

**Analytical Two-valued Potential Energy Functions for the  
Ground State Surfaces of  $\text{CO}_2(\tilde{\text{X}}^1\Sigma_g^+)$  and  $\text{CS}_2(\tilde{\text{X}}^1\Sigma_g^+)$**

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A potential model for two-valued triatomic surfaces is reviewed with reference to the ground state potentials of  $\text{CO}_2(\tilde{\text{X}}^1\Sigma_g^+)$  and  $\text{CS}_2(\tilde{\text{X}}^1\Sigma_g^+)$ . A comparison is made between the observed  $J = 0$  vibrational spectra and those calculated from the derived potentials by a variational method. For  $\text{CO}_2$  the strong Fermi-resonance in the (10<sup>0</sup>) and (02<sup>0</sup>) vibrational states is confirmed for the first time using a full three-dimensional potential and a complete vibrational hamiltonian.

#### INTRODUCTION

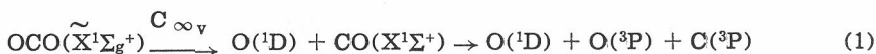
In a recent publication,<sup>1</sup> a method was outlined for the construction of two-valued potential energy functions which represent the adiabatic ground states of polyatomic molecules whose surfaces intersect and/or avoid in some regions of coordinate space. In a subsequent publication,<sup>2</sup> this method was enhanced by the inclusion of a variational procedure<sup>3</sup> which enabled the resulting functions to be refined to the experimental vibrational spectra of the molecule. In this paper, we use these techniques to refine ground state potential functions for  $\text{CO}_2(\tilde{\text{X}}^1\Sigma_g^+)$  and  $\text{CS}_2(\tilde{\text{X}}^1\Sigma_g^+)$ .

A ground state polyatomic surface can be considered to be two (or multi)-valued if there is a crossing of the potential surfaces of two eigenstates in some configurations but an avoided crossing in others. For example, the ground state of linear HOH is  $^1\Sigma^+$  for short OH bond distances but  $^1\Pi$  towards the linear H+OH asymptote. On bending, the  $^1\Pi$  surface splits into  $^1A'$  and  $^1A''$ , and the  $^1A'$  component shows an avoided crossing

with the  ${}^1A'$  surface arising from  ${}^1\Sigma^+$ . There is a conical intersection of these  ${}^1A'$  surfaces in linear configurations.<sup>4</sup> There is also a crossing at infinity on the singlet  $H_2O$  surface. At the  $O+H_2$  limit spin conservation requires either the oxygen to be in an excited state,  $O({}^1D)$  or the  $H_2$  to be in an excited state,  $H_2(\tilde{a}^3\Sigma_u^+)$ . The energy of the latter depends on the H—H distance so the asymptotic limit of the ground state surface produces either a ground state,  $O({}^3P)$  or excited state,  $O({}^1D)$ .

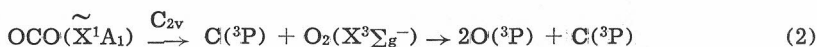
#### DISSOCIATION SCHEMES OF $CO_2$ AND $CS_2$

The topologies of the  $CO_2(\tilde{X}^1\Sigma_g^+)$  and  $CS_2(\tilde{X}^1\Sigma_g^+)$  potential surfaces are very similar, as are those of their respective dissociation fragments. We will therefore investigate the nature of these surfaces from an analysis of the adiabatic dissociation processes for  $CO_2(\tilde{X}^1\Sigma_g^+)$ , and consider first the dissociation of linear  $OCO$  into  $O+CO$  along a  $C_{\infty v}$  channel. For  $(r(CO) \sim r_e)$ , the lowest-energy fragments that maintain  ${}^1\Sigma^+$  symmetry arise for the process



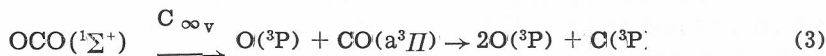
The  $O({}^1D) - O({}^3P)$  separation is 1.958 eV,<sup>5</sup> but the lowest-energy triplet state of  $CO(a^3\Pi)$  is some 6 eV higher in energy<sup>6</sup> than  $CO(X^1\Sigma^+)$  at  $r_e$ , hence there are no lower energy channels that can give  $O({}^3P)$  for the initial dissociation.

If we now consider the adiabatic dissociation of  $OCO$  into  $C+O_2$  along a  $C_{2v}$  channel, the lowest energy fragments that maintain  ${}^1A_1$  symmetry<sup>7</sup> arise for the process

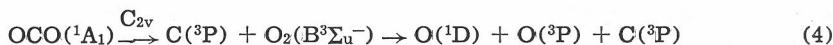


At these are all ground state fragments there are no lower energy channels. A comparison of (1) and (2) shows that the ground state surface of  $CO_2(\tilde{X}^1\Sigma_g^+)$  must be two-valued because there are two sets of atomic states that can be reached by adiabatic processes.

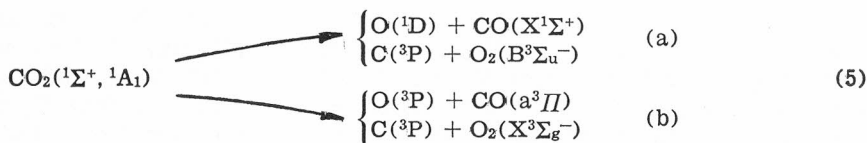
The minimum energy  $C_{\infty v}$  dissociation process which results in the formation of the atomic fragments (2) along a  ${}^1\Sigma^+$  surface is<sup>6</sup>



Similarly, the minimum energy  $C_{2v}$  dissociation process which results in the formation of the atomic fragments (1) along a  ${}^1A_1$  surface is<sup>8</sup>



The asymptotic two-valued nature of  $CO_2$  is now completely specified, and we can write the complete sets of dissociation channels for  $CO_2$  (and likewise for  $CS_2$ ) as follows



These dissociation channels are in important first step in deriving a two-valued potential function for polyatomic molecules.<sup>1</sup> In subsequent sections we will frequently make reference to these dissociation channels as (a) or (b), whereby arguments relating to both CO<sub>2</sub> and CS<sub>2</sub> will be implied.

CONSTRUCTION OF THE POTENTIAL ENERGY FUNCTIONS FOR CO<sub>2</sub> AND CS<sub>2</sub>

The potential function of a 2-valued surface is given by eigenvalues of a 2 × 2 potential energy matrix

$$V_{L/U} = 1/2 \{ V_a + V_b \pm [(V_a - V_b)^2 + 4V_c^2]^{1/2} \} \quad (6)$$

where V<sub>a</sub> and V<sub>b</sub> are diabatic potentials which dissociate according to schemes (a) and (b), respectively, and V<sub>c</sub> the mixing term, is particularly important in regions where the diabatic states intersect. We define the potential functions as follows

$$V_a, V_b = V^{(1)} + \sum_{i=1}^3 V_{AB}^{(2)}(R_i) + V_{ABC}^{(3)}(R_1, R_2, R_3) \quad (7)$$

$$V_c = V_{ABC}^{(3)}(R_a, R_2, R_3) \quad (8)$$

V<sup>(1)</sup> are atomic energies relative to ground states, V<sub>AB</sub><sup>(2)</sup>(R<sub>i</sub>) are two-body terms for the diatomic fragments appearing in the dissociation schemes (a) and (b) and V<sub>ABC</sub><sup>(3)</sup>(R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>) are three-body terms. The off-diagonal term is necessarily 3-body. We have found the following forms for V<sub>AB</sub><sup>(2)</sup>(R) and V<sub>ABC</sub><sup>(3)</sup>(R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>) to be particularly useful

$$V_{AB}^{(2)}(R) = -D_e (1 + \sum_{j=1}^3 a_j \rho^j) \exp(-a_1 \rho) \quad (9)$$

where D<sub>e</sub> is a dissociation energy and ρ = R - R<sub>e</sub> is a displacement coordinate measured relative to the equilibrium bond length R<sub>e</sub>.

$$\begin{aligned}
 V_{ABC}^{(3)}(R_1, R_2, R_3) = \prod_{i=1}^3 [1 - \tanh(\gamma_i \rho_i / 2)] V_o (1 + \sum_j C_j \rho_j + \\
 \sum_{j \leq k} C_{jk} \rho_j \rho_k + \dots) \quad (10)
 \end{aligned}$$

where ρ<sub>i</sub> = R<sub>i</sub> - R<sub>i</sub><sup>o</sup> are displacement coordinates measured relative to a suitable reference R<sub>i</sub><sup>o</sup>, and γ<sub>i</sub> are adjustable parameters. In (9) and (10), the coefficients a<sub>j</sub>, and V<sub>o</sub>, C<sub>j</sub>, C<sub>jk</sub>, ... are determined from the appropriate diatomic and triatomic data, respectively.

It can be seen from (9) and (10) that if any bond distance  $R_i$  becomes infinite, all of the  $V_{ABC}^{(3)}(R_1, R_2, R_3)$  in (7) and (8) become zero, as do those two-body terms  $V_{AB}^{(2)}(R_i)$  (one for each of  $V_a$  and  $V_b$ ) that are parametric on  $R_i$ . It follows, from (6), (7) and (8), that  $V_L$  and  $V_U$  will never intersect, provided that all three bonds are finite, but there can be intersections, corresponding to the crossings of diatomic potentials, if the third atom is removed to infinity. A close inspection of the dissociation processes (1) — (4) suggests that this correctly defines the topology of  $\text{CO}_2(\tilde{X}^1\Sigma_g^+)$  and  $\text{CS}_2(\tilde{X}^1\Sigma_g^+)$ .

Whilst it is a straight-forward matter<sup>9</sup> to determine the diatomic coefficients  $a_j$  in (9), the determination of the coefficients  $V_c, c_j, c_{jk}, \dots$  in (10) requires some clarification. These coefficients<sup>1</sup>, appropriate to  $V_a, V_b$  and  $V_c$ , were determined from a least-squares fit to a wide range of ab initio data for the  $\tilde{X}^1A_1$  and  $\tilde{B}^1A_1$  states of  $\text{H}_2\text{O}$ , corresponding to  $V_L$  and  $V_U$  in (6) respectively. This method leads to globally approximate potentials for both ground ( $V_L$ ) and excited ( $V_U$ ) states. They were determined<sup>2</sup> from spectroscopic data for stationary points on just  $V_L$ , the ground  $\tilde{X}^1A_1$  state of  $\text{O}_3$ , making use of a variational procedure<sup>3</sup> to refine  $V_L$  to the experimental vibrational spectrum of the ground state equilibrium structure. This method leads to a reliable ground state potential ( $V_L$ ) only. The coefficients cannot be uniquely determined, however, by either method, since there are only two equations ( $V_L$  and  $V_U$  in (6)) in three unknowns ( $V_a, V_b$  and  $V_c$ ). We will explain how this problem can be overcome by describing the second of the above methods for  $\text{CO}_2$  and  $\text{CS}_2$ , our principle aim being to derive ground state potentials which are particularly accurate in regions of the equilibrium structures.

If data exist for the states  $V_L$  and/or  $V_U$  in regions where their symmetries differ,  $V_c$  in (6) is identically zero, and  $V_L, V_U$  can be represented by the appropriate potentials  $V_a, V_b$  (depending on their respective dissociation schemes).<sup>1</sup> Furthermore, if  $V_L$  and  $V_U$  are far enough apart such that  $V_c$  has only a minute effect on their energies, then their potentials in such regions can again be approximated by  $V_a$  and  $V_b$ . As we have seen, for  $\text{CO}_2$  and  $\text{CS}_2$  there are no regions in which the symmetry of  $V_L$  differs from that of  $V_U$ . However, at the equilibrium configuration, the first excited singlet state lies above the  $\tilde{X}^1\Sigma_g^+$  ground state by some 5.7 eV for both  $\text{CO}_2$  and  $\text{CS}_2$ .<sup>7</sup> This is a sufficient energy difference to be able to neglect the effect of  $V_c$  initially.

If we compare the atomic and diatomic contributions to the energy in (5) at the equilibrium  $\tilde{X}^1\Sigma_g^+$  geometry of  $\text{CO}_2$  for schemes (a) and (b), those for (a) come closest to the true energy by some 9 eV. This might have been anticipated from valence considerations, and so we can obtain approximate potentials  $V_a$  for  $\text{CO}_2$  (and  $\text{CS}_2$ ) by fitting the parameters in (10) to the ground state equilibrium properties. This technique is now standard to our method, and is explained fully elsewhere.<sup>10</sup>

The equilibrium  $\tilde{X}^1A_1$  state of  $\text{O}_3$  was found<sup>2</sup> to correspond to one potential ( $V_a$ , say) and the metastable  $D_{3h}$  structure to  $V_b$ , both minima

lying on the overall adiabatic ground state by virtue of an avoided intersection. Initial potentials  $V_a$  and  $V_b$  could therefore be obtained from data for these two minima. In  $\text{CO}_2$  and  $\text{CS}_2$ , we have already seen that there are no surface intersections in interaction regions of the potential, and so we must investigate other means of defining  $V_b$ . The first excited state has  ${}^1B_2$  ( ${}^1\Delta_u$ ) symmetry,<sup>7</sup> and will, of course, dissociate to the same asymptotes as the ground state (the  $C_{\infty,v}$   $\text{CO} + \text{O}$  asymptote in 5 (a) has  ${}^1\Delta$ ,  ${}^1\Pi$ ,  ${}^1\Sigma^+$  components, and the  $C_{2v}$   $\text{O}_2 + \text{C}$  asymptote in 5 (b) has  ${}^1A_1$ ,  ${}^1A_2$ ,  ${}^1B_2$  components). However, in  $C_s$  symmetry, this will be the closest state that interacts with the ground state ( ${}^1A'$ ) and so we have chosen this  $\tilde{A} {}^1B_2$  state to initially define  $V_b$ , by fitting to the geometry and energy of its equilibrium structure.<sup>10</sup> A least-squares procedure is now used to refine  $V_c$  and re-refine  $V_a$  and  $V_b$  such that the  $\tilde{X} {}^1\Sigma_g^+$  and  $\tilde{A} {}^1B_2$  data are reproduced by  $V_L$  and  $V_U$ , respectively in (6).<sup>1,2</sup>

One unfortunate aspect of fitting two-valued potentials is that, of necessity all dissociation channels (a) and (b) must be included, and both  $V_a$  and  $V_b$  must be assigned values, even if this means using data of doubtful validity. However, in such circumstances, the excited state will never be intended to be reliable and so, in principle, any data can be used. Our choice of the  $\tilde{A} {}^1B_2$  state to define  $V_b$  does however mean that the excited state  $V_U$  will have some regions of validity, notably around the excited state equilibrium structure, the exceptions being the dissociation products. On the other hand, the ground state will be valid over all space by virtue of channels (a) and (b) for the dissociation limits, the equilibrium ground state data which defines  $V_L$  for short  $R$ , and the correct symmetry of the cross-term  $V_c$ .

#### REFINEMENT OF THE $\text{CO}_2$ AND $\text{CS}_2$ POTENTIALS

The spectroscopic data for the equilibrium configurations of  $\text{CO}_2$  ( $\tilde{X} {}^1\Sigma_g^+$ ) and  $\text{CS}_2$  ( $\tilde{X} {}^1\Sigma_g^+$ ) were taken from references [11] and [12], respectively. The data for the excited  $\tilde{A} {}^1B_2$  states were taken from reference [7]. They are summarized in Table I. The atomic energies of  $\text{O}({}^1D)$  and  $\text{S}({}^1D)$  were taken from reference [5], and the diatomic potentials for all of the dissociation products in (5) and (6) were constructed<sup>9</sup> from data taken from reference [6]. These potentials are collected in Table II.

Inserting the initial potentials  $V_a$  and  $V_b$  into (6) and choosing some arbitrary values for the parameters in  $V_c$  (8), (10) (our starting values were taken to be  $\gamma_1 = 2\text{\AA}^{-1}$ ,  $R_1^0 = 1\text{\AA}$ ,  $V_0 = 0.5$  eV,  $c_j, c_{jk}, \dots = 0$ ) the parameters in the three-body terms of  $V_a$  and  $V_b$  were re-refined by a non-linear least-squares procedure such that  $V_L$  and  $V_U$  reproduced all of the data in Table I for the  $\tilde{X} {}^1\Sigma_g^+$  and  $\tilde{A} {}^1B_2$  states, respectively. This process utilizes only a few select coefficients  $V_0, c_j, c_{jk}, \dots$  (10) for  $V_a$  and  $V_b$ .<sup>10</sup>

TABLE I  
 Experimental Data for CO<sub>2</sub> and CS<sub>2</sub>

	$\tilde{X}^1\Sigma_g^+$	
	CO <sub>2</sub> [11]	CS <sub>2</sub> [12]
$r_e(\text{CX})/\text{\AA}$	1.160	1.553
$\alpha_e(\text{XCX})/\text{deg}$	180.0	180.0
$D_e/\text{eV}$	16.856	12.070
$f_{rr}/\text{aJ}\text{\AA}^{-2}$	16.032	7.666
$f_{\alpha\alpha}/\text{aJ}$	0.783	0.569
$f_{rr'}/\text{aJ}\text{\AA}^{-2}$	1.250	0.848
	$\tilde{A}^1B_2$	
	CO <sub>2</sub> [7]	CS <sub>2</sub> [7]
$r_e(\text{CX})/\text{\AA}$	1.246	1.660
$\alpha_e(\text{XCX})/\text{deg}$	122.0	153.0
$D_e/\text{eV}$	11.153	6.373

TABLE II

One- and Two-Body Terms in the Expression (7) for the Potential Function of CO<sub>2</sub> and CS<sub>2</sub> Corresponding to the Dissociation Channels (5). The Two-Body Terms are Defined by Equation (9) of the Text.

	$V^{(1)}/\text{eV}$	$D_e/\text{eV}$	$a_1/\text{\AA}^{-1}$	$a_2/\text{\AA}^{-2}$	$a_3/\text{\AA}^{-3}$	$R_e/\text{\AA}$
O( <sup>1</sup> D)	1.985					
CO(X <sup>1</sup> Σ <sup>+</sup> )		11.226	3.897	2.305	1.898	1.128
O <sub>2</sub> (B <sup>3</sup> Σ <sub>u</sub> <sup>-</sup> )		0.998	3.802	0.000	0.000	1.604
CO(a <sup>3</sup> Π)		5.162	5.671	8.654	6.359	1.206
O <sub>2</sub> (X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )		5.213	6.080	11.477	11.003	1.208
S( <sup>1</sup> D)	1.146					
CS(X <sup>1</sup> Σ <sup>+</sup> )		7.435	3.445	2.370	1.238	1.535
S <sub>2</sub> (B <sup>3</sup> Σ <sub>u</sub> <sup>-</sup> )		1.613	2.579	0.000	0.000	2.170
CS(a <sup>3</sup> Π)		3.991	4.790	6.293	4.111	1.568
S <sub>2</sub> (X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )		4.414	3.954	4.312	2.332	1.889

A variational procedure<sup>3</sup> was then used to calculate the J=0 vibrational spectrum of the  $\tilde{X}^1\Sigma_g^+$  states and a further least-squares procedure was carried out in order to minimise the errors between calculated and observed frequencies for CO<sub>2</sub><sup>13</sup> and CS<sub>2</sub>.<sup>14</sup> In this refinement, all of the parameters ( $R_i^o$ ,  $\gamma_i$ ,  $V_o$ ,  $c_j$ ,  $c_{jk}$ , ...) in  $V_c$  and all of the parameters in  $V_a$ , with the exception of those coefficients  $V_o$ ,  $c_j$ ,  $c_{jk}$ , required to fit the  $\tilde{X}^1\Sigma_g^+$  data were allowed to relax, the polynomials being extended to quartic in both cases. It was not felt necessary to relax any further parameters in  $V_b$  since this approximates almost exclusively to the  $\tilde{A}^1B_2$  state. For every iteration of the variables, the same coefficients in  $V_a$  and  $V_b$  were again re-refined to fit the data in Table I. (A full account of this technique is given in reference [2]).

TABLE III

Three-Body Terms, Defined by Equation (10), for the Potential Functions of CO<sub>2</sub> and CS<sub>2</sub>. The Adiabatic Ground State Potentials are Obtained from the Parameters in Tables II and III by Substituting the Expressions for V<sub>a</sub>, V<sub>b</sub> and V<sub>c</sub> in (7) and (8) into V<sub>L</sub> in Equation (6).

	CO <sub>2</sub>			CS <sub>2</sub>		
	V <sub>a</sub>	V <sub>b</sub>	V <sub>c</sub>	V <sub>a</sub>	V <sub>b</sub>	V <sub>c</sub>
<sup>+</sup> C <sub>1</sub> = C <sub>2</sub> /Å <sup>-1</sup>	2.617	5.246	-0.623	2.753	-0.655	0.107
C <sub>3</sub>	-2.019	7.752	-0.272	-1.590	0.384	0.031
C <sub>11</sub> = C <sub>22</sub> /Å <sup>-2</sup>	0.627	—	-1.539	1.246	—	0.235
C <sub>33</sub>	0.223	—	-0.278	0.311	13.042	0.180
C <sub>12</sub>	0.837	—	0.026	3.500	—	0.192
C <sub>13</sub> = C <sub>23</sub>	0.076	—	-0.496	0.215	—	0.209
C <sub>111</sub> = C <sub>222</sub> /Å <sup>-3</sup>	-0.002	—	-0.704	3.212	—	0.363
C <sub>333</sub>	-0.069	—	-0.676	-0.900	—	0.339
C <sub>112</sub> = C <sub>122</sub>	0.076	—	-1.723	-0.863	—	0.365
C <sub>133</sub> = C <sub>233</sub>	0.151	—	-0.795	0.658	—	0.336
C <sub>113</sub> = C <sub>223</sub>	0.128	—	-0.342	2.634	—	0.197
C <sub>123</sub>	0.076	—	-0.838	-0.467	—	0.319
C <sub>1111</sub> = C <sub>2222</sub> /Å <sup>-4</sup>	-0.038	—	-0.822	-0.738	—	0.054
C <sub>3333</sub>	0.048	—	-0.997	-0.452	—	0.181
C <sub>1112</sub> = C <sub>1222</sub>	0.061	—	-0.902	0.061	—	0.187
C <sub>1333</sub> = C <sub>2333</sub>	0.110	—	-0.523	-0.737	—	0.346
C <sub>1113</sub> = C <sub>2223</sub>	0.079	—	-0.341	-0.181	—	0.150
C <sub>1122</sub>	0.058	—	-0.656	0.315	—	0.174
C <sub>1133</sub> = C <sub>2233</sub>	0.210	—	-0.318	-0.528	—	0.170
C <sub>1123</sub> = C <sub>1223</sub>	0.037	—	-0.809	0.427	—	0.178
C <sub>1233</sub>	-0.004	—	-0.981	0.395	—	0.282
V <sub>0</sub> /eV	4.361	-0.771	-0.261	2.143	1.742	0.640
γ <sub>1</sub> = γ <sub>2</sub> /Å <sup>-1</sup>	2.357	2.000	2.271	2.0	2.0	1.771
γ <sub>3</sub>	0.959	12.000	1.988	2.0	2.0	2.054
R <sub>1</sub> <sup>0</sup> = R <sub>2</sub> <sup>0</sup> /Å	1.117	1.246	1.527	1.553	1.660	1.293
R <sub>3</sub> <sup>0</sup>	2.226	2.180	3.053	3.105	3.228	2.586

<sup>+</sup> Bond definitions: R<sub>1</sub> ≡ R(CX), R<sub>2</sub> ≡ R(CX'), R<sub>3</sub> ≡ R(XX')

Finally, the input harmonic force constants in Table I were adjusted to give added flexibility to the fitting procedure, and the resulting three-body terms so obtained are given in Table III. In Table IV, we present a comparison between the observed and calculated J=0 vibrational spectra for several isotopes of CO<sub>2</sub> and CS<sub>2</sub>. The mean error is 3.7 cm<sup>-1</sup> for the CO<sub>2</sub> spectra and 8.8 cm<sup>-1</sup> for CS<sub>2</sub>. This suggests that the potential functions given in Tables II and III are accurate representations of the complete three-dimensional ground state surfaces, especially at the equilibrium configurations and at the dissociation limits. They should therefore be particularly useful in dynamical studies.

TABLE IV

Comparison Between Experimental and Calculated  $J = 0$  Vibrational Spectra of  $\text{CO}_2(\tilde{X}^1\Sigma_g^+)$  and  $\text{CS}_2(\tilde{X}^1\Sigma_g^+)$ .

$\text{CO}_2(\tilde{X}^1\Sigma_g^+)$			$\text{CO}_2(\tilde{X}^1\Sigma_g^+)$			$\text{CO}_2(\tilde{X}^1\Sigma_g^+)$		
$^{16}\text{O}^{12}\text{C}^{16}\text{O}$			$^{16}\text{O}^{12}\text{C}^{16}\text{O}$			$^{16}\text{O}^{13}\text{C}^{16}\text{O}$		
Assign- ment	Calc.	Expt. [13]	Assign- ment	Calc.	Expt. [13]	Assign- ment	Calc.	Expt. [13]
(100) <sub>II</sub>	1286	1285	(301) <sub>IV</sub>	6075	6076	(100) <sub>II</sub>	1268	1266
(100) <sub>I</sub>	1389	1388	(301) <sub>III</sub>	6217	6228	(100) <sub>I</sub>	1369	1370
(200) <sub>III</sub>	2550	2548	(301) <sub>II</sub>	6339	6348	(001)	2282	2283
(200) <sub>II</sub>	2667	2671	(301) <sub>I</sub>	6505	6503	(101) <sub>II</sub>	3528	3528
(200) <sub>I</sub>	2800	2797	(003)	6970	6973	(101) <sub>I</sub>	3628	3633
(300) <sub>IV</sub>	3795	3792	(401) <sub>V</sub>	7284	7284	(201) <sub>III</sub>	4750	4748
(300) <sub>III</sub>	3935	3942	(401) <sub>IV</sub>	7455	7460	(201) <sub>II</sub>	4880	4887
(300) <sub>II</sub>	4095	4064	(401) <sub>III</sub>	7585	7594	(201) <sub>I</sub>	4987	4991
(300) <sub>I</sub>	4229	4224	(401) <sub>II</sub>	7729	7734	(301) <sub>IV</sub>	5954	5952
(002)	4671	4673	(401) <sub>I</sub>	7924	7921	(301) <sub>III</sub>	6113	6120
(400) <sub>V</sub>	5024	5022 <sup>c</sup>	(103) <sub>II</sub>	8192	8193	(301) <sub>II</sub>	6230	6242
(400) <sub>IV</sub>	5188	5197	(103) <sub>I</sub>	8292	8294	(301) <sub>I</sub>	6361	6364
(400) <sub>III</sub>	5315	5329 <sup>c</sup>				(003)	6777	6780
(400) <sub>II</sub>	5470	5476				(401) <sub>V</sub>	7145	7143 <sup>c</sup>
(400) <sub>I</sub>	5672	5668 <sup>c</sup>				(401) <sub>IV</sub>	7329	7333 <sup>c</sup>
(102) <sub>II</sub>	5912	5915	$^{18}\text{O}^{12}\text{C}^{18}\text{O}$			(401) <sub>III</sub>	7473	7482
(102) <sub>I</sub>	6013	6016	Assign- ment	Calc.	Expt. [13]	(401) <sub>II</sub>	7592	7600
(202) <sub>III</sub>	7132	7134	(100) <sub>II</sub>	1229	1230	(401) <sub>I</sub>	7748	7748 <sup>c</sup>
(202) <sub>II</sub>	7251	7260 <sup>c</sup>	(100) <sub>I</sub>	1350	1347	(103) <sub>II</sub>	7982	7981
(202) <sub>I</sub>	7377	7377	(001)	2312	2314	(103) <sub>I</sub>	8084	8089
(004)	9248	9247	(101) <sub>II</sub>	3521	3575			
			(101) <sub>I</sub>	3639	3638			
(001)	2347	2349	(201) <sub>III</sub>	4716	4721			
(101) <sub>II</sub>	3611	3612	(201) <sub>II</sub>	4828	4833			
(101) <sub>I</sub>	3713	3715	(201) <sub>I</sub>	4993	4989			
(201) <sub>III</sub>	4852	4854	(003)	6866	6870			
(201) <sub>II</sub>	4970	4978						
(201) <sub>I</sub>	5100	5100						
$\text{CS}_2(\tilde{X}^1\Sigma_g^+)$								
$^{32}\text{S}^{12}\text{C}^{32}\text{S}$			$^{32}\text{S}^{13}\text{C}^{32}\text{S}$					
Assignment	Calc.	Expt. [14]	Assignment	Calc.	Expt. [14]			
(100)	660	658	(100)	659	657			
(020)	811	802	(020)	786	776 <sup>c</sup>			
(200)	1316	1314						
(120)	1459	1447 <sup>c</sup>	(001)	1471	1485			
(040)	1642	1620 <sup>c</sup>	(101)	2123	2135			
			(021)	2245	2250			
(001)	1521	1535	(201)	2771	2782			
(101)	2173	2185	(121)	2884	2887			
(021)	2320	2325	(041)	3038	3031 <sup>c</sup>			
(201)	2822	2833	(301)	3415	3425			
(121)	2960	2962	(221)	3521	3521 <sup>c</sup>			
(041)	3138	3130	(141)	3669	3659 <sup>c</sup>			
(301)	3467	3478	(061)	3846	3825 <sup>c</sup>			
(221)	3597	3597						
(141)	3769	3757						
(061)	3972	3948 <sup>c</sup>						
(003)	4559	4566						
(103)	5195	5201						
(023)	5332	5331 <sup>c</sup>						

<sup>c</sup> calculated by the authors in references [13] and [14].



## CONCLUDING REMARKS

In this paper, we have attempted to outline in some detail the step by step analysis of two-valued triatomic potential surfaces; how a two-valued surface can be recognised and the procedures required in order to construct its potential energy function. We have also highlighted the main areas which are involved in refining the potential to the observed vibrational spectrum of the molecule.

In this and other work<sup>2,15</sup> we have found that much more accurate vibrational spectra can be obtained by directly iterating to the observed spectrum variationally, rather than by more standard perturbation techniques.<sup>16</sup> The failure of the perturbation method lies in the truncation both of the data and of the potential,<sup>2</sup> whereas in the method described here, both are infinite expansions. Even at the harmonic level, small differences in the force constants are to be found. This is illustrated in Table V, where we give the harmonic force constants predicted for CO<sub>2</sub> and CS<sub>2</sub>.

TABLE V

*Comparison Between Experimental and Calculated Harmonic Force Constants for CO<sub>2</sub> ( $\tilde{X}^1\Sigma_g^+$ ) and CS<sub>2</sub> ( $\tilde{X}^1\Sigma_u^+$ )*

	CO <sub>2</sub> ( $\tilde{X}^1\Sigma_g^+$ )		CS <sub>2</sub> ( $\tilde{X}^1\Sigma_u^+$ )	
	<i>calc.</i>	<i>expt.</i> [11]	<i>calc.</i>	<i>expt.</i> [12]
$f_{rr}/aJ \text{ \AA}^{-2}$	15.995	16.032	7.781	7.666
$f_{\sigma a}/aJ$	0.791	0.783	0.577	0.569
$f_{rr'}/aJ \text{ \AA}^{-2}$	1.252	1.250	0.790	0.848

Finally, the use of a variational procedure to calculate the vibrational spectra produces a means of investigating the extent to which vibrational states interact. CO<sub>2</sub> is the classic example of such interactions, known as Fermi-resonance in the vibrational spectra. For CO<sub>2</sub>( $X^1\Sigma_g^+$ ) the two normal mode vibrations (10<sup>0</sup>0) and (02<sup>0</sup>0) are degenerate, as are all multiples thereof. This results in heavy mixing which make it impossible to assign the spectrum along conventional normal mode lines (see [3] and references therein). In Table VI, we give the contributions to the variational (J=0) vibrational wavefunctions for <sup>12</sup>C<sup>16</sup>O<sub>2</sub>, calculated from our potential. In order to investigate the interactions between the vibrational motions, it is most appropriate to use a method of calculation that employs normal coordinate basis functions,<sup>3</sup> since these are diagonal (unmixed) at the harmonic level. Our analysis appears to be the first time that such an investigation of the CO<sub>2</sub> spectrum has been carried out using the complete vibrational hamiltonian, coupled with a full three-dimensional potential.

TABLE VI

*Coefficients of Basis Functions, Corresponding to the Fermi-Resonant Normal Coordinate Eigenstates, in the Normalised  $J=0$  Vibrational Wavefunctions of  $^{12}\text{C}^{16}\text{O}_2$  ( $\tilde{X}^1\Sigma_g^+$ ). Coefficients are Underlined When There are Larger Single Contributions Elsewhere in the Wavefunction.*

Conventional Assignment	Coefficient of Normal Mode basis function*					Conventional Assignment	Coefficient of Normal Mode basis function*				
	**(100) (020)**						(001)**				
** (100) <sub>I</sub>	-0.75	-0.64				** (001)	-0.98				
(100) <sub>II</sub>	-0.75	-0.64					(101) (021)				
	(200) (120) (040)					(101) <sub>I</sub>	-0.60	0.75			
(200) <sub>I</sub>	-0.30	0.66	-0.68			(101) <sub>II</sub>	0.70	0.65			
(200) <sub>II</sub>	-0.76	0.20	0.56				(201) (121) (041)				
(200) <sub>III</sub>	-0.49	-0.72	-0.46			(201) <sub>I</sub>	-0.26	0.63	-0.67		
	(300) (220) (140) (060)					(201) <sub>II</sub>	-0.66	0.17	0.56		
(300) <sub>I</sub>	0.11	-0.40	0.66	-0.60		(201) <sub>III</sub>	-0.42	-0.70	-0.48		
(300) <sub>II</sub>	0.48	-0.60	0.04	0.56			(301) (221) (141) (061)				
(300) <sub>III</sub>	0.69	0.24	-0.40	-0.43		(301) <sub>I</sub>	0.09	-0.36	0.65	-0.59	
(300) <sub>IV</sub>	0.30	0.62	0.62	0.33		(301) <sub>II</sub>	0.38	-0.53	0.01	0.56	
	(002)					(301) <sub>III</sub>	0.53	0.25	-0.38	-0.45	
(002)	0.94					(301) <sub>IV</sub>	-0.73	-0.58	-0.63	-0.34	
	(400) (320) (240) (160) (080)						(003)				
(400) <sub>I</sub>	0.04	0.20	0.47	0.64	0.53		-0.89				
(400) <sub>II</sub>	0.22	-0.55	0.49	0.08	-0.56		(401) (321) (241) (161) (081)				
(400) <sub>III</sub>	0.57	-0.33	-0.33	0.28	0.42	(401) <sub>I</sub>	0.03	-0.17	0.44	-0.64	0.53
(400) <sub>IV</sub>	-0.51	-0.49	0.09	0.45	0.34	(401) <sub>II</sub>	-0.16	0.46	-0.44	-0.11	0.56
(400) <sub>V</sub>	0.17	0.48	0.63	0.48	0.22	(401) <sub>III</sub>	0.40	-0.21	-0.35	0.24	0.43
	(102) (022)					(401) <sub>IV</sub>	-0.32	-0.47	0.03	0.47	0.37
(102) <sub>I</sub>	-0.52	0.71				(401) <sub>V</sub>	0.11	0.42	0.63	0.51	0.23
(102) <sub>II</sub>	-0.61	-0.64					(103) (023)				
	(202) (122) (042)					(103) <sub>I</sub>	-0.44	0.65			
(202) <sub>I</sub>	-0.20	0.57	-0.63			(103) <sub>II</sub>	-0.49	-0.64			
(202) <sub>II</sub>	0.51	-0.12	-0.56								
(202) <sub>III</sub>	-0.32	-0.65	-0.49								
	(004)										
(004)	-0.83										

\* $\nu_1$  = symmetric stretch,  $\nu_2$  linear angle bend,  $\nu_3$  = asymmetric stretch  
 \*\* $l = 0$  is assumed in the assignments:  $(n_1 n_2 n_3) \equiv (n_1 n_2 n_3)$ .

It is obviously impossible to assign the  $\text{CO}_2$  spectrum according to its normal modes, and in this respect, our potential function appears valid.

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## SAŽETAK

Analitičke dvovrijednosne potencijalne energijske funkcije  
za površine temeljnog stanja od  $\text{CO}_2(\tilde{\text{X}}^1\Sigma_g^+)$  i  $\text{CS}_2(\tilde{\text{X}}^1\Sigma_g^+)$

*S. Carter i J. N. Murrell*

Potencijalni model za dvovrijednosne troatomske površine opisan je s obzirom na potencijale temeljnog stanja za  $\text{CO}_2(\tilde{\text{X}}^1\Sigma_g^+)$  i  $\text{CS}_2(\tilde{\text{X}}^1\Sigma_g^+)$ . Uspoređeni su zapaženi vibracijski spektri  $J=0$  s onima koji su izračunani iz izvedenih potencijala s pomoću varijacijske metode. Po prvi puta je utvrđena jaka Fermijeva resonancija u vibracijskim stanjima ( $10^0$  i  $02^0$ ) upotrebljavajući potpuni tro-dimenzijski potencijal i vibracijski hamiltonian.