.65*		1.3392
7	e(11)	-2.36(24)	-26.2(27)	1.2650
8	e(12)	-4.03*		1.2830
9	e(14)	3.48*		1.2723
10	e(15)	4.328(25)	-25.28(15)	1.2841
11	e(17)	-3.79*		1.2747
12	e(18)	-3.78*		1.2854
13	e(19)	-3.13*		1.2971
14	e(21)	3.07*		1.2882
15	e(22)	2.148(32)	-23.68(35)	1.3017
16	e(24)	-2.22*		1.2933
17	e(25)	-1.24(5)	-23.5(9)	1.3128
18	e(27)	1.25*		1.3049

Table I: (continued)

$A^1\Pi (v)$	Perturber ( $v'$ )	$A$ ( $\text{cm}^{-1}$ )	$A/\langle v v'\rangle$ ( $\text{cm}^{-1}$ )	$r$ -centroid ( $\text{\AA}$ )
0	d(4)	-12.439(29)	-33.70(8)	1.2200
1	d(5)	-9.769(39)	-33.90(14)	1.2298
2	d(7)	6.2*		1.2226
3	d(8)	0.532(64)	-28.3(34)	1.2994
4	d(9)	-4.04*		1.2193
6	d(12)	6.338(11)	-34.20(6)	1.2227
8	d(15)	-6.074(39)	-33.51(22)	1.2221
9	d(16)	5.15*		1.2308
11	d(19)	3.551(18)	-32.31(16)	1.2290
13	d(22)	-2.234(65)	-37.0(11)	1.2309
16	d(26)	-1.15*		1.1957
18	d(29)	1.200(41)	a –	a –
		$\beta(\text{cm}^{-1})$	$\beta/\langle v B v'\rangle$ (unitless)	
0	I(1)	-0.0539(9)	.114(2)	1.2929
1	I(2)	.056*		1.2966
2	I(3)	.0231(55)	.061(15)	1.3105
4	I(6)	.0121(10)	.156(13)	1.2707
6	I(9)	-.031*		1.2952
7	I(10)	-.036*		1.3083
8	I(12)	.034*		1.2987
9	I(13)	.0212(65)	.091(28)	1.3117
10	I(15)	-.027*		1.3028
11	I(16)	-.0128(36)	.091(26)	1.3196
13	I(19)	.006*		1.3514
14	I(21)	-.0068*		1.3376
15	I(22)	-.0032*		1.2151
16	I(24)	-.0025*		1.1898
1	D(1)	.0746(25)	a –	a –

Uncertainties in ( ) correspond to one standard deviation.

\* Fixed at calculated values.

a. Vibrational wavefunctions not available.

Table II:  $a^3\Pi$  Perturbation Parameters

$a^3\Pi(v)$	Perturber( $v'$ )	$\alpha$ ( $\text{cm}^{-1}$ )	$\beta$ ( $\text{cm}^{-1}$ )	$\alpha/\langle v v'\rangle$ ( $\text{cm}^{-1}$ )	$\beta/\langle v \beta v'\rangle$ (unitless)	$r$ -centroid ( $\text{\AA}$ )
4	$a'(0)$	-7.476(9)	.0819(4)	-17.77(2)	0.1544(8)	1.3955
5	$a'(1)$	-8.016*	.0874*			1.4058
6	$a'(3)$	4.226*	-.0473*			1.3833
7	$a'(4)$	5.601(16)	-.0609(6)	-17.53(5)	0.1512(15)	1.3964
8	$a'(5)$	4.64*	-.0506*			1.4095
10	$a'(8)$	-4.066*	.0447*			1.4026
13	$a'(12)$	2.183*	-.0239*			1.4160
15	$a'(15)$	-1.959*	.0216*			1.4129
11	$e(2)$	-3.956(34)	.0353(12)	-17.55(15)	0.1587(54)	1.5759
14	$e(6)$	-4.52*	.0405*			1.5895
9	$d(2)$	-9.258(21)	.0889(32)	-24.84(6)	0.222(8)	1.5122
12	$d(6)$	1.856(57)	-.019*	-22.8(7)	—	1.4785
15	$d(15)$	0.83*	-.008*			1.4202
		$A(\text{cm}^{-1})$		$A/\langle v v'\rangle (\text{cm}^{-1})$		
10	$I(0)$	-0.886*				1.5856
11	$I(1)$	-2.168*				1.5965
13	$I(4)$	-9.88(32)		-24.7(8)		1.5924
14	$I(5)$	-9.42(9)		-23.61(23)		1.6045

Table III: Normalized, antisymmetrized wavefunctions for the  $\sigma\pi^*$  and  $\pi^3\pi^*$  configurations

State	$\Omega$	wavefunctions for	$\dots (\pi 2p)^4 (\sigma 2p) (\pi^* 2p)$
${}^3\Pi_2$	+2	$A  1^+1^- - 1^+ - 1^-0^+1^{*+}\rangle$	
	-2	$A  1^+1^- - 1^+ - 1^-0^- - 1^{*-}\rangle$	
${}^3\Pi_1$	+1	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^+ - 1^-0^-1^{*+}\rangle +  1^+1^- - 1^+ - 1^-0^+1^{*-}\rangle]$	
	-1	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^+ - 1^-0^- - 1^{*+}\rangle +  1^+1^- - 1^+ - 1^-0^+ - 1^{*-}\rangle]$	
${}^3\Pi_0$	$0^+$	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^+ - 1^-0^-1^{*-}\rangle -  1^+1^- - 1^+ - 1^-0^+ - 1^{*+}\rangle]$	
	$0^-$	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^+ - 1^-0^-1^{*-}\rangle +  1^+1^- - 1^+ - 1^-0^+ - 1^{*+}\rangle]$	
${}^1\Pi$	+1	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^+ - 1^-0^-1^{*+}\rangle -  1^+1^- - 1^+ - 1^-0^+1^{*-}\rangle]$	
	-1	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^+ - 1^-0^- - 1^{*+}\rangle -  1^+1^- - 1^+ - 1^-0^+ - 1^{*-}\rangle]$	
		wavefunctions for	$\dots (\pi 2p)^3 (\sigma 2p)^2 (\pi^* 2p)$
${}^3\Delta_3$	+3	$A  1^+1^- - 1^+0^+0^-1^{*+}\rangle$	
	-3	$A  1^- - 1^+ - 1^-0^+0^-1^{*-}\rangle$	
${}^3\Delta_2$	+2	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^-0^+0^-1^{*+}\rangle +  1^+1^- - 1^+0^+0^-1^{*-}\rangle]$	
	-2	$A \frac{1}{\sqrt{2}} [ 1^- - 1^+ - 1^-0^+0^- - 1^{*+}\rangle +  1^+ - 1^+ - 1^-0^+0^- - 1^{*-}\rangle]$	
${}^3\Delta_1$	+1	$A  1^+1^- - 1^-0^+0^-1^{*-}\rangle$	
	-1	$A  1^+ - 1^+ - 1^-0^+0^- - 1^{*+}\rangle$	
${}^1\Delta$	+2	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^-0^+0^-1^{*+}\rangle -  1^+1^- - 1^+0^+0^-1^{*-}\rangle]$	
	-2	$A \frac{1}{\sqrt{2}} [ 1^- - 1^+ - 1^-0^+0^- - 1^{*+}\rangle -  1^+ - 1^+ - 1^-0^+0^- - 1^{*-}\rangle]$	
${}^3\Sigma^+$	+1	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^+0^+0^- - 1^{*+}\rangle +  1^+ - 1^+ - 1^-0^+0^-1^{*+}\rangle]$	
	$0^-$	$A \frac{1}{2} [ 1^+1^- - 1^-0^+0^- - 1^{*+}\rangle +  1^+1^- - 1^+0^+0^- - 1^{*-}\rangle +  1^- - 1^+ - 1^-0^+0^-1^{*+}\rangle +  1^+ - 1^+ - 1^-0^+0^-1^{*-}\rangle]$	
	-1	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^-0^+0^- - 1^{*-}\rangle +  1^- - 1^+ - 1^-0^+0^-1^{*-}\rangle]$	
${}^3\Sigma^-$	+1	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^+0^+0^- - 1^{*+}\rangle -  1^+ - 1^+ - 1^-0^+0^-1^{*+}\rangle]$	
	$0^+$	$A \frac{1}{2} [ 1^+1^- - 1^-0^+0^- - 1^{*+}\rangle +  1^+1^- - 1^+0^+0^- - 1^{*-}\rangle -  1^- - 1^+ - 1^-0^+0^-1^{*+}\rangle -  1^+ - 1^+ - 1^-0^+0^-1^{*-}\rangle]$	
	-1	$A \frac{1}{\sqrt{2}} [ 1^+1^- - 1^-0^+0^- - 1^{*-}\rangle -  1^- - 1^+ - 1^-0^+0^-1^{*-}\rangle]$	
${}^1\Sigma^+$	$0^+$	$A \frac{1}{2} [ 1^+1^- - 1^-0^+0^- - 1^{*+}\rangle +  1^- - 1^+ - 1^-0^+0^-1^{*+}\rangle]$	$-  1^+1^- - 1^+0^+0^-1^{*-}\rangle -  1^+ - 1^+ - 1^-0^+0^-1^{*-}\rangle]$
${}^1\Sigma^-$	$0^-$	$A \frac{1}{2} [ 1^+1^- - 1^-0^+0^- - 1^{*+}\rangle -  1^- - 1^+ - 1^-0^+0^-1^{*+}\rangle]$	$-  1^+1^- - 1^+0^+0^- - 1^{*-}\rangle +  1^+ - 1^+ - 1^-0^+0^-1^{*-}\rangle]$

Table IV: Electronic Perturbation Matrix Elements.

$\langle {}^3\Pi_{1\pm}, v \mid \left[ \sum_{i=1}^6 a_i \boldsymbol{\ell}_i \cdot \mathbf{s}_i + B(\mathbf{L}_+ \mathbf{S}_- + \mathbf{L}_- \mathbf{S}_+) \right] \mid {}^3\Sigma_1^{\pm}, v' \rangle$	$= \frac{1}{4}a \langle v v' \rangle - B_{vv'}b$
$\langle {}^3\Pi_{1\pm}, v \mid \left[ \sum_{i=1}^6 a_i \boldsymbol{\ell}_i \cdot \mathbf{s}_i + B(\mathbf{L}_+ \mathbf{S}_- + \mathbf{L}_- \mathbf{S}_+) \right] \mid {}^3\Sigma_1^{\mp}, v' \rangle$	$= -\frac{1}{4}a \langle v v' \rangle + B_{vv'}b$
$\langle {}^3\Pi_{1\pm}, v \mid \left[ \sum_{i=1}^6 a_i \boldsymbol{\ell}_i \cdot \mathbf{s}_i + B(\mathbf{L}_+ \mathbf{S}_- + \mathbf{L}_- \mathbf{S}_+) \right] \mid {}^3\Delta_{1\pm}, v' \rangle$	$= \frac{1}{4}\sqrt{2}a \langle v v' \rangle - \sqrt{2}B_{vv'}b$
$\langle {}^3\Pi_{0-}, v \mid \sum_{i=1}^6 a_i \boldsymbol{\ell}_i \cdot \mathbf{s}_i \mid {}^1\Sigma^{-}, v' \rangle$	$= -\frac{1}{4}\sqrt{2}a \langle v v' \rangle$
$\langle {}^3\Pi_{2\pm}, v \mid \sum_{i=1}^6 a_i \boldsymbol{\ell}_i \cdot \mathbf{s}_i \mid {}^1\Delta_{\pm}, v' \rangle$	$= \frac{1}{4}\sqrt{2}a \langle v v' \rangle$
$\langle {}^1\Pi_{\pm}, v \mid \sum_{i=1}^6 a_i \boldsymbol{\ell}_i \cdot \mathbf{s}_i \mid {}^3\Sigma_1^{\pm}, v' \rangle$	$= \frac{1}{4}a \langle v v' \rangle$
$\langle {}^1\Pi_{\pm}, v \mid \sum_{i=1}^6 a_i \boldsymbol{\ell}_i \cdot \mathbf{s}_i \mid {}^3\Sigma_1^{\mp}, v' \rangle$	$= -\frac{1}{4}a \langle v v' \rangle$
$\langle {}^1\Pi_{\pm}, v \mid \sum_{i=1}^6 a_i \boldsymbol{\ell}_i \cdot \mathbf{s}_i \mid {}^3\Delta_{1\pm}, v' \rangle$	$= -\frac{1}{4}\sqrt{2}a \langle v v' \rangle$
$\langle {}^1\Pi_{-}, v \mid -B(\mathbf{J}_+ \mathbf{L}_- + \mathbf{J}_- \mathbf{L}_+) \mid {}^1\Sigma^{-}, v' \rangle$	$= -B_{vv'}bx^{\frac{1}{2}}$
$\langle {}^1\Pi_{\pm}, v \mid -B(\mathbf{J}_+ \mathbf{L}_- + \mathbf{J}_- \mathbf{L}_+) \mid {}^1\Delta_{\pm}, v' \rangle$	$= B_{vv'}b(x-2)^{\frac{1}{2}}$
$x = J(J+1)$	

Table V: Electronic Perturbation Paramaters

Perturbations	Correspondences <sup>a</sup>	Experimental Value
${}^3\Pi, {}^3\Sigma^+$	$a = -4\sqrt{2} \alpha_0^+ / \langle v v' \rangle$	$a = 100.3$
	$b = \sqrt{2} B_0^+ / B_{vv'}$	$b = 0.217$
${}^3\Pi, {}^3\Sigma^-$	$a = -4\sqrt{2} \alpha_0^- / \langle v v' \rangle$	$a = 99.3$
	$b = \sqrt{2} \beta_0^- / B_{vv'}$	$b = 0.224$
${}^3\Pi, {}^3\Delta$	$a = -4 \alpha_2 / \langle v v' \rangle$	$a = 99.3$
	$b = \beta_2 / B_{vv'}$	$b = 0.222$
${}^3\Pi, {}^1\Sigma^-$	$a = -4 A_{01}^- / \langle v v' \rangle$	$a = 94.8$
${}^3\Pi, {}^1\Delta$	$a = 2\sqrt{2} A_{21} / \langle v v' \rangle$	no perturbation analyzed
${}^1\Pi, {}^3\Sigma^+$	$a = -4 A_{10}^+ / \langle v v' \rangle$	$a = 83.4$
${}^1\Pi, {}^3\Sigma^-$	$a = -4 A_{10}^- / \langle v v' \rangle$	$a = 99.0$
${}^1\Pi, {}^3\Delta$	$a = -2\sqrt{2} A_{12} / \langle v v' \rangle$	$a = 95.8$
${}^1\Pi, {}^1\Sigma$	$b = 2 \beta_{10}^- / B_{vv'}$	$b = 0.228$
${}^1\Pi, {}^1\Delta$	$b = -\beta_{12} / B_{vv'}$	vibrational wavefunctions not available for ${}^1\Delta$

<sup>a</sup>For definitons of the parameters  $\alpha$ ,  $\beta$ , etc. see Freed,[6] Wicke *et al.*[2] and Field [1].

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