

THE POTENTIAL ENERGY SURFACE FOR THE C<sub>3</sub> MOLECULE  
 DETERMINED FROM EXPERIMENTAL DATA.  
 EVIDENCE FOR A BENT EQUILIBRIUM STRUCTURE

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The Morse oscillator-rigid bender internal dynamics (MORBID) Hamiltonian for triatomic molecules (Jensen P.: *J. Mol. Spectrosc.* 128, 478 (1988)) has been used to refine the potential energy function for the  $X^1\Sigma_g^+$  electronic ground state of C<sub>3</sub> by fitting to experimental data. In accordance with previous *ab initio* calculations by Kraemer W. P., Bunker P. R., and Yoshimine M. (*J. Mol. Spectrosc.* 107, 191 (1984)), C<sub>3</sub> is found to have a bent equilibrium structure. The MORBID calculation reported here yields a barrier to linearity of 16.5(3.6) cm<sup>-1</sup> and an equilibrium bond angle of 162.5°(1.0°) with one standard error given in parentheses.

The C<sub>3</sub> molecule has been generally believed to have a linear equilibrium configuration in its ground electronic state (see Sørensen<sup>1</sup> and references therein). The *ab initio* calculation by Kraemer et al.<sup>2</sup>, however, predicted a barrier to linearity of 21 cm<sup>-1</sup> and an equilibrium bond angle of 162°. According to this calculation, C<sub>3</sub> is a quasi-linear molecule with bending potential energy function similar to that determined for the CCC chain in carbon suboxide C<sub>3</sub>O<sub>2</sub> (refs<sup>3-5</sup>) on the basis of experimental data. The C<sub>3</sub>O<sub>2</sub> molecule is found<sup>5</sup> to have a barrier to linearity of 28 cm<sup>-1</sup> and an equilibrium bond angle of 156°.

Matsumura et al.<sup>6</sup> have observed the  $\nu_3$  band of C<sub>3</sub> in high resolution using a diode laser. When analyzing this band in terms of spectroscopic parameters, they found that their fitted *D* values (for the vibrational ground state and for the  $\nu_3$  state) were considerably larger than the value obtained from the theoretical expression

$$D = \frac{4B_c^3}{\omega_1^2} \quad (1)$$

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and that the  $B$  value in the  $\nu_3$  state was larger than the  $B$  value in the vibrational ground state. A similar behaviour is found for  $C_3O_2$  (refs<sup>3,7,8</sup>), and therefore the analysis of the  $\nu_3$  band also suggests that  $C_3$  is quasilinear.

Quite recently, Smith et al.<sup>9</sup> reassigned a wavelength resolved laser induced fluorescence emission spectrum, initially believed to be due to the furan cation  $C_4H_4O^+$ , to transitions in  $C_3$ . They obtained a large number of bend-stretch term values in the  $X^1\Sigma_g^+$  electronic ground state of  $C_3$ . The vibrational states identified include  $20\nu_2$ ,  $14\nu_2 + 2\nu_3$ , and  $8\nu_2 + 4\nu_3$ . In the present work these data are used for determining the potential surface for the electronic ground state of  $C_3$  using the Morse oscillator-rigid bender internal dynamics (MORBID) Hamiltonian for triatomic molecules<sup>10,11</sup>. Similar determinations of the potential energy surface have already been carried out for  $CH_2$  (ref.<sup>12</sup>) and for  $H_2O$  (ref.<sup>13</sup>). Also, MORBID has been used for calculating rotation-vibration energies for  $C_3$  (ref.<sup>14</sup>) using the *ab initio* data of Kraemer et al.<sup>2</sup>. The shape of the bending potential energy function determined in this *ab initio* study is confirmed by the calculations reported in the present work; from the fitting to experimental data we obtain a barrier to linearity of  $16.5(3.6) \text{ cm}^{-1}$  and an equilibrium bond angle of  $162.5^\circ(1.0^\circ)$  with one standard error given in parentheses.

## THEORETICAL AND CALCULATIONS

### *The Model*

Description of the MORBID approach have been given in refs<sup>10,11</sup>, and we refer the reader to these publications for details. The potential energy function is represented by the following analytical expression

$$V(\Delta r_{12}, \Delta r_{32}, \bar{\varrho}) = V_0(\bar{\varrho}) + \sum_j F_j(\bar{\varrho}) y_j + \sum_{j \leq k} F_{jk}(\bar{\varrho}) y_j y_k + \sum_{j \leq k \leq m} F_{jkm}(\bar{\varrho}) y_j y_k y_m + \sum_{j \leq k \leq m \leq n} F_{jkmn}(\bar{\varrho}) y_j y_k y_m y_n, \quad (2)$$

where all of the indices  $j$ ,  $k$ ,  $m$ , and  $n$  assume the values 1 or 3. In Eq.(2),  $y_j = 1 - \exp(-a_j \Delta r_{j2})$ , where the  $a_j$  are molecular constants and the  $\Delta r_{j2} = r_{j2} - r_{j2}^e$ ,  $j = 1$  or  $3$ , are defined as displacements from the equilibrium value  $r_{j2}^e$  of the distance between the outer nucleus  $j$  and the centre nucleus 2. The quantity  $\bar{\varrho}$  is the supplement of the instantaneous value of the bond angle (see Fig. 1 of ref.<sup>10</sup>). The  $F_{jkm\dots}$  expansion coefficients of Eq. (2) are functions of  $\bar{\varrho}$ , and we define them as

$$F_j(\bar{\varrho}) = \sum_{i=1}^4 f_j^{(i)} (\cos \varrho_e - \cos \bar{\varrho})^i, \quad (3)$$

and

$$F_{jkm\dots}(\bar{\varrho}) = f_{jkm\dots}^{(0)} + \sum_{i=1}^N f_{jkm\dots}^{(i)} (\cos \varrho_e - \cos \bar{\varrho})^i, \quad (4)$$

where  $\varrho_e$  is the equilibrium value of  $\bar{\varrho}$ . The function  $F_{jk}(\bar{\varrho})$  has  $N = 3$ ,  $F_{jkl}(\bar{\varrho})$  has  $N = 2$ , and  $F_{jklm}(\bar{\varrho})$  has  $N = 1$ . The function  $V_0(\bar{\varrho})$  is the potential energy for the molecule bending with its bond lengths fixed at their equilibrium values. In the present work we parameterize this function as

$$V_0(\bar{\varrho}) = \sum_{i=1}^8 f_0^{(i)} (1 - \cos \bar{\varrho})^i. \quad (5)$$

This parameterization is equally well suited for linear and bent molecules<sup>10</sup>. In the refinement of the  $f_0^{(i)}$  (using the least squares fitting technique) the sign of the non-zero  $f_0^{(i)}$  parameter of lowest order,  $f_0^{(k)}$  say, determines the sign of the first non-vanishing derivative of  $V_0(\bar{\varrho})$  at  $\bar{\varrho} = 0$ , and thus the variation of  $V_0(\bar{\varrho})$  for small  $\bar{\varrho}$  values. The function  $V_0(\bar{\varrho})$  will vary as  $f_0^{(k)} (\bar{\varrho}^2/2)^k$  for  $\bar{\varrho} \simeq 0$ , so that for  $f_0^{(k)} < 0$  a barrier exists, whereas for  $f_0^{(k)} > 0$  there is no barrier.

The analytical potential energy expansion given by Eqs (2–5) is chosen such that it behaves in a physically reasonable way at all coordinate boundaries: it approaches a constant when a bond length is stretched, it approaches a very large (albeit not infinite) value for short bond lengths, and, as required by symmetry, it has zero slope at  $\bar{\varrho} = 0$  and  $\bar{\varrho} = \pi$  for all  $\Delta r_{12}$  and  $\Delta r_{32}$ .

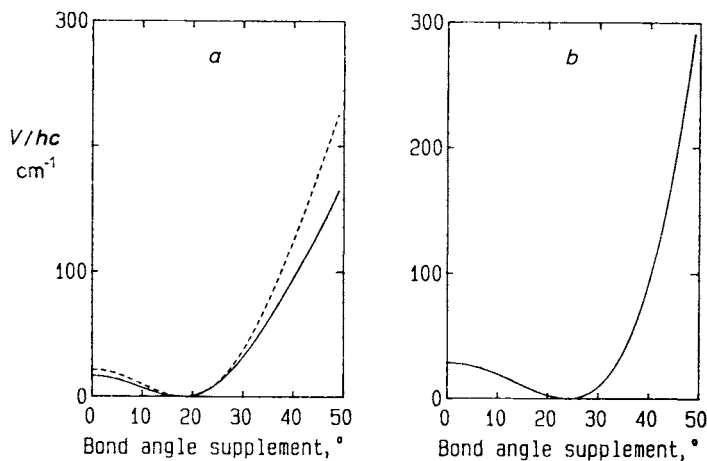


FIG. 1

Comparison of bending potential function for  $C_3$  and for the CCC chain in  $C_3O_2$ . *a* Bending potential function for  $C_3$  determined in the present work (solid curve), and the function computed *ab initio* by Kraemer *et al.*<sup>2</sup>; *b* the bending potential energy for the CCC chain in  $C_3O_2$  determined by Jensen and Johns<sup>5</sup>

We use the  $\Delta r_{j2}$ ,  $j = 1$  or  $3$ , as vibrational coordinates together with a bending coordinate  $\varrho$  defined as in the work by Hougen et al.<sup>15</sup>. The coordinate  $\varrho$  is almost, but not quite, equal to  $\bar{\varrho}$ . The molecular rotation is described by Euler angles. We expand the total Hamiltonian to quartic terms (with  $\varrho$ -dependent expansion coefficients) in the  $y_i$ , and we obtain its eigenvalues by diagonalizing its matrix representation in a truncated basis of Morse oscillator functions describing the stretching motion, numerically integrated bending functions<sup>10,16</sup> and usual symmetric top rotational functions<sup>17</sup>.

The vibrational basis functions used in the MORBID approach describe the stretches as two non-interacting Morse oscillators and the bending as being isolated from the stretching motion. This is a so-called "local mode" basis (see Mills and Robiette<sup>18</sup>), and for some triatomic molecules such as  $\text{H}_2\text{O}$ , already these zero order functions are rather good approximations to the true vibrational wavefunctions of the molecule. In  $\text{C}_3$ , however, there is a strong kinetic energy coupling between the stretches of the two bonds through the off-diagonal element of the  $\mathbf{G}$  matrix (see Eq. (57) of ref.<sup>10</sup>), this matrix element being of the same order of magnitude as the two diagonal matrix elements. Consequently, even though the two isolated Morse oscillators in the zero order approximation have fundamental energy spacings around  $1\,600\text{ cm}^{-1}$ , the stretch-stretch interaction places the fundamental stretching energies of  $^{12}\text{C}_3$  at  $1\,225\text{ cm}^{-1}$  (refs<sup>9,19</sup>) and  $2\,040\text{ cm}^{-1}$  (ref.<sup>6</sup>), respectively. This fact, together with the fact that the potential energy function of  $\text{C}_3$  contains rather strong bend-stretch interactions, makes it necessary to use very many vibrational basis functions in order to obtain converged energies in the calculations reported here. We have carried out these calculations with a basis set of 91 Morse oscillator functions determined such that the Morse oscillator quantum numbers  $n_1$  and  $n_3$  fulfill  $n_1 + n_3 \leq 12$ , and the 13 lowest bending eigenfunctions were determined using a grid of 1 000 points in the numerical integration procedure (see ref.<sup>10</sup>). In determining the final energies we used the 13 lowest bending eigenfunctions together with the 28 lowest stretching eigenfunctions. With this basis set,  $J = 0$  states involving two stretching quanta are converged to better than  $1.0\text{ cm}^{-1}$ . In order to obtain a similar convergence for  $J = 0$  states involving three stretching quanta, a considerable extension of the basis set (at least to  $n_1 + n_3 \leq 16$ ) turned out to be necessary, and with the computer facilities available (a CDC Cyber 180-860 installation) it was not feasible to carry out calculations with this large basis set. We have therefore limited the calculations reported here to states with up to two stretching quanta. For higher-lying states the convergence is probably not better than  $25\text{ cm}^{-1}$ .

### *Input Data and Fitting*

As input data for the least squares fitting we have used the  $^{12}\text{C}_3$  term values (relative to the  $(0, 0, 0)^0$   $J = 0$  level) with  $v_1 + v_3 \leq 2$  from Smith et al.<sup>9</sup>. The higher energy

levels were excluded since they were not satisfactorily converged in the MORBID calculation (see the preceding section). These data were supplemented with the  $J = 1$  term values of the  $(0, 1, 0)^1 \Pi_u$ (ref.<sup>20</sup>) and the  $(0, 3, 0)^1 \Pi_u$ (ref.<sup>21</sup>) states together with the hypothetical (Pauli forbidden)  $J = 0$  level of the  $(0, 0, 1)$  state<sup>6</sup>. In ref.<sup>14</sup>, we used the *ab initio* data of Kraemer et al.<sup>2</sup> to obtain parameters for the analytical potential energy expansion used in the MORBID approach. The parameterization of the pure bending potential energy  $V_0(\bar{\varrho})$  used in that work was an expansion in  $\cos \varrho_e - \cos \bar{\varrho}$ , appropriate only for a bent molecule. In the present work we use the expansion of Eq. (5), which can be used for both linear and bent molecules, so in order to get a starting point for the least squares fitting we have transformed the  $f_0^{(i)}$  parameters given in Table VIII of ref.<sup>14</sup> into values consistent with the expansion of Eq. (5).

In the final least squares fitting, we found it possible to vary usefully the parameters  $f_0^{(i)}$ ,  $i = 1, \dots, 8$ , together with  $f_{11}^{(0)}$  and  $f_{13}^{(0)}$ . The residuals (Observed - Calculated) of this fitting are given in Table I, and Table II contains the values of the fitted parameters together with the *ab initio* starting values. The standard deviation

TABLE I  
Experimental term values for  $^{12}C_3$

$(v_1, v_2, v_3)^t$	$J$	Observed <sup>a</sup> cm <sup>-1</sup>	Obs - Calc cm <sup>-1</sup>	$(v_1, v_2, v_3)^t$	$J$	Observed <sup>a</sup> cm <sup>-1</sup>	Obs - Calc cm <sup>-1</sup>
$(0, 1, 0)^1$	1	64 <sup>b</sup>	1	$(0, 20, 0)^0$	0	2 034	-3
$(0, 2, 0)^0$	0	133	-5	$(0, 0, 1)^0$	0	2 040 <sup>d</sup>	3
$(0, 3, 0)^1$	1	208 <sup>c</sup>	1	$(1, 10, 0)^0$	0	2 192	-3
$(0, 4, 0)^0$	0	287	-3	$(2, 0, 0)^0$	0	2 433	-5
$(0, 6, 0)^0$	0	459	6	$(2, 2, 0)^0$	0	2 667	-3
$(0, 8, 0)^0$	0	644	2	$(2, 4, 0)^0$	0	2 884	10
$(0, 10, 0)^0$	0	846	0	$(0, 0, 2)^0$	0	4 022	6
$(0, 12, 0)^0$	0	1 068	8	$(0, 2, 2)^0$	0	4 088	-6
$(1, 0, 0)^0$	0	1 225	5	$(0, 4, 2)^0$	0	4 191	-2
$(0, 14, 0)^0$	0	1 285	-1	$(0, 6, 2)^0$	0	4 323	5
$(1, 2, 0)^0$	0	1 409	3	$(0, 8, 2)^0$	0	4 473	8
$(0, 16, 0)^0$	0	1 525	3	$(0, 10, 2)^0$	0	4 635	5
$(1, 4, 0)^0$	0	1 585	-2	$(0, 12, 2)^0$	0	4 823	11
$(1, 6, 0)^0$	0	1 776	-4	$(0, 14, 2)^0$	0	5 017	7
$(1, 8, 0)^0$	0	1 982	-3				

<sup>a</sup> From Smith et al.<sup>9</sup> except where otherwise indicated; <sup>b</sup> from Jungen and Merer<sup>20</sup>; <sup>c</sup> from Gausset et al.<sup>21</sup>; <sup>d</sup> from Matsumura et al.<sup>6</sup>.

of the fitting ( $5.9 \text{ cm}^{-1}$ ) is comparable to the  $\pm 5 \text{ cm}^{-1}$  estimated accuracy<sup>22</sup> of the data from Smith et al.<sup>9</sup>.

Figure 1a shows the pure bending potential energy function  $V_0(\bar{q})$  determined in the present work through least squares fitting to experimental data (solid curve) and the corresponding function obtained from the *ab initio* data of Kraemer et al.<sup>2</sup> (dashed curve). In Fig. 1b, we show the potential energy function for the CCC chain

TABLE II  
Values of the potential energy parameters for the electronic ground state of  $\text{C}_3$

Parameter	<i>Ab initio</i> <sup>a</sup>	Fitted
$r_{12}^e/\text{\AA}$	1.289726	1.289726 <sup>b</sup>
$a_1/\text{\AA}^{-1}$	2.1	2.1 <sup>b</sup>
$f_0^{(1)}/\text{cm}^{-1c}$	-913	-777(91) <sup>d</sup>
$f_0^{(2)}/\text{cm}^{-1c}$	11 966	10 759(414)
$f_0^{(3)}/\text{cm}^{-1c}$	-38 132	-38 889(866)
$f_0^{(4)}/\text{cm}^{-1c}$	63 289	67 082(105)
$f_0^{(5)}/\text{cm}^{-1c}$	-42 461	-49 903(2 039)
$f_0^{(6)}/\text{cm}^{-1c}$	17 844	19 146(483)
$f_0^{(7)}/\text{cm}^{-1c}$		-12 519(3 892)
$f_0^{(8)}/\text{cm}^{-1c}$		7 252(2 720)
$f_1^{(1)}/\text{cm}^{-1}$	-2 086	-902 <sup>e</sup>
$f_1^{(2)}/\text{cm}^{-1}$		-5 024 <sup>e</sup>
$f_{11}^{(0)}/\text{cm}^{-1}$	62 332	57 391(172)
$f_{11}^{(1)}/\text{cm}^{-1}$	-1 857	-1 857 <sup>b</sup>
$f_{13}^{(0)}/\text{cm}^{-1}$	179	-1 503(290)
$f_{111}^{(0)}/\text{cm}^{-1}$	8 036	8 073 <sup>e</sup>
$f_{1111}^{(0)}/\text{cm}^{-1}$	30 239	30 239 <sup>b</sup>
$q_e/\text{deg}^f$	18.18	17.5(10)
$H/\text{cm}^{-1g}$	21	16.5(36)

<sup>a</sup> Obtained in ref.<sup>14</sup> from the *ab initio* data by Kraemer et al.<sup>2</sup>; <sup>b</sup> parameter constrained to the *ab initio* value; <sup>c</sup> coefficients for the expansion in  $1 - \cos \bar{q}$  given by Eq. (5); the *ab initio* values are calculated from the expansion coefficients (appropriate for an expansion in  $\cos q_e - \cos \bar{q}$ ) given in Table VIII of ref.<sup>14</sup>; <sup>d</sup> Quantities in parentheses are one standard error in units of the last digit; <sup>e</sup> constrained to value determined in a preliminary least squares fit; <sup>f</sup> equilibrium value of  $\bar{q}$ ; the fitted value is calculated from the fitted values of the parameters  $f_0^{(i)}$ ,  $i = 1, \dots, 8$ ; <sup>g</sup> barrier to linearity; the fitted value is calculated from the fitted values of the parameters  $f_0^{(i)}$ ,  $i = 1, \dots, 8$ .

of C<sub>3</sub>O<sub>2</sub> determined by Jensen and Johns<sup>5</sup> by combining their results with those of Bunker<sup>3</sup> and Jensen<sup>4</sup>.

## DISCUSSION

The potential energy function obtained through the fitting in the present work (Table II) yields a barrier to linearity of 16.5(3.6) cm<sup>-1</sup> (one standard error given in parentheses) and an equilibrium  $\bar{\varrho}$  value of 17.5°(1.0°) (i.e., an equilibrium bond angle of 162.5° (1.0°)). These results agree well with the *ab initio* calculations of Kraemer et al.<sup>2</sup> Table III contains a comparison between experimentally determined *B* values for <sup>12</sup>C<sub>3</sub> and the corresponding values predicted by the MORBID program with the fitted parameters of Table II. It is seen that the predicted *B* constants are systematically larger than the experimental values. A large part of this discrepancy could probably be removed by adjusting the equilibrium bond length  $r_{12}^e$  in the least squares fitting. This adjustment would require that the input data be supplemented with more energy spacings involving non-zero *J* values, but with the huge basis sets necessary for the C<sub>3</sub> molecule the calculations would then become computationally unfeasible. However, the MORBID calculation predicts correctly the *variation* of the *B* parameter with the vibrational quantum numbers. In particular it predicts that the *B* value for the  $\nu_3$  state is larger than that in the vibrational ground state as observed by Matsumura et al.<sup>6</sup>.

We have used the nonrigid bender program NRBI (refs<sup>16,23</sup>) to calculate the effective bending potential energy function  $V_{\text{eff}}^{(\nu_1, \nu_3)}(\varrho)$  in the stretching states  $(\nu_1, \nu_3) = (0, 0), (1, 0),$  and  $(0, 1)$ . The resulting functions are shown in Fig. 2. As input for the NRBI program we used the coefficients in a fourth order Taylor expansion (in  $\bar{\varrho}, \Delta r_{12},$  and  $\Delta r_{32}$ ) of the potential energy function given by Eqs (2–5) with the fitted parameters of Table II. The effective potential energy functions are obtained by averaging over the (small amplitude) stretching motion. Figure 2 shows that excitation of the  $\nu_1$  mode removes the barrier to linearity of 13 cm<sup>-1</sup> found for  $V_{\text{eff}}^{(0,0)}(\varrho)$ . As already pointed out by Beardsworth et al.<sup>23</sup>, excitation of  $\nu_3$  bends the molecule;  $V_{\text{eff}}^{(0,1)}(\varrho)$  has a barrier to linearity of 36 cm<sup>-1</sup>. This latter effect explains why the *B* constant increases when  $\nu_3$  is excited.

Two recent papers<sup>24,25</sup> advocate a linear structure for C<sub>3</sub>. Jones<sup>24</sup> has carried out *ab initio* calculations leading to minimum potential energy at linearity, and Plesser et al.<sup>25</sup> have used the “Coulomb explosion” experimental technique to investigate the structure of C<sub>3</sub>. The situation concerning *ab initio* calculations of C<sub>3</sub> is perhaps similar to that for C<sub>3</sub>O<sub>2</sub>, where several calculations<sup>26–29</sup> failed to produce a barrier to linearity in accordance with experimental results<sup>5</sup>. Lozes et al.<sup>30</sup>, however, obtained an *ab initio* bending potential energy function for C<sub>3</sub>O<sub>2</sub> in qualitative agreement with the function derived from experiment. The “Coulomb explosion” technique of ref.<sup>25</sup> appears to yield a vibrationally averaged structure, and since excitation of

the lowest stretching mode  $\nu_1$  removes the barrier to linearity, the vibrationally averaged bond angle is possibly so close to  $180^\circ$  that the deviation cannot be measured.

It is conceivable that the least squares refinement of the potential energy parameters has multiple solutions, and we have exerted considerable effort to find them by varying the starting values of the parameters. When we constrained  $f_0^{(1)}$  to zero, a solution with a linear equilibrium structure was obtained. This fitting had a standard deviation of about  $20 \text{ cm}^{-1}$ , so that it was much poorer than that reported in Tables I–II. For other values of the starting parameters, the fitting either converged

TABLE III  
Values of the  $B$  constant for  $^{12}\text{C}_3$  (in  $\text{cm}^{-1}$ )

$(\nu_1, \nu_2, \nu_3)^{\dagger}$	Observed <sup>a</sup>	Predicted
$(0, 0, 0)^0$	$0.430445^b$	0.4343
$(0, 1, 0)^1$	0.4421	0.4451
$(0, 2, 0)^0$	0.4519	0.4564
$(0, 3, 0)^1$	0.4600	0.4670
$(0, 4, 0)^0$	0.4675	0.4738
$(0, 6, 0)^0$	$0.4807^c$	0.4851
$(1, 0, 0)^0$	$0.4257^c$	0.4297
$(0, 0, 1)^0$	$0.435565^b$	0.4418

<sup>a</sup> From Gausset et al.<sup>21</sup> except where otherwise indicated; <sup>b</sup> from Matsumura et al.<sup>6</sup>; <sup>c</sup> from Merer<sup>19</sup>.

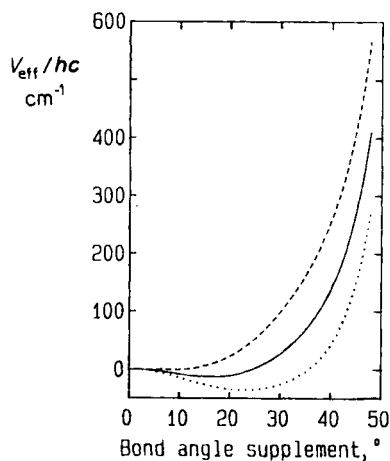


FIG. 2

Effective bending potential energy functions for  $\text{C}_3$  in different  $(\nu_1, \nu_3)$  stretching states from the nonrigid bender program NRBI (refs<sup>16,23</sup>). The solid curve (barrier to linearity  $13 \text{ cm}^{-1}$ ) shows the effective bending potential energy in the  $(0, 0)$  state, the dashed curve (barrier to linearity  $0 \text{ cm}^{-1}$ ) shows that of the  $(1, 0)$  state, and the dotted curve (barrier to linearity  $36 \text{ cm}^{-1}$ ) shows that of the  $(0, 1)$  state. The curves are drawn using a common energy scale so that the energy at the linear configuration is zero



to the fitted parameters values of Table II, or it diverged. Even though we were not able to locate a solution with a linear equilibrium structure, we cannot entirely rule out its existence. However, the fact that the fitted potential energy function correctly predicts the variation of the *B* constant with the vibrational quantum numbers (without any rotational structure being fitted) lends credibility to the results of the present work. These results, together with the *ab initio* calculations of Kraemer et al.<sup>2</sup> and the observations of Matsumura et al.<sup>6</sup>, which demonstrate the analogy with C<sub>3</sub>O<sub>2</sub>, provide strong evidence for a small barrier to linearity in the ground electronic state of C<sub>3</sub>.

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