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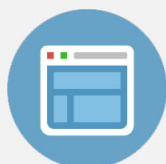
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A study of the bending motion in tetratomic molecules by the algebraic operator expansion method

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We study the bending motion in the tetratomic molecules C_2H_2 ($\tilde{X}^1\Sigma_g^+$), C_2H_2 (\tilde{A}^1A_u) *trans*- S_1 , C_2H_2 (\tilde{A}^1A_2) *cis*- S_1 , and \tilde{X}^1A_1 H_2CO . We show that the algebraic operator expansion method with only linear terms comprised of the basic operators is able to describe the main features of the level energies in these molecules in terms of two (linear) or three (*trans*-bent, *cis*-bent, and branched) parameters. By including quadratic terms, the rms deviation in comparison with experiment goes down to typically ~ 10 cm^{-1} over the entire range of energy 0–6000 cm^{-1} . We determine the parameters by fitting the available data, and from these parameters we construct the algebraic potential functions. Our results are of particular interest in high-energy regions where spectra are very congested and conventional methods, force-field expansions or Dunham-expansions plus perturbations, are difficult to apply. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4856115>]

I. INTRODUCTION

A unified description of tetratomic molecules is a challenging problem. For these molecules, several geometric configurations are possible: linear, *cis*-bent, *trans*-bent, nonplanar, and branched, as schematically depicted in Fig. 1. In addition, molecular species exist with a non-rigid structure, intermediate between the configurations of Fig. 1, and even more complicated configurations may occur, in which the potential function has coexisting minima corresponding to linear, *cis*-bent and *trans*-bent configurations.^{1–8} Also a molecule may change its point group symmetry upon electronic excitation as shown many years ago^{9–11} and as demonstrated recently.¹²

A commonly used method to describe tetratomic molecules is the force-field method.¹³ This method is an expansion in terms of curvilinear internal coordinates, three stretching and four bending for tetratomic molecules. Another commonly used method is the Dunham expansion plus perturbations,¹² that is, an expansion in terms of spectroscopic constants ω_r , χ_{rs} , ... to which perturbations are applied. In this article we describe another, less widely explored method, the algebraic operator expansion method, described in detail below.

While the three stretching vibrations of tetratomic molecules have similar properties for all configurations of Fig. 1 (linear, *cis*-bent, *trans*-bent, nonplanar, and branched), the bending vibrations have markedly different properties, as will be shown in Secs. II and III. In the present study, which is devoted to the understanding of the differences in spectroscopic properties of linear, *cis*-bent and *trans*-bent molecules, we therefore concentrate on bending vibrations. Both the force-field approach^{13,14} and the Dunham plus resonance approach¹² have also been used recently to study

bending vibrations in *cis* and *trans* tetratomic molecules and thus our work can be compared with those approaches. Also, semiclassical methods have been used.^{15,16}

Extensive work on the dynamics of tetratomic molecules related to both spectra and potential surfaces has been done,^{15,16} especially from the point of view of “bifurcations” of normal modes.^{17–19} This work is particularly important and relevant to the study of quantum phase transitions in tetratomic molecules,^{20–22} which may provide a guide of how the method presented here could be extended. Also, van Vleck perturbation theory has been used in the study of the mid-size molecules^{23,24} CHF_3 and $HFCO$ by a combination of perturbative and variational methods within the framework of the “polyad” method of Kellman *et al.*^{25,26} The algebraic expansion operator method can be viewed as a generalization of the van Vleck approach to anharmonic potentials.

In 1996 one of the authors (F.I.) with Oss²⁷ introduced an algebraic approach to benders, the two-dimensional vibron model. The model, based on the algebra $U(3)$ for single-benders and $U(3) \times U(3)$ for coupled benders, has been the subject of many investigations. For single-benders it has been used to study non-rigid molecules^{28,29} and quantum phase transitions.^{20–22} For coupled benders after the original treatment of linear molecules,²⁷ it was used to treat nonplanar molecules (H_2O_2) by Oss and co-workers.^{30,31} In recent years it has been used to provide a systematic approach^{32,33} to all configurations of Fig. 1. The phase diagram between linear, bent, and nonplanar has been explored using this method.³⁴

The scheme^{27,32,33} amounts to an expansion of the Hamiltonian in terms of Lie algebraic operators and we therefore call it the “algebraic method” or the “operator expansion method.” The method is in spirit identical to the force field method to which it reduces in the harmonic limit. Its essence is that while the force field method is an expansion

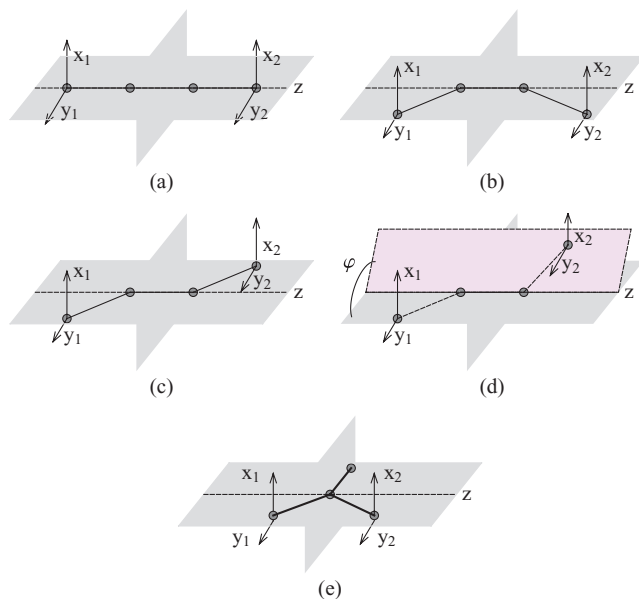


FIG. 1. Schematic representation of geometric configurations of two coupled benders (ABBA type) tetratomic molecules: (a) linear, (b) *cis*-bent, (c) *trans*-bent, (d) nonplanar, and (e) branched molecules.

of the potential function in powers of r , where r denotes an intrinsic coordinate, the operator expansion method is an expansion of group theoretical operators, which effectively reduces to an expansion in powers of functions of the type $f(r) = r^2/(1 + r^2)$.

A description of the $\tilde{X}^1\Sigma_g^+$ state of acetylene (linear configuration)^{27,32} and an algebraic analysis of the full vibrational spectrum of formaldehyde (without rotational levels) with a local model based on a coordinate-momenta representation of coupled U(2) algebras³⁵ have been performed previously. In this article, we use a bosonic-vibronic realization of coupled U(3) algebras to address the more challenging problem of providing a description of the \tilde{A}^1A_u state of acetylene. Our aim is to show that a description of the main features of the *trans*-spectrum of this state can be obtained in terms of four parameters. In addition, in order to show the versatility of our method, we also provide a description of the \tilde{A}^1A_2 *cis*-state of acetylene and of the spectrum of \tilde{X}^1A_1 formaldehyde, H₂CO, in terms of four parameters. Our results when combined with the study of the $\tilde{X}^1\Sigma_g^+$ state of acetylene (linear) demonstrate that the operator expansion method (in the present context of the two-dimensional vibron model) can provide a simple description of coupled benders in tetratomic molecules which includes linear, *cis*-bent, *trans*-bent, and branched molecules. This simple method can be used for more elaborate descriptions that include higher order terms and other relevant degrees of freedom.

After these introductory comments, the algebraic expansion method, for single and coupled benders, is first reviewed (Sec. II). A longer review is given in the supplementary material,³⁶ which also contains some formal details about the structure of the two-dimensional vibron model. Then, results are summarized for the ground electronic state, $\tilde{X}^1\Sigma_g^+$, of acetylene in Sec. III A, while the results for the two configurations of the first excited electronic state, \tilde{A}^1A_u and \tilde{A}^1A_2 ,

are presented in Sec. III B. The ground electronic state \tilde{X}^1A_1 of formaldehyde is described in Sec. III C and concluding remarks are given in Sec. IV.

II. THE OPERATOR EXPANSION METHOD

The operator expansion method is an expansion of the Hamiltonian operator \hat{H} in elements of a Lie algebra,³⁷ their powers, and products. The energy levels are obtained by diagonalizing the matrix of \hat{H} in an appropriate basis (as defined below). Application of the method is straightforward, since it amounts to the construction of the basis and the evaluation of the matrix elements of \hat{H} in this basis. From the Hamiltonian \hat{H} one can also construct both the kinetic and the potential functions by making use of the method of coherent^{38–46} (or intrinsic) states. In this section, we briefly review the operator expansion method for single and coupled benders,²⁷ treated as two-dimensional problems. We summarize all technical aspects required for generating and diagonalizing the Hamiltonian matrix for these problems, and for constructing the corresponding potential.

A. Single bender

We consider first the case of a single bender, shown in Fig. 2(a). The Lie algebra for this case is U(3) whose elements are explicitly written up in the supplementary material.³⁶ The Hamiltonian \hat{H} up to quadratic terms in the elements of U(3) is

$$\hat{H} = \varepsilon \hat{n} + \alpha \hat{n}(\hat{n} + 1) + \beta \hat{\ell}^2 + A \hat{W}^2, \quad (1)$$

where $\varepsilon, \alpha, \beta$, and A are fitting parameters, and \hat{n} , $\hat{\ell}^2$, \hat{W}^2 are the operators onto which the Hamiltonian is expanded. (Instead of \hat{W}^2 , one can use the pairing operator $\hat{P} = N(N + 1) - \hat{W}^2$, which is proportional to \hat{W}^2 , to within a constant (diagonal) term.) The Hamiltonian \hat{H} is diagonalized in the basis $[N]$ of the two-dimensional truncated harmonic oscillator $[[N]; n^\ell] \equiv |n, \ell\rangle$, with $n = N, N - 1, \dots, 0$, $\ell = \pm n, \pm(n - 2), \dots, \pm 1$ or 0. Matrix elements of the operators \hat{n} , $\hat{\ell}^2$, and \hat{W}^2 in this basis are given in the supplementary material.³⁶ A computer code has been written to diagonalize \hat{H} and used to study a variety of single benders.^{21,22,47} To the Hamiltonian \hat{H} of Eq. (1) there corresponds a potential function which can be obtained by the method of coherent^{38,41–46} states. These states are labeled by $|r, \theta\rangle$. The potential function is only a function of the intrinsic variable r of Fig. 2(a), and we therefore drop the label θ from the coherent state. The potential function corresponding to the

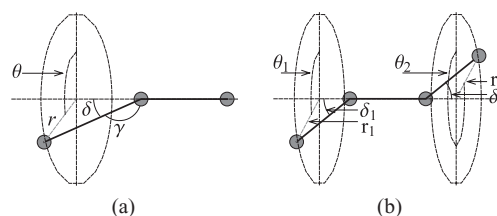


FIG. 2. Schematic drawings of (a) a single bender molecule and (b) two coupled bending sites in a tetratomic molecule.

Hamiltonian of Eq. (1) is

$$V(r) = \varepsilon N \frac{r^2}{1+r^2} + \alpha \left[N(N-1) \frac{r^2}{1+r^2} + 2N \right] \frac{r^2}{1+r^2} + \beta N \frac{r^2}{1+r^2} + A N(N-1) \left(\frac{1-r^2}{1+r^2} \right)^2. \quad (2)$$

The intrinsic variable r is related to the physical variable δ (the bending angle) by a constant scale transformation factor Θ , $\delta = \Theta r$. The expansion given in Eq. (2) is similar to the force field expansion

$$V(r) = E_0 + f_{rr}r^2 + f_{rrrr}r^4 + \dots \quad (3)$$

except for the use of $r^2/(1+r^2)$ instead of r^2 .

The potential function obtained from the Hamiltonian \hat{H} by Eq. (2) has been investigated for a variety of single benders.^{21,22} It has been shown that the simple Hamiltonian (1) with four adjustable parameters, $\varepsilon, \alpha, \beta, A$, in addition to the vibron number N , is capable of describing the main features of the bending motion from rigidly linear, to non-rigid linear, to non-rigid bent, to rigidly bent molecules.

B. Coupled benders

We consider next the case of two coupled benders, shown in Fig. 2(b). The Lie algebra for this case is $U_1(3) \times U_2(3)$ whose elements are explicitly written up elsewhere.^{27,32} The Hamiltonian \hat{H} is expanded into operators of the two bending systems denoted by 1 and 2, their products, and their powers. Up to quadratic terms the Hamiltonian is

$$\begin{aligned} \hat{H} = & \varepsilon_1 \hat{n}_1 + \alpha_1 \hat{n}_1(\hat{n}_1 + 1) + \beta_1 \hat{\ell}_1^2 + A_1 \hat{P}_1 \\ & + \varepsilon_2 \hat{n}_2 + \alpha_2 \hat{n}_2(\hat{n}_2 + 1) + \beta_2 \hat{\ell}_2^2 + A_2 \hat{P}_2 \\ & + \alpha_{12} \hat{n}_1 \hat{n}_2 + \beta_{12} \hat{\ell}_1 \hat{\ell}_2 + A_{12} \hat{P}_{12} \\ & + \lambda \hat{M}_{12} + B_{12} \hat{Q}_1 \cdot \hat{Q}_2, \end{aligned} \quad (4)$$

where \hat{M}_{12} is the so-called Majorana operator.³⁷ This operator conserves the polyad number of Kellman^{15,16,25} and it allows a description of both local and normal behaviors. When viewed from the normal basis, it induces Darling-Dennison couplings, as has been shown.³⁷ Further details of the operators in Eq. (4) are given in the supplementary material.³⁶

The basis upon which \hat{H} is diagonalized is denoted by $[N_1, N_2]$, where N_i ($i = 1, 2$) is the vibron number for the i th bender. The most convenient basis for the diagonalization of \hat{H} is the product of two two-dimensional oscillator bases $|[N_1, N_2]; n_1^{\ell_1}, n_2^{\ell_2}\rangle \equiv |n_1^{\ell_1}, n_2^{\ell_2}\rangle \equiv |n_1, \ell_1; n_2, \ell_2\rangle$ with $n_i = N_i, N_i - 1, \dots, 0$; $\ell_i = \pm n_i, \pm(n_i - 2), \dots, \pm 1$ or 0, for $i = 1, 2$. Matrix elements of the operators in Eq. (4) are given elsewhere.^{32,33,36} Here we only note that the term $\hat{W}_1 \cdot \hat{W}_2$ allows the description of *cis*-bent and *trans*-bent configurations, the term \hat{M}_{12} leads from local to normal configurations, and that the operator $\hat{Q}_1 \cdot \hat{Q}_2$ produces vibrational ℓ resonances.⁴⁸ This last terms conserves the polyad number²⁵ and can describe nonplanar configurations.^{30,31}

The potential functions can be obtained from the Hamiltonian \hat{H} by the method of coherent^{38,41-46} states. These states can be denoted by the displacement r_1 and r_2 and by their angles of orientation θ_1 and θ_2 , $|r_1, \theta_1, r_2, \theta_2\rangle$. However, the potential functions are invariant under an overall rotation of the molecule, and thus depend only on the dihedral angle $\varphi = \theta_2 - \theta_1$. For purposes of evaluating the potential function, one of the angles θ_1 or θ_2 may be chosen arbitrarily, and the intrinsic state may be written as $|r_1, r_2, \varphi\rangle$. The expectation value of the various terms in the general Hamiltonian equation, Eq. (4), are given in the supplementary material,³⁶ and the resulting potential function is

$$\begin{aligned} V(r_1, r_2, \varphi) = & \sum_{i=1}^2 \varepsilon_i N_i \frac{r_i^2}{1+r_i^2} + \sum_{i=1}^2 \beta_i N_i \frac{r_i^2}{1+r_i^2} \\ & + \sum_{i=1}^2 \alpha_i N_i \left[(N_i - 1) \frac{r_i^2}{1+r_i^2} + 1 \right] \frac{r_i^2}{1+r_i^2} \\ & + \alpha_{12} N_1 N_2 \frac{r_1^2 r_2^2}{(1+r_1^2)(1+r_2^2)} \\ & + \sum_{i=1}^2 A_i N_i (N_i - 1) \left(\frac{1-r_i^2}{1+r_i^2} \right)^2 \\ & + 4A_{12} N_1 N_2 \left(\prod_{i=1}^2 \frac{r_i}{1+r_i^2} \right) \cos \varphi \\ & + \lambda N_1 N_2 \left(\prod_{i=1}^2 \frac{r_i}{1+r_i^2} \right) \cos \varphi \\ & + B_{12} N_1 N_2 \left(\prod_{i=1}^2 \frac{r_i^2}{1+r_i^2} \right) \cos 2\varphi, \end{aligned} \quad (5)$$

which is the expectation value of the Hamiltonian \hat{H} of Eq. (4) in the intrinsic state $|r_1, r_2, \varphi\rangle$. The displacements r_1, r_2 are related to the physical bending angles δ_1, δ_2 by a scale transformation $\delta_1 = \Theta_1 r_1, \delta_2 = \Theta_2 r_2$, and can be both positive and negative. For planar configurations we have four possible sign combinations as shown in Fig. 3. The two *trans* configurations in Fig. 3 are equivalent to each other, as they are obtained from one another by a rotation, and the two *cis* configurations in Fig. 3 are equivalent to each other as well. To fix $\varphi = 0$, we thus adopt the sign convention that

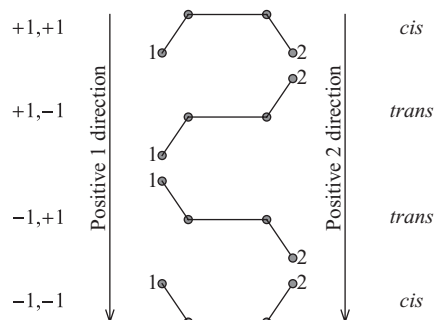


FIG. 3. Four possible sign combinations for planar configurations of tetratomic molecules.

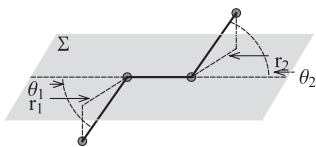


FIG. 4. Schematic drawing of a nonplanar configuration.

r_1 is positive, but r_2 may be either negative (for *trans* configurations) or positive (for *cis* configurations). For nonplanar configurations, the situation is slightly more complicated. In this case we need to look at the projection of the displacements in the plane Σ of Fig. 4. We use the following convention: we take (a) the angle φ as $0 \leq \varphi \leq \pi/2$; (b) r_1 positive and r_2 negative (nonplanar *trans*-like) or positive (nonplanar *cis*-like). The expansion of $V(r_1, r_2, \varphi)$ of Eq. (5) is similar to the conventional expansion,⁴⁹ except that the expansion is not in powers of r_1, r_2 , and φ but in terms of functions of r_1, r_2 , and φ .

C. Coupled identical benders

We now treat a special case on coupled benders (Sec. II B) by requiring the two benders to be identical, e.g., ABBA molecules. For coupled identical benders, as in ABBA molecules, the states must be representations of the appropriate point group. The permutation-inversion formalism^{50,51} has been forwarded as a robust method and a discussion of the symmetry operations used here is available,³² so here we briefly review only the two operations used in this work. Operationally, we introduce two symmetry operations on the basis $|n_1^{\ell_1}, n_2^{\ell_2}\rangle$. The first is the transposition (12):

$$(12) |n_1^{\ell_1}, n_2^{\ell_2}\rangle = |n_2^{\ell_2}, n_1^{\ell_1}\rangle. \quad (6)$$

The second is the operator (σ),

$$(\sigma) |n_1^{\ell_1}, n_2^{\ell_2}\rangle = (-1)^{\ell_1 + \ell_2} |n_1^{-\ell_1}, n_2^{-\ell_2}\rangle, \quad (7)$$

which is identical to the permutation-inversion symmetry operator E^* .^{51,52} We identify the symmetry of the states on the basis of the eigenvalues of these operators. Note that, since the Hamiltonian \hat{H} is rotationally invariant, the total two-dimensional angular momentum $\ell_{12} = \ell_1 + \ell_2$ is conserved.

- Linear case, $D_{\infty, h}$:** The irreducible representations of $D_{\infty, h}$ are labeled by $\Sigma_{g/u}^{\pm}$ for $\ell_{12} = 0$, $\Pi_{g/u}$ for $\ell_{12} = 1$, $\Delta_{g/u}$ for $\ell_{12} = 2$, and so on. For $\ell_{12} \neq 0$ the label g/u is given by the eigenvalues of operator (12): $g \rightarrow +1$, $u \rightarrow -1$. For $\ell_{12} = 0$ the labels $g/u, \pm$ are given by the eigenvalues of operators ((12), (σ)) and the following symmetry assignments can be associated with the eigenvalue pairs: $\Sigma_g^+ \rightarrow (+1, +1)$, $\Sigma_g^- \rightarrow (+1, -1)$, $\Sigma_u^+ \rightarrow (-1, +1)$, $\Sigma_u^- \rightarrow (-1, -1)$.
- Cis-bend, C_{2v} :** The irreducible representations are labeled by A_1, A_2, B_1, B_2 . They are associated with the eigenvalue pairs ((12), (σ)) = $(+1, +1), (+1, -1), (-1, +1), (-1, -1)$, respectively.
- Trans-bend, C_{2h} :** The irreducible representations are labeled by A_g, A_u, B_g, B_u . They are associated with the

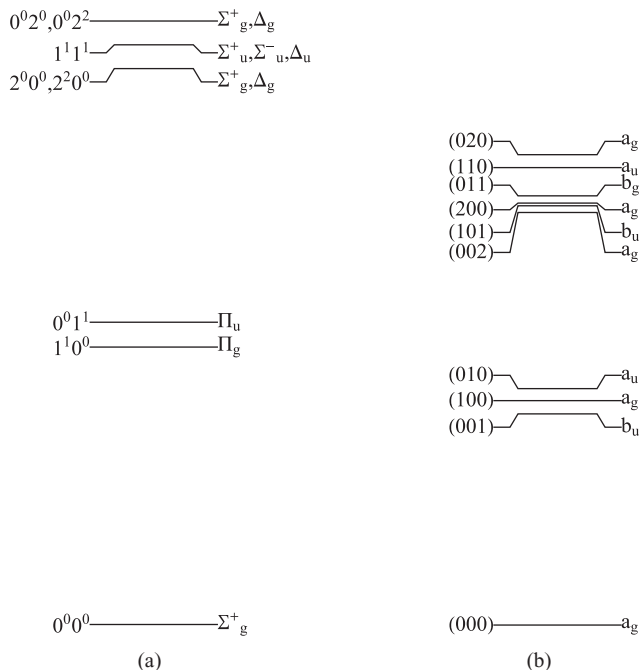


FIG. 5. Example of (a) linear and (b) bent spectra. Linear spectra has $\varepsilon = 700 \text{ cm}^{-1}$ and $\lambda = -2.5 \text{ cm}^{-1}$, while the bent spectrum shows $A = 1.0 \text{ cm}^{-1}$, $A_{12} = 20.0 \text{ cm}^{-1}$, and $\lambda = -2.5 \text{ cm}^{-1}$; both have $N_1 = N_2 = 12$.

eigenvalue pairs ((12), (σ)) = $(+1, +1), (+1, -1), (-1, +1), (-1, -1)$, respectively.

For identical benders, $\varepsilon_1 = \varepsilon_2 = \varepsilon$, $\alpha_1 = \alpha_2 = \alpha$, $\beta_1 = \beta_2 = \beta$, $A_1 = A_2 = A$; $N_1 = N_2 = N/2$ and the Hamiltonian simplifies to

$$\begin{aligned} \hat{H} = & \varepsilon(\hat{n}_1 + \hat{n}_2) + \alpha[\hat{n}_1(\hat{n}_1 + 1) + \hat{n}_2(\hat{n}_2 + 1)] + \beta(\hat{\ell}_1^2 + \hat{\ell}_2^2) \\ & + A(\hat{P}_1 + \hat{P}_2) + \alpha_{12} \hat{n}_1 \hat{n}_2 + \beta_{12} \hat{\ell}_1 \hat{\ell}_2 + A_{12} \hat{P}_{12} \\ & + \lambda \hat{M}_{12} + B_{12} \hat{Q}_1 \cdot \hat{Q}_2, \end{aligned} \quad (8)$$

with a corresponding simplification of the potential function, Eq. (5).

The equilibrium configuration of the molecule is obtained by minimizing $V(r_1, r_2, \varphi)$ with respect to the variables r_1, r_2 , and φ . For ABBA molecules and with the sign convention of Sec. II B, we can put $r_{1,e} = |r_{2,e}| = r_e$. The equilibrium configuration depends on the values of the parameters. One can see that the potential function (5) includes the following cases: (a) $r_e = 0$ (linear configuration), Fig. 1(a); (b) $r_e \neq 0$, $r_{1,e} = r_{2,e} = r_e$, $\varphi = 0$, the benders are displaced in the same direction (planar *cis*-configuration Fig. 1(b)); (c) $r_e \neq 0$, $r_{1,e} = -r_{2,e} = r_e$, $\varphi = 0$, the benders are displaced in opposite directions (planar *trans*-configuration Fig. 1(c)); (d) $r_e \neq 0$, $r_{1,e} = -r_{2,e} = r_e$, $\varphi \neq 0$, $0 \leq \varphi \leq \pi/2$ (nonplanar *cis*-like configuration); (e) $r_e \neq 0$, $r_{1,e} = r_{2,e} = r_e$, $\varphi \neq 0$, $0 < \varphi \leq \pi/2$ (nonplanar *trans*-like configuration).

The Hamiltonian (8) provides a description of the bending vibrations of all ABBA molecules: linear, quasi-linear, *cis*-bent, *cis* quasi-bent, *trans*-bent, *trans* quasi-bent, nonplanar, and branched in terms of the nine parameters $\varepsilon, \alpha, \beta, A, \alpha_{12}, \beta_{12}, A_{12}, \lambda, B_{12}$. However, it turns out that a

TABLE I. Best-fit values of Hamiltonian parameters for linear acetylene. Parameters and σ_{rms} in cm^{-1} units.

Parameter	$H^{(0)}$	$H^{(1)}$	$H^{(2)}$	$H^{(3)}$
ε	671.5	670.8	666.3	666.3
α				-1.28
β			4.93	4.66
λ	-1.82	-1.91	-1.83	1.90
A_{12}				
A				
α_{12}				6.78
β_{12}				2.40
B_{12}		3.27	3.81	4.37
No. of parameters	2	3	4	7
σ_{rms}	21.0	15.8	12.4	7.1

description which brings in the main features of the level structure can be obtained in terms of the simple Hamiltonian,

$$\hat{H}^{(0)} = \varepsilon(\hat{n}_1 + \hat{n}_2) + A(\hat{P}_1 + \hat{P}_2) + A_{12} \hat{P}_{12} + \lambda \hat{M}_{12}, \quad (9)$$

which we shall call the “essential” Hamiltonian, or the level zero $\hat{H}^{(0)}$. With this Hamiltonian we can obtain energy levels of linear molecules when $A = A_{12} = 0$ with essential

Hamiltonian,

$$\hat{H}_{\text{linear}}^{(0)} = \varepsilon(\hat{n}_1 + \hat{n}_2) + \lambda \hat{M}_{12}, \quad (10)$$

and energy levels of bent molecules (*cis* and *trans*) when $\varepsilon = 0$ with essential Hamiltonian,

$$\hat{H}_{\text{bent}}^{(0)} = A(\hat{P}_1 + \hat{P}_2) + A_{12} \hat{P}_{12} + \lambda \hat{M}_{12}. \quad (11)$$

To illustrate this point we show in Fig. 5(a) the spectrum obtained by setting $A = A_{12} = 0$ in (9) and $\varepsilon = 700 \text{ cm}^{-1}$, $\lambda = -2.5 \text{ cm}^{-1}$ (linear molecule) and in Fig. 5(b) the spectrum obtained by setting $\varepsilon = 0$, $A = 1.0$, $A_{12} = 20.0$, $\lambda = -2.5 \text{ cm}^{-1}$ (bent molecule). These spectra are obtained by diagonalizing the Hamiltonian $\hat{H}^{(0)}$ in the oscillator basis $|n_1^{\ell_1}, n_2^{\ell_2}\rangle$ and identifying the symmetry of the states by applying the operators ((12), (σ)). When using the essential Hamiltonians (10) and (11) the values of the parameters ε and λ can be obtained from the energies of the fundamental $v_4^{\ell_4} v_5^{\ell_5} = 1^1 0^0$ and $0^0 1^1$ states (two parameters – two quantities to fit), while for bent molecules A, A_{12} , and λ can be obtained from the energies of the fundamentals $(v_3 v_4 v_6) = (100)$, (010) , and (001) states (three parameters – three quantities to fit). The extracted values are useful as starting values for more detailed fits.

The operator expansion method is a systematic procedure for expanding the Hamiltonian \hat{H} . Up to quadratic terms in the elements of the Lie algebra there are nine terms in (8). Up

TABLE II. Results of linear acetylene fits. Calculated levels up to 6000 cm^{-1} are compared to experimental data.^{54–58}

Γ	$(v_4^{\ell_4} v_5^{\ell_5})$	Expt.	$H^{(0)}$	Results	$H^{(3)}$	Results	Γ	$(v_4^{\ell_4} v_5^{\ell_5})$	Expt.	$H^{(0)}$	Results	$H^{(3)}$	Results
Σ bands							Π_u	$3^1 0^0$	1960.87	1965.41	-4.54	1955.19	5.68
Σ_g^+	$0^0 0^0$	0	0	0	0	0	Π_g	$1^1 2^0$	2049.06	2063.54	-14.48	2045.84	3.22
Σ_g^+	$2^0 0^0$	1230.39	1242.95	-12.56	1232.53	-2.14	Π_g	$1^1 2^2$	2066.99	2063.59	3.40	2059.78	7.21
Σ_u^+	$1^1 1^1$	1328.08	1342.99	-14.91	1324.99	3.09	Π_u	$0^0 3^1$	2170.34	2161.77	8.57	2169.50	0.84
Σ_u^-	$1^1 1^1$	1340.55	1342.99	-2.44	1332.58	7.97	Δ bands						
Σ_g^+	$0^0 2^0$	1449.11	1443.02	6.09	1442.51	6.60	Δ_g	$2^2 0^0$	1233.52	1242.95	-9.43	1240.57	-7.05
Σ_u^+	$1^1 3^1$	2560.60	2589.72	-29.12	2562.29	-1.69	Δ_u	$1^1 1^1$	1347.52	1342.99	4.53	1343.64	3.88
Σ_u^-	$1^1 3^1$	2583.84	2589.58	-5.74	2577.90	5.94	Δ_g	$0^0 2^2$	1463.02	1443.02	20.00	1449.07	13.95
Σ_g^+	$2^2 2^2$	2648.02	2685.97	-37.95	2652.02	-4.00	Δ_u	$3^3 1^1$	2561.53	2589.58	-28.05	2569.89	-8.36
Σ_g^-	$2^2 2^2$	2661.19	2685.97	-24.78	2657.26	3.93	Δ_u	$3^1 1^1$	2589.68	2589.72	-0.04	2587.95	1.73
Σ_u^+	$3^1 1^1$	2757.80	2782.23	-24.43	2769.66	-11.86	Δ_g	$2^2 2^0$	2666.15	2685.97	-19.82	2672.10	-5.95
Σ_u^-	$3^1 1^1$	2783.65	2782.37	1.28	2784.41	-0.76	Δ_u	$1^1 3^3$	2773.19	2782.23	-9.04	2771.76	1.43
Σ_g^+	$0^0 4^0$	2880.22	2878.69	1.53	2895.90	-15.68	Δ_u	$1^1 3^1$	2795.50	2782.37	13.13	2793.86	1.64
Σ_g^+	$6^0 0^0$	3765.99	3750.91	15.08	3765.00	0.99	Δ_g	$0^0 4^2$	2894.07	2878.69	15.38	2902.49	-8.42
Σ_u^+	$5^1 1^1$	3818.43	3843.95	-25.52	3819.55	-1.12	Δ_g	$6^2 0^0$	3769.12	3750.91	18.21	3773.40	-4.28
Σ_u^-	$5^1 1^1$	3850.32	3843.52	6.80	3844.17	6.15	Δ_u	$5^3 1^1$	3820.24	3843.52	-23.28	3828.09	-7.85
Σ_g^+	$4^0 2^0$	3940.48	3936.56	3.92	3935.70	4.78	Δ_u	$5^1 1^1$	3855.82	3843.95	11.87	3853.80	2.02
Σ_g^+	$8^0 0^0$	5066.97	5015.93	51.04	5060.92	6.05	Δ_g	$4^0 2^2$	3947.38	3936.56	10.82	3945.31	2.07
Σ_u^+	$7^1 1^1$	5098.38	5105.71	-7.33	5093.70	4.68	Δ_g	$8^2 0^0$	5070.31	5104.82	-34.51	5069.80	0.51
Σ_u^-	$7^1 1^1$	5137.37	5104.82	32.55	5129.38	7.99	Δ_u	$7^3 1^1$	5100.92	5105.71	-4.79	5103.21	-2.29
Σ_g^+	$6^0 2^0$	5216.22	5194.83	21.39	5212.77	3.45	Δ_u	$7^1 1^1$	5142.62	5193.79	-51.17	5138.92	3.70
Σ_u^+	$5^1 3^1$	5254.53	5282.98	-28.45	5266.54	-12.01	Δ_g	$6^0 2^2$	5221.83	5194.83	27.00	5222.39	-0.56
Σ_u^-	$5^1 3^1$	5298.93	5283.20	15.73	5304.51	-5.58	Δ_u	$5^1 3^1$	5226.71	5194.23	32.48	5232.76	-6.05
Π bands							Δ_u	$5^1 3^3$	5262.39	5282.83	-20.44	5252.40	9.99
Π_g	$1^1 0^0$	612.87	620.56	-7.69	615.36	-2.49	Δ_u	$5^1 3^1$	5306.21	5283.50	22.71	5314.27	-8.06
Π_u	$0^0 1^1$	730.33	722.43	7.90	721.51	8.82	Φ bands						
Π_g	$2^2 1^1$	1855.72	1867.19	-11.47	1859.44	-3.72	Φ_g	$3^3 0^0$	1861.93	1867.19	-5.26	1875.63	-13.70
Π_u	$2^0 1^1$	1941.18	1965.36	-24.18	1942.74	-1.56	Φ_u	$2^2 1^1$	1972.59	1965.41	7.18	1975.65	-3.06
							Φ_g	$1^1 2^2$	2084.85	2063.54	21.31	2077.95	6.90
							Φ_u	$0^0 3^3$	2198.13	2161.77	36.36	2182.66	15.47

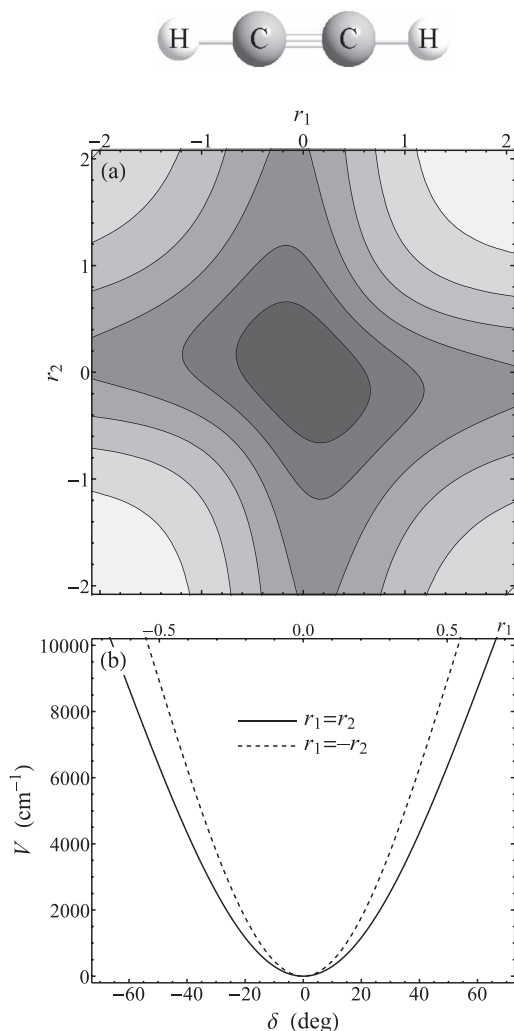


FIG. 6. Potential function for $\tilde{X}^1\Sigma_g^+$ state C_2H_2 using parameters from $\hat{H}^{(3)}$ in Table I with contour plot setting $\varphi = 0$ in (a) and the cuts $r_1 = r_2$ and $r_1 = -r_2$ in panel (b). A schematic of the geometry of the molecule is provided. In the contour plot the equipotential curves are spaced by 5000 cm^{-1} .

to quartic terms there are $9 + 9 \times 10/2 = 54$ terms. However, only some of the higher order terms are found to be important. We mention here the high order terms which play a role in the analysis of the molecules studied in this article. For linear molecules, the relevant quadratic terms are

$$\kappa(\hat{n}_1 + \hat{n}_2)\hat{M}_{12} + \lambda^{III}\hat{M}_{12}^2. \quad (12)$$

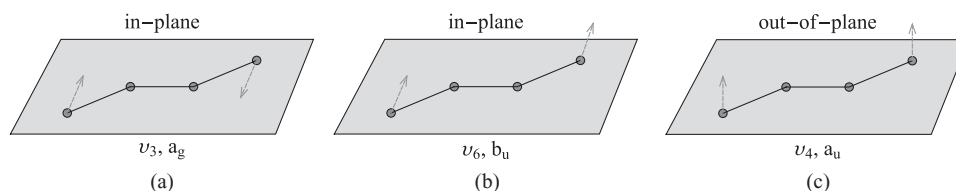


FIG. 7. The fundamental vibrations of \tilde{A}^1A_u state C_2H_2 *trans*- S_1 : (a) shows a_g symmetry (*trans*-bend), (b) b_u symmetry (antisymmetrical bend), and (c) a_u symmetry (torsion).

TABLE III. Scaling values used for linear $\tilde{X}^1\Sigma_g^+$ acetylene and the other molecules presented here.

Molecule	g	Θ (rad)	δ_e (deg)	$\delta_{e,\text{expt.}}$ (deg)
$C_2H_2 \tilde{X}^1\Sigma_g^+$	1.203	1.8358	0	0
$C_2H_2 \tilde{A}^1A_u$ <i>trans</i> - S_1	1.044	1.1048	54.0	57.5
$C_2H_2 \tilde{A}^1A_2$ <i>cis</i> - S_1	1.067	0.8002	-13.8	-47.3
$H_2CO \tilde{X}^1A_1$	1.741	1.1417	-59.5	-58.3

For bent molecules the relevant quadratic terms are

$$\begin{aligned} & A^I (\hat{P}_1 + \hat{P}_2)^2 + A^{II} \hat{P}_{12}(\hat{P}_1 + \hat{P}_2) \\ & + A^{III} (\hat{P}_1 \hat{P}_2) + A_{12}^I (\hat{P}_{12})^2 \\ & + \lambda^I \frac{1}{2} (\hat{M}_{12} \hat{P}_{12} + \hat{P}_{12} \hat{M}_{12}) \\ & + \lambda^{II} \frac{1}{2} [\hat{M}_{12}(\hat{P}_1 + \hat{P}_2) + (\hat{P}_1 + \hat{P}_2)\hat{M}_{12}] + \lambda^{III} (\hat{M}_{12})^2. \end{aligned} \quad (13)$$

III. RESULTS

In this section, we show the results of the application of the algebraic operator expansion method to a linear, a *trans*-bent, a *cis*-bent, and a branched molecule. All calculations are done using a computer code written for the present work. The matrix representations of all operators are built up by composition (array multiplication) of the matrix representations of the creation and annihilation operators on Fock space. Matrices are stored in a compressed sparse row format, and the lowest eigenvalues are found using the Arnoldi method. The code was implemented in its final form on Yale's High Performance Computing BulldogL computer on Mathematica⁵³ and run on 64 cores with the largest matrix dimension 22 776.

A. Linear molecule: Bending vibrations of C_2H_2 ($\tilde{X}^1\Sigma_g^+$)

To illustrate the algebraic approach to bending vibrations in linear tetratomic molecules, we perform here a calculation of acetylene, C_2H_2 , in its electronic ground state $\tilde{X}^1\Sigma_g^+$. Although we have previously³² reported calculations for this molecule, it is illustrative to present an expanded treatment here, making use of a larger basis and showing a description of the main features can be found with only two parameters. This treatment is more suitable for comparison with the bent molecules considered in Secs. III B and III C. We consider a

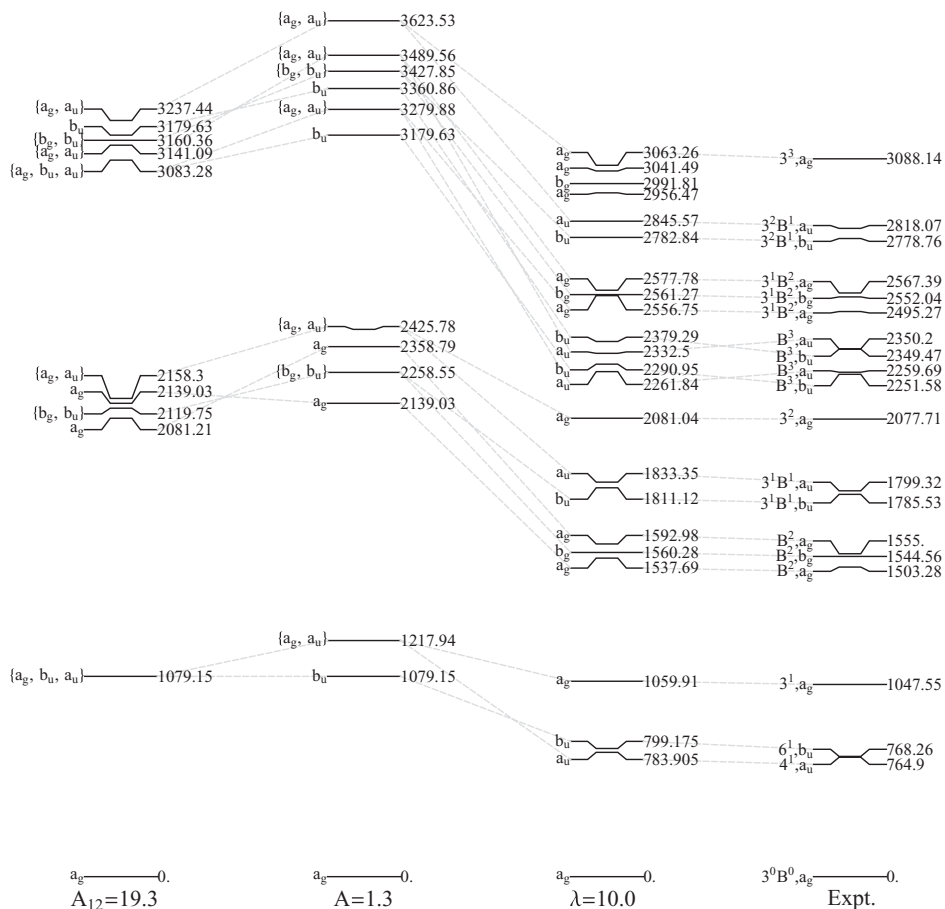


FIG. 8. The three parameter spectrum for $N_1 = N_2 = 28$ is built from single parameters to show the effect of each. All states up to the third polyad $\nu_3 + \nu_4 + \nu_6 = 3$ are shown in this figure.

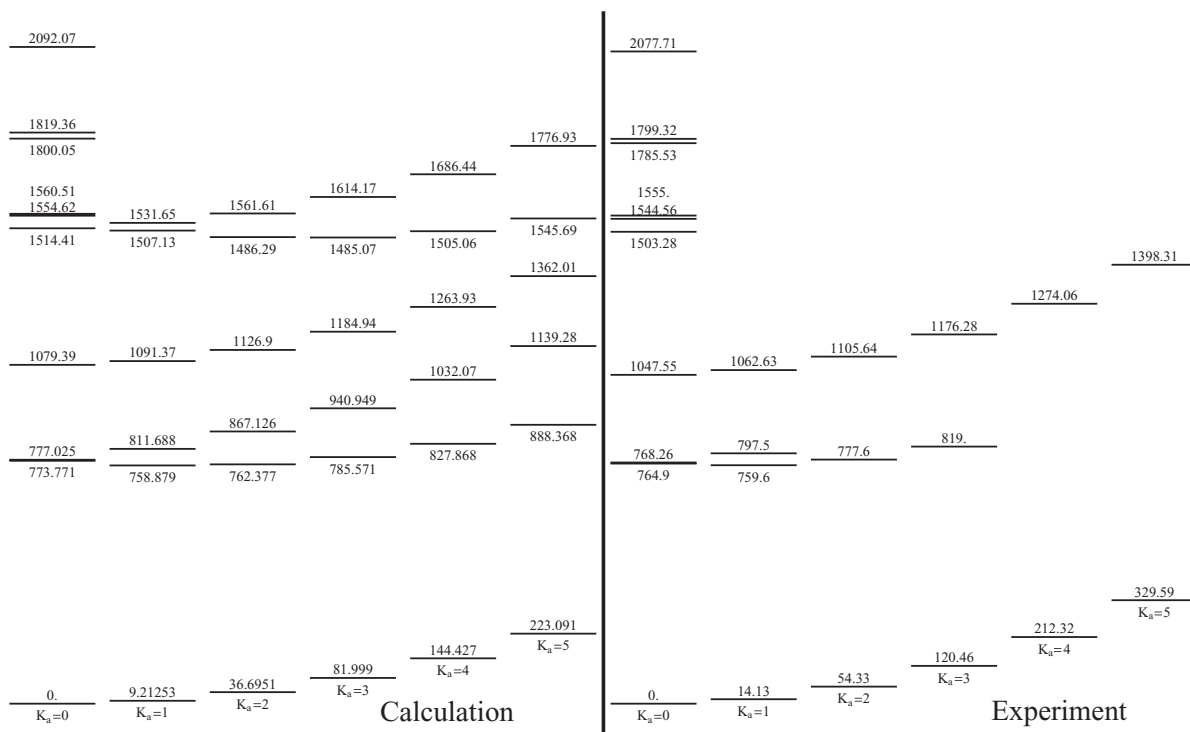


FIG. 9. The rotational behavior for $\tilde{A}^1 A_u$ state of C_2H_2 is smooth for the $(3^0 4^0 6^0)$ state but appears staggered for the 4^1 and 6^1 states.

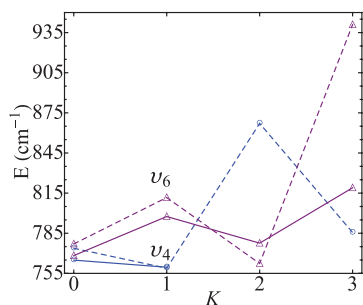


FIG. 10. The staggering in the experimental rotational levels of \tilde{A}^1A_u C_2H_2 as reproduced by the Hamiltonian (15). The purple solid (dashed) line represents experimental (calculated) energies for the ν_6 mode as a function of K , while the blue solid (dashed) line shows experimental (calculated) values for ν_4 mode.

total number of 54 term values^{54–58} below 6000 cm^{-1} . All fits are done within a model space with $N_1 = N_2 = 28$.

The parameter values obtained including different physically relevant operators are given in Table I, starting with the essential Hamiltonian $H^{(0)}$.

One can see from these fits that the essential Hamiltonian with two parameters gives a description of the 54 levels with $\sigma_{\text{rms}} = 21.0\text{ cm}^{-1}$, where σ_{rms} is defined as

$$\sigma_{\text{rms}} = \sqrt{\frac{\sum_{i=1}^j (E_{\text{expt},i} - E_{\text{calc},i})^2}{j - n_{\text{param}}}}. \quad (14)$$

TABLE V. Results of *trans* acetylene fits to $K = 0$ vibrational levels. Calculated levels are compared to experiment.^{12,14,59–66}

Γ	$(\nu_3\nu_4\nu_6)$	Expt.	$H_{\text{bent}}^{(0)}$	Results	$H^{(2)}$	Results	Γ	$(\nu_3\nu_4\nu_6)$	Expt.	$H_{\text{bent}}^{(0)}$	Results	$H^{(2)}$	Results
a_g	$3^04^06^0$	0	0	0	0	0	b_u	3^1B^3 (I)	3200.24	3274.5	-74.26	3206.9	-6.66
							a_u	3^1B^3 (II)	3246.7	3273.96	-27.26	3205.91	40.79
a_u	4^1	764.9	783.9	-19	774.75	-9.85	b_u	3^1B^3 (III)	3340.93	3307.55	33.38	3319.55	21.38
b_u	6^1	768.26	799.17	-30.91	776.77	-8.51	a_u	3^1B^3 (IV)	3348.3	3298.79	49.51	3320.04	28.26
a_g	3^1	1047.55	1059.91	-12.36	1083.38	-35.83	a_g	3^2B^2 (I)	3446.57	3485.53	-38.96	3405.3	41.27
							b_g	$3^24^16^1$	3538.5	3523.56	14.94	3492.26	46.24
a_g	B^2 (I)	1503.28	1537.69	-34.41	1517.79	-14.51	a_g	3^2B^2 (III)	3569.1	3575.72	-6.62	3503.09	66.01
b_g	4^16^1	1544.56	1560.28	-15.72	1558.7	-14.14	b_u	3^36^1	3740.19	3820.77	-80.58	3788.61	-48.42
a_g	B^2 (III)	1555	1592.98	-37.98	1563.4	-8.4	a_u	3^34^1	3818.79	3784.92	33.87	3805.31	13.48
b_u	3^16^1	1785.53	1811.12	-25.59	1804.25	-18.72	a_g	3^4	4072.95	4043.22	29.73	4102.81	-29.86
a_u	3^14^1	1799.32	1833.35	-34.03	1825.4	-26.08							
a_g	3^2	2077.71	2081.04	-3.33	2099.77	-22.06	b_u	B^5 (I)	3692.51	3720.69	-28.18	3711.53	-19.02
							a_u	B^5 (II)	3721.71	3713.92	7.79	3703.42	18.29
b_u	B^3 (I)	2251.58	2290.95	-39.37	2285.66	-34.08	b_u	B^5 (III)	3810.01	3854	-43.99	3971.85	-161.84
a_u	B^3 (II)	2259.69	2261.84	-2.15	2246.46	13.23	a_u	B^5 (IV)	3824.77	3925.95	-101.18	3971.97	-147.2
b_u	B^3 (III)	2349.47	2379.29	-29.82	2355.49	-6.02	a_g	3^1B^4 (I)	3877.81	3953.4	-75.59	3891.61	-13.8
a_u	B^3 (IV)	2350.2	2332.5	17.7	2353.14	-2.94	b_g	3^1B^4 (II)	3955.73	3958.33	-2.6	3917.07	38.66
a_g	3^1B^2 (I)	2495.27	2556.75	-61.48	2506.45	-11.18	b_u	B^5 (V)	3993.12	4201.54	-208.42	4080.85	-87.73
b_g	$3^14^16^1$	2552.04	2561.27	-9.23	2558.06	-6.02	a_u	B^5 (VI)	3993.44	4182.18	-188.74	4044.13	-50.69
a_g	3^1B^2 (III)	2567.39	2577.78	-10.39	2561.22	6.17	a_g	3^1B^4 (III)	4012.13	4006.36	5.77	3923.49	88.64
b_u	3^26^1	2778.76	2782.84	-4.08	2760.42	18.34	b_u	3^2B^3 (I)	4089.48	4274.18	-184.7	4238.96	-149.48
a_u	3^24^1	2818.07	2845.57	-27.5	2806.4	11.67	b_g	3^1B^4 (IV)	4142.43	4016.56	125.87	4103.06	39.37
a_g	3^3	3088.14	3063.26	24.88	3048.68	39.46	a_g	3^1B^4 (V)	4149.43	4257.28	-107.85	4214.71	-65.28
							a_u	3^2B^3 (II)	4200.26	4233.18	-32.92	4235.81	-35.55
a_g	B^4 (I)	2974.98	2956.47	18.51	2948.76	26.22	b_u	3^2B^3 (III)	4313.4	4601.08	-287.68	4483.43	-170.03
b_g	B^4 (II)	3009.33	2991.81	17.52	3015.75	-6.42	a_g	3^36^2	4317.18	4370.44	-53.26	4281.93	35.25
a_g	B^4 (III)	3042.23	3041.49	0.74	3040.65	1.58	a_u	3^2B^3 (IV)	4344.36	4603.8	-259.44	4444.56	-100.2
b_g	B^4 (IV)	3164.03	3097.37	66.66	3156.38	7.65							
a_g	B^4 (V)	3165.63	3157.24	8.39	3157.09	8.54	a_g	3^46^2	4997.23	4943.81	53.42	5015.49	-18.26

TABLE IV. Best-fit values of Hamiltonian parameters for *trans* acetylene. Parameters and σ in cm^{-1} units.

Parameters	$H_{\text{bent}}^{(0)}$	$H^{(0)}$	$H^{(1)}$	$H_{\text{bent}}^{(2)}$	$H^{(2)}$
A_{12}	19.27	20.08	21.22	18.29	19.64
A	1.261	2.94	-1.10	1.59	3.22
λ	10.03	15.90	3.46	9.75	16.03
ε		393.5			392.8
α					
$A^I/10^4$			-2.2		
$A^{II}/10^3$			1.5		
$A_{12}^I/10^4$			-4.0		
$\lambda^I/10^3$			-6.5		
$\lambda^{II}/10^3$			6.9		
$\lambda^{III}/10^3$			9.4		
$\lambda^{IV}/10^5$				1.4	0.63
No. of parameters	3	4	9	4	5
σ	56.0	27.5	44.9	53.8	27.4

Adding the parameter B_{12} (ℓ -resonance) brings this down to 15.8 cm^{-1} . The introduction of the parameter β brings the deviation down to 12.4 cm^{-1} . We have investigated the effect of introducing the (polyad breaking) parameters A and A_{12} but found no gain in the rms deviation. Inclusion of additional parameters $\alpha, \alpha_{12}, \beta_{12}$ brings the deviation down to 7.1 cm^{-1} . Table II shows the experimental term values and the

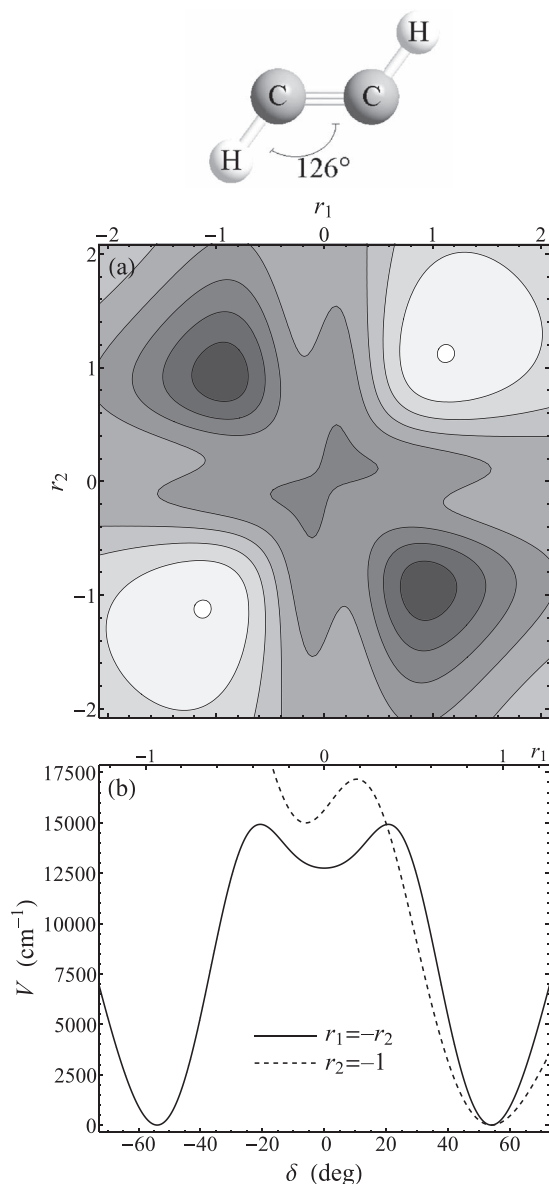


FIG. 11. The best fit potential function for $\tilde{A}^1 A_u$ state C_2H_2 $trans$ - S_1 (a), and its cuts along the lines $r_1 = -r_2$ and $r_2 = -1$ in (b). The geometric configuration of the molecule is also shown. The contour curves in (a) are spaced by 5000 cm^{-1} .

residuals $\Delta E = E_{\text{expt.}} - E_{\text{calc.}}$ obtained in the calculations $H^{(0)}$ and $H^{(3)}$.

The values of the parameters in Table I support a linear normal configuration for C_2H_2 ($\tilde{X}^1 \Sigma_g^+$) for the term energies below 6000 cm^{-1} . In Fig. 6 we show the potential function (5) for $\phi = 0$ (i.e., in the plane Σ) in a two-dimensional plot,

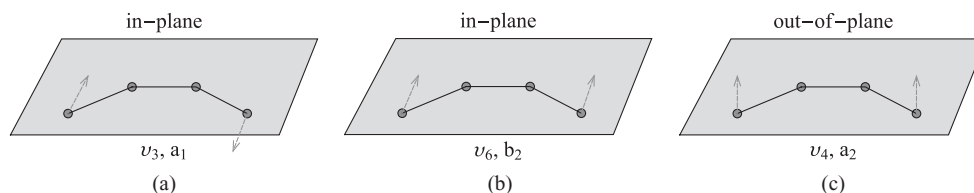


FIG. 12. The fundamental vibrations of $\tilde{A}^1 A_2$ state C_2H_2 cis - S_1 : (a) shows a_1 symmetry ($trans$ bend), (b) b_2 symmetry (antisymmetric bend), and (c) a_2 symmetry (torsion).

TABLE VI. Best-fit values of Hamiltonian parameters for cis acetylene. Parameters and σ in cm^{-1} units.

Parameters	$\hat{H}_{\text{bent}}^{(0)}$	$\hat{H}^{(1)}$	$\hat{H}^{(2)}$
A_{12}	20.0	21.0	20.0
A	4.0	4.3	3.8
λ	-12.1	-75.1	-65.5
A^{III}			0.07
λ^{III}		0.54	0.44
σ	55	28	15

Fig. 6(a). Its properties can be further elucidated by cutting it along the lines $r_1 = r_2 = r$ (appropriate for cis -vibrations) and $r_1 = -r_2 = r$ (appropriate for $trans$ -vibrations), Fig. 6(b). Note the slight difference between the potential functions, Fig. 6(b), also seen as an asymmetry in Fig. 6(a). The potential functions shown in Fig. 6(b) can be converted to the bending angle δ in radians by using the scaling^{21,22} $\delta = \Theta r$. The value of Θ can be obtained using the established method for linear molecules²¹ and is 1.836 rad, as shown in Table III. With this value we can plot the potential functions shown in Fig. 6(b). In the same Table III we show also the scaling values for all other molecules presented in this article. A discussion of the obtained values is given in Secs. III B and III C.

B. Bent molecule: Bending vibrations of C_2H_2 ($\tilde{A}^1 A_u$)

1. Description of $trans$ - S_1 bending spectrum

The $\tilde{A}^1 A_u$ state of acetylene has been studied for over 60 years with almost 100 vibrational levels assigned, and complete assignments up to 4300 cm^{-1} above the zero-point level.^{12,14,59-66} This state therefore provides optimal testing ground of the algebraic method. There are three fundamental bending vibrations of $trans$ - S_1 with symmetry a_u, b_u, a_g as shown in Fig. 7. We use the conventional labeling (ν_3, ν_4, ν_6) $\equiv (a_g, a_u, b_u)$. Since the vibrations ν_4 and ν_6 are strongly mixed it is convenient to introduce a notation B^n where $n = \nu_4 + \nu_6$ with a Roman numeral indicating ascending energy order within a polyad.¹⁴ This notation is used in the supplementary material,³⁶ where the calculated term energies are compared to experiment.

a. Essential Hamiltonian for $trans$ - S_1 C_2H_2 . We consider here a fit to all vibrational states for $K = 0$ with the Hamiltonian (11) with three parameters A, A_{12} , and λ . This fit has a deviation σ_{rms} of 56.0 cm^{-1} for all levels and 32.9 cm^{-1} for the lowest four polyads.

TABLE VII. The *cis*-well levels of C₂H₂.

($\nu_3\nu_4\nu_6$)	Γ	Expt.	Expt. $-T_0^a - 2702^b$	$\hat{H}_{\text{bent}}^{(0)}$	Results	$\hat{H}^{(2)}$	Results
000	a_1	44 900	0	0	0	0	0
100	a_1	45 610	710	738	-28	700	10
010	a_2	45 735	835	880	-45	835	0
002	a_1	46 114	1214	1213	1	1209	5
101	b_2	46 175	1275	1323	-48	1286	-11
200	a_1	46 347	1447	1410	37	1447	0
011	b_1	46 394	1494	1445	49	1494	0

^aEnergy of *trans* well above electronic ground state.⁶⁵^bEstimation of energy of the bottom of the *cis* well above the *trans* well.¹⁴

Because of its extreme simplicity, it is instructive to display how the spectrum of a *trans* molecule is built up term by term. In Fig. 8 we show in the first column the spectrum of $A_{12} \hat{P}_{12}$, in the second column the spectrum of $A_{12} \hat{P}_{12} + A(\hat{P}_1 + \hat{P}_2)$, in the third column the spectrum of $A_{12} \hat{P}_{12} + A(\hat{P}_1 + \hat{P}_2) + \lambda \hat{M}_{12}$, and in the fourth column the experimental spectrum. It appears that the essential Hamiltonian produces the main features of the spectrum of states, including Darling-Dennison couplings with only three parameters. A conventional Dunham-like expansion would require three ω_i ($i = 3, 4, 6$), 21 χ_{ij} ($i, j = 3, 4, 6$) plus the parameter κ_{4466} of the Darling-Dennison coupling. We consider next a fit to all states $K = 0$ and $K \neq 0$ with Hamiltonian

$$\hat{H}^{(0)} = \hat{H}_{\text{bent}}^{(0)} + \varepsilon(\hat{n}_1 + \hat{n}_2). \quad (15)$$

This fit has an rms deviation of 27.5 cm⁻¹. It is instructive to display the rotational behavior, Fig. 9. While for the (3⁰4⁰6⁰) state the rotational behavior is smooth, for the vibrations 4¹ and 6¹ a staggering is observed, Fig. 10.

b. Higher order terms for trans-S₁ C₂H₂. In order to improve the description we introduce higher order terms. At level 1 we have the terms from Eq. (13):

$$\begin{aligned} \hat{H}^{(1)} = & \hat{H}^{(0)} \\ & + A^I(\hat{P}_1 + \hat{P}_2)^2 + A^{II} \hat{P}_{12}(\hat{P}_1 + \hat{P}_2) + A_{12}^I(\hat{P}_{12})^2 \\ & + \lambda^I \frac{1}{2} [\hat{M}_{12} \hat{P}_{12} + \hat{P}_{12} \hat{M}_{12}] + \lambda^{II} \frac{1}{2} [\hat{M}_{12}(\hat{P}_1 + \hat{P}_2) \\ & + (\hat{P}_1 + \hat{P}_2) \hat{M}_{12}] + \lambda^{III} (\hat{M}_{12})^2. \end{aligned} \quad (16)$$

A fit to all vibrational levels with $K = 0$ gives an rms deviation of 44.9 cm⁻¹. At level 2 we have all cubic terms and at level 3 we have all quartic terms. An analysis of the effect of the various terms reveals that only one term at level 2 plays a role. We have therefore considered fits to all states with $K = 0$ and $K \neq 0$ with the Hamiltonian:

$$\begin{aligned} \hat{H}^{(2)} = & A(\hat{P}_1 + \hat{P}_2) + A_{12} \hat{P}_{12} + \lambda \hat{M}_{12} \\ & + \varepsilon(\hat{n}_1 + \hat{n}_2) \\ & + \lambda^{IV} \frac{1}{2} \left(\left[\hat{P}_{12} - \frac{1}{4}(\hat{P}_1 + \hat{P}_2) \right]^2 \hat{M}_{12} \right. \\ & \left. + \hat{M}_{12} \left[\hat{P}_{12} - \frac{1}{4}(\hat{P}_1 + \hat{P}_2) \right]^2 \right). \end{aligned} \quad (17)$$

This fit does not much improve the overall rms deviation, $\sigma_{\text{rms}} = 27.4$ cm⁻¹, which is dominated by the lowest polyads, but it improves considerably the polyads with $\nu_3 + \nu_4 + \nu_6 \geq 4$, which are those of major interest to the experimental groups studying this state.¹⁴ All best-fit values of model parameters are summarized in Table IV and are for $N_1 = N_2 = 28$. A comparison between experiment and calculation is shown in Table V for $K = 0$ levels and in the supplementary material³⁶ for levels with $K > 0$.

2. Potential functions for trans-S₁ C₂H₂

In Fig. 11 we show the contour plot of the potential function for the best fit of Table IV as a function of $r_1 \propto \angle CCH_1$ and $r_2 \propto \angle CCH_2$. The potential function has minima at around $r_{e,1} = -r_{e,2} \cong 1$ (*trans* configuration). The properties of the potential function can be further elucidated by cutting it along some lines. In Fig. 11 we show two cuts, one along the line $r_1 = -r_2$, showing the barrier to linearity and one along the line $r_2 = -1$, showing the *trans-cis* potential, in Fig. 11(b). Both can be converted to scaled potentials by $\delta = \Theta r$, where $\Theta = 1.1048$ rad using a method for bent molecules²² adapted to nonlinear coupled benders as

$$\Theta = 5.7737 \sqrt{\frac{(2 - \xi)N_1 g}{(1 - \xi)\varepsilon + \xi N_1(2A_{12} + 4A)}} \quad (18)$$

with the adapted definition of ξ ,

$$\xi = \frac{(A + \frac{1}{2}A_{12})(N_1 - 1)}{\varepsilon + (A + \frac{1}{2}A_{12})(N_1 - 1)}. \quad (19)$$

Our calculated equilibrium angle is 54.0°, which is in good agreement with the reported value 57.5°.⁶⁷ The value of Θ and the equilibrium angle are also shown in Table III.

3. Description of cis-S₁ bending spectrum

Contrary to the previous case of *trans*-S₁, only seven levels have been observed in the *cis*-well.^{66,68} There are three fundamental bending vibrations of *cis*-S₁, with symmetry a_2, b_2, a_1 , as shown in Fig. 12. We use again the conventional labeling (ν_3, ν_4, ν_6) \equiv (a_1, a_2, b_2). The zero-point level of the *cis*-well is not known but it has been estimated⁶⁸ to be 3267 cm⁻¹ above the zero-point level of the *trans* well.

For this configuration we do a fit with $\hat{H}_{\text{bent}}^{(0)}$, Eq. (11), and the resulting rms deviation is 55 cm⁻¹. We note that the inclusion of the Hamiltonian parameter ε (that is, using $\hat{H}^{(0)}$, Eq. (15)) does not improve the fit. The large deviation of the $\hat{H}_{\text{bent}}^{(0)}$ fit may be due to the fact that the spectrum of the *cis*-S₁ configuration is strongly affected by the coupling to the neighboring *trans* levels. In order to simulate these effects we introduce higher order terms and consider the Hamiltonian $\hat{H}^{(2)}$:

$$\hat{H}^{(2)} = \hat{H}_{\text{bent}}^{(0)} + \lambda^{III} (\hat{M}_{12})^2 + A^{III} \hat{P}_1 \hat{P}_2. \quad (20)$$

However, this latter fit has an unusually large value of the parameter λ and should be considered with caution. The

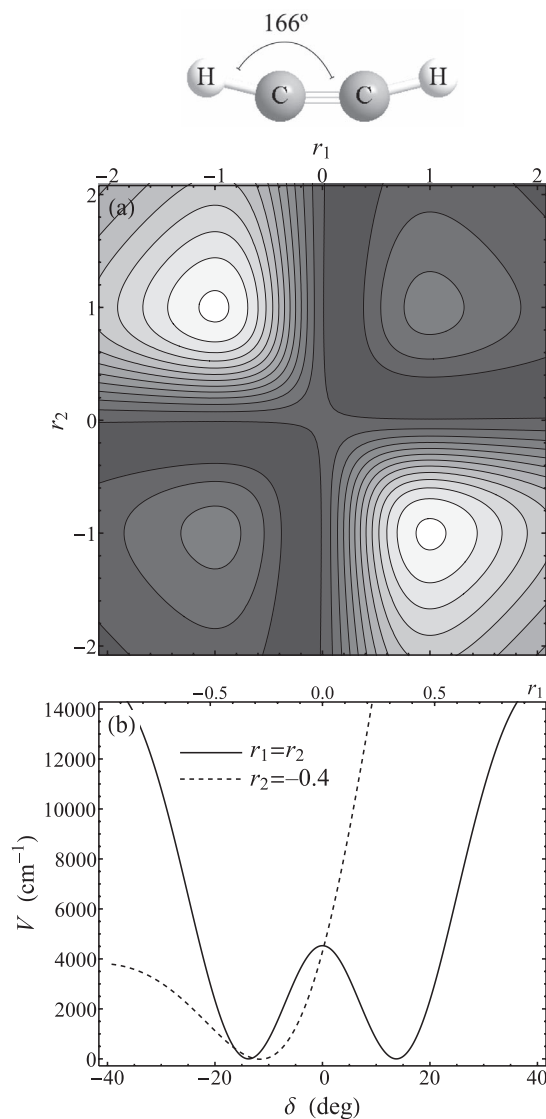


FIG. 13. Potential function for *cis* C₂H₂ using parameters from $\hat{H}^{(2)}$ in Table VI in (a), the cuts $r_1 = r_2$ and $r_2 = -0.4$ in (b), and a schematic drawing of the geometric configuration of the molecule. The contour curves in (a) are spaced by 10 000 cm⁻¹.

resulting parameters are shown in Table VI and the calculated level energies are given in Table VII.

The potential energy function is shown for the fit $\hat{H}^{(2)}$ in Fig. 13(a), together with the cuts $r_1 = r_2 = r$ (barrier to linearity) and $r_2 = -1$ (*trans-cis* potential) in Fig. 13(b), and a schematic drawing of the geometric configuration of the molecule. The scaled potentials are also shown in Fig. 13(b) where $\Theta = 0.8002$ rad has been used to scale r . The calculated *cis* angle is -13.8° and is in poor agreement with the reported

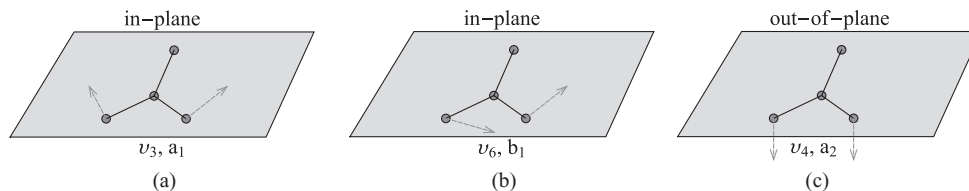


FIG. 15. The fundamental vibrations of H₂CO: (a) shows a_1 symmetry bend, (b) b_1 symmetry bend, and (c) a_2 symmetry bend.

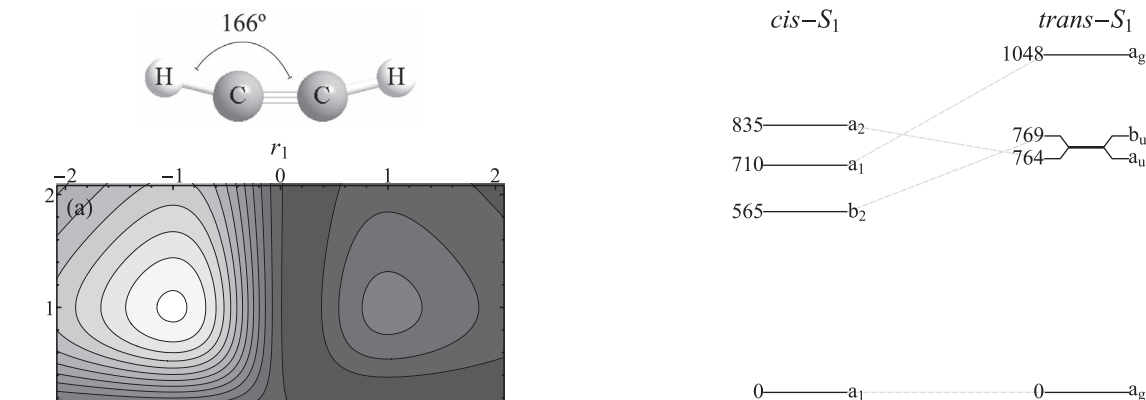


FIG. 14. Comparison of the fundamentals of *trans*-S₁ \tilde{A}^1A_u and *cis*-S₁ \tilde{A}^1A_2 state C₂H₂. The term value for the b_2 vibrational in *cis*-S₁ is the one estimated previously.⁶⁷

value -47.4° .⁶⁷ As stated above, the parameters derived for *cis*-S₁ acetylene should be taken with caution because of the unusual value of λ .

It is of interest to contrast the fundamentals for *trans*-S₁ and *cis*-S₁ configurations. The out of plane vibration has the highest energy for *cis*-bent and the lowest for *trans*-bent, as seen in Fig. 14. This is reflected in the sign of the coefficient λ of the \hat{M}_{12} term in $\hat{H}^{(0)}$, which is positive for *trans* C₂H₂ and negative for the *cis* configuration of C₂H₂.

Cis-bent and *trans*-bent configurations have been treated here and elsewhere¹⁴ as separate configurations. In a more complete treatment they should be treated as part of the same potential energy surface. Within the algebraic approach the combined *cis-trans* description might be approached in two ways: (1) by adding terms to \hat{H} of higher order; (2) by the method of eigenpotentials used in nuclear physics.⁶⁹

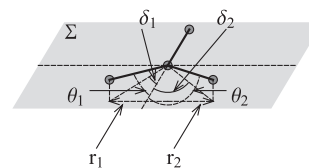
C. Bent molecules: Bending vibrations of formaldehyde, H₂CO

In order to explore the range of applicability of the algebraic method we study the \tilde{X}^1A_1 state of formaldehyde, H₂CO, for which a large number of experimental data exist.⁷⁰ This molecule has three fundamental bending vibrations as shown in Fig. 15. We denote the three vibrations in the conventional way (ν_3 , ν_4 , ν_6). We do three fits to the observed levels, with the essential Hamiltonian $\hat{H}_{\text{bent}}^{(0)}$, the Hamiltonian at level 1 with all the terms from Eq. (13), and with the Hamiltonian $\hat{H}^{(1)'} = \hat{H}^{(1)} + \varepsilon(\hat{n}_1 + \hat{n}_2)$. The corresponding parameters are shown in Table VIII. We note that adding the term $\varepsilon(\hat{n}_1 + \hat{n}_2)$ has no effect on the rms deviation; hence, H₂CO is strictly bent. The fits at

TABLE VIII. Best-fit values of Hamiltonian parameters for H₂CO. Parameters and σ in cm⁻¹ units.

Fit $N_1 = N_2$	$\hat{H}^{(0)}$ 40	$\hat{H}^{(1)}$ 40	$\hat{H}^{(1)'}$ 40
ε			111.79
A_{12}	19.6	15.39	15.29
A	1.0	3.44	3.55
λ	8.3	9.52	9.60
$A^I/10^3$		-2.10	-1.92
$A^{II}/10^3$		1.54	1.23
$A^{III}/10^3$		1.54	1.90
$A_{12}^I/10^3$		2.14	1.94
$\lambda^I/10^3$		2.88	2.13
$\lambda^{II}/10^3$		-2.45	-2.21
$\lambda^{III}/10^3$		-2.07	-2.19
σ	50.6	7.05	7.07

levels 0 and 1 are compared with experimental data in Table IX. The potential function for H₂CO can be constructed with the method of Sec. II B. The displacements r_1, θ_1 and r_2, θ_2 for this molecule are shown in Fig. 16. The potential energy function in the plane $\Sigma, \varphi = 0$ is shown for the fit using $\hat{H}^{(1)}$ in Fig. 17(a) and scaled to bending angle in Fig. 17(b). The scaling constant is $\Theta = 1.1417$ rad and is

FIG. 16. The displacements r_1, r_2 and angles δ_1, δ_2 for branched tetratomic molecules. Our sign convention, r_2 positive to the right and r_1 positive to the left, is also shown.

calculated using the method²¹ for rigidly bent molecules. The equilibrium angle $\angle HCH = 119^\circ$ is in good agreement with the reported angle $\angle HCH = 116.5^\circ$.⁷¹

IV. DISCUSSION

In this article we have presented applications of the algebraic method to the study of tetratomic molecules, C₂H₂ ($\tilde{X}^1\Sigma_g^+$), C₂H₂ (\tilde{A}^1A_u) *trans*-S₁, C₂H₂ (\tilde{A}^1A_2) *cis*-S₁, H₂CO, and shown that the basic properties of all of them can be obtained in terms of four parameters $\varepsilon, A, A_{12}, \lambda$ (level 0 of the algebraic method). The values obtained are summarized in Table X. The number of essential parameters is two (ε, λ) for linear molecules and three (A, A_{12}, λ) for bent molecules. This level should be compared with Dunham-like

TABLE IX. Calculated levels compared to experimental levels for formaldehyde.

Γ	$(v_3 v_4 v_6)$	Expt.	$\hat{H}^{(0)}$	Results	$\hat{H}^{(1)}$	Results	Γ	$(v_3 v_4 v_6)$	Expt.	$\hat{H}^{(0)}$	Results	$\hat{H}^{(1)}$	Results
a_1	0 0 0	0	0	0	0	0	b_1	0 5 0	5771	5815.2	-44.2	5772.4	-1.4
							b_2	0 4 1	5891.8	5868.9	22.9	5890.3	1.5
b_1	0 1 0	1176.4	1236.1	-59.7	1167.7	8.7	a_1	1 4 0	6123.6	6180	-56.4	6123.2	0.4
b_2	0 0 1	1249.6	1219.5	30.1	1251.7	-2.1	a_2	1 3 1	6189.1	6183.1	6	6191.5	-2.4
a_1	1 0 0	1500.2	1547.9	-47.7	1498.1	2.1	a_1	1 2 2	6263.1	6260.9	2.2	6253.4	9.7
							a_1	1 0 4	6373.4	6208.1	165.3	6376.1	-2.7
a_1	0 2 0	2327.5	2406.7	-79.2	2328.1	-0.6	b_2	2 2 1	6508.8	6487.7	21.1	6509.5	-0.7
a_2	0 1 1	2422.2	2429.2	-7	2421.8	0.4	b_1	2 1 2	6553.1	6520.1	33	6549.9	3.2
a_1	0 0 2	2496.1	2463.4	32.7	2505.7	-9.6	a_1	3 2 0	6815.2	6838	-22.8	6815.5	-0.3
b_1	1 1 0	2667.1	2738	-70.9	2667.6	-0.5							
b_2	1 0 1	2718.6	2759	-40.4	2713.8	4.8	a_1	0 6 0	6909	6886.1	22.9	6909.8	-0.8
a_1	2 0 0	2998.1	3057.4	-59.3	3000.6	-2.5	a_2	0 5 1	7036	7010	26	7034.2	1.8
							a_1	0 4 2	7151.3	7089.1	62.2	7145.1	6.2
b_1	0 3 0	3480.7	3589.9	-109.2	3482	-1.3	b_1	1 5 0	7264.8	7263.6	1.2	7260.1	4.7
b_2	0 2 1	3586.6	3562	24.6	3584.6	2	b_2	1 4 1	7328.2	7295.5	32.7	7334.3	-6.1
b_1	0 1 2	3673.5	3680.9	-7.4	3676.3	-2.8	a_1	2 4 0	7616.3	7608.9	7.4	7609.1	7.2
a_1	1 2 0	3825.3	3918.5	-93.2	3827.7	-2.4	a_2	2 3 1	7641.7	7630.5	11.2	7652	-10.3
a_2	1 1 1	3886.5	3922.5	-36	3882.1	4.4	a_1	2 2 2	7709.2	7659.5	49.7	7696.5	12.7
a_1	1 0 2	3937.4	3937.5	-0.1	3932.6	4.8							
							b_1	0 7 0	8041	8055.7	-14.7	8042.4	-1.4
a_1	0 4 0	4629	4685.6	-56.6	4629.9	-0.9	b_2	0 6 1	8172.7	8141.3	31.4	8172.6	0.1
a_2	0 3 1	4741.9	4718.5	23.4	4740.6	1.3	a_1	1 6 0	8399.2	8442.9	-43.7	8390.4	8.8
a_1	0 2 2	4842	4888.1	-46.1	4839.4	2.6	a_2	1 5 1	8456.2	8500	-43.8	8469.9	-13.7
b_1	1 3 0	4977.1	5069.1	-92	4979.3	-2.2							
b_2	1 2 1	5043.7	5069.3	-25.6	5041	2.7	a_1	0 8 0	9167.6	9161.8	5.8	9170.4	-2.8
b_1	1 1 2	5104	5097.3	6.7	5097.6	6.4	a_2	0 7 1	9312.5	9262	50.5	9305.6	6.9
b_2	1 0 3	5151	5088.2	62.8	5153.5	-2.5	b_2	1 6 1	9577.8	9619	-41.2	9598.7	-20.9
a_1	2 2 0	5321.3	5337.6	-16.3	5325.6	-4.3							
a_2	2 1 1	5353.2	5378.5	-25.3	5357	-3.8	a_1	1 8 0	10652.3	10640.7	11.6	10632.9	19.4
a_1	2 0 2	5389.4	5429	-39.6	5392.6	-3.2	a_1	0 10 0	11407	11351.3	55.7	11412.8	-5.8

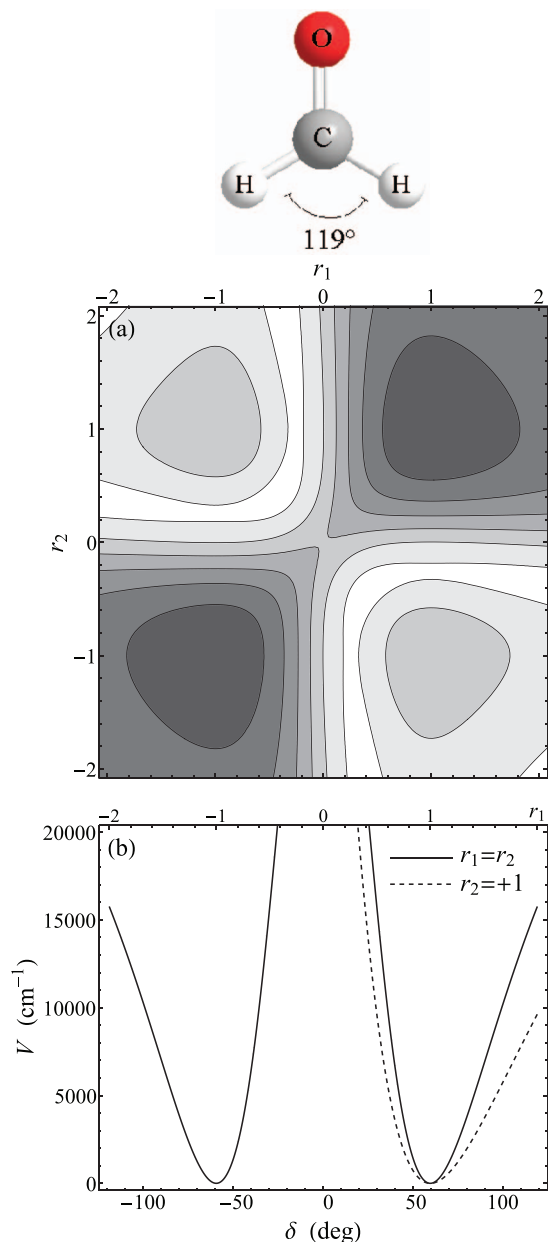


FIG. 17. Potential function for $\tilde{X}^1\Sigma_g^+$ state H_2CO using parameters from $\hat{H}^{(1)}$ in Table VIII in (a), the cuts $r_1 = r_2$ and $r_2 = +1$ in panel (b), and a schematic drawing of the molecule. The contour curves in (a) are spaced by 10000 cm^{-1} .

expansions to level zero with parameters ω_4, ω_5 for linear and $\omega_3, \omega_4, \omega_6$ for bent. At level 1 of the algebraic theory we obtain descriptions with the rms deviation of the order 7 cm^{-1} , except in C_2H_2 (\tilde{A}^1A_u) trans-S_1 where the rms deviation is of the order 27 cm^{-1} . Level 1 of the algebraic theory should be compared with Dunham-like expansions with parameters $\omega_4, \omega_5, \chi_{44}, \chi_{45}, \chi_{55}$ for linear molecules and $\omega_3, \omega_4, \omega_6, \chi_{33}, \chi_{34}, \chi_{36}, \chi_{44}, \chi_{46}, \chi_{66}$ for bent molecules.

We note that the algebraic method also provides the symmetry of the states and the potential functions in terms of the bending angles. These functions should be compared with force-field expansions, in terms of the angles δ_1, δ_2, ϕ , the only difference being that we expand onto functions of δ_1, δ_2, ϕ rather than in powers of them $(\delta_1)^{n_1}, (\delta_2)^{n_2}, (\phi)^{n_\phi}$.

TABLE X. Optimized parameter values for tetratomic molecules. Parameters and σ in cm^{-1} units.

Parameters	C_2H_2	C_2H_2	C_2H_2	H_2CO
	($\tilde{X}^1\Sigma_g^+$)	(\tilde{A}^1A_u) trans-S_1	(\tilde{A}^1A_2) cis-S_1	
ϵ	671.5			
A_{12}		19.3	20.0	19.6
A		1.3	4.0	1.0
λ	-1.8	10.0	-12.1	8.3
No. of levels	54	117	7	52
σ	21.0	56.0	55.0	50.6

The results we obtain support previous studies, namely, (1) the ground electronic state $\tilde{X}^1\Sigma_g^+$ of C_2H_2 is linear with a small contribution to nonlinearity; (2) the excited electronic state of C_2H_2 has two configurations, trans-S_1 \tilde{A}^1A_u and cis-S_1 \tilde{A}^1A_2 . The configuration trans-S_1 is not rigidly bent but soft and has a complex surface with a second minimum. The precise properties of the configuration cis-S_1 cannot be determined because of the lack of experimental data; (3) the H_2CO molecule is rigidly bent.

Our calculated values can be used to estimate the location of unknown states and thus serve as a guide for further experimental studies. To this end, we give, in the supplementary material,³⁶ all our calculated term values for $\tilde{X}^1\Sigma_g^+$ C_2H_2 , \tilde{A}^1A_u C_2H_2 trans-S_1 , \tilde{A}^1A_2 C_2H_2 cis-S_1 , and H_2CO .

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