Computational Study of the Rovibrational Spectra of CO₂-C₂H₂ and CO₂-C₂D₂

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(Dated: June 23, 2016)

An intermolecular potential energy surface and rovibrational transition frequencies are computed for CO₂-C₂H₂. An interpolating moving least squares method is used to fit ab initio points at the explicitly correlated coupled-cluster level. The rovibrational Schrödinger equation is solved with a symmetry-adapted Lanczos algorithm. The computed disrotatory and torsion vibrational levels of both CO₂-C₂H₂ and CO₂-C₂D₂ differ from those obtained by experimentalists by less than 0.5 cm⁻¹. CO₂-C₂H₂ has two equivalent minima with the monomers perpendicular to the inter-monomer axis. In contrast to many other Van der Waals dimers there is no disrotatory path that connects the minima. The tunnelling path follows the torsional coordinate over a high barrier and the splitting is therefore tiny. Using vibrational parent analysis we are able to fit and thus obtain rotational constants and centrifugal distortion constants. Calculated rotational constants differ from their experimental counterparts by less than 0.001 cm⁻¹.

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I. INTRODUCTION

For decades scientists have been measuring and analysing high-resolution spectra of Van der Waals dimers.¹⁻⁴ Experiments are challenging in part because the complexes are so weakly bound that only low number density is easily achievable. The intermolecular modes are so weak that they are usually studied by measuring combination bands that also involve intramolecular vibrations.^{5,6} Theoretically, Van der Waals dimers are difficult to model because they typically have several stable structures and undergo large amplitude motion, and therefore standard approximations based on harmonic oscillators and rigid rotors work poorly. Some dimers have been observed in space, and they are studied because their spectra reveal information about interactions between molecules as well as the chemistry and history of the universe.^{7,8}

In recent years, we have demonstrated that by combining high-level *ab initio* calculations, an accurate method for generating potential energy surfaces (PESs) and an exact ro-vibrational variational method for the intermolecular coordinates, it is possible to compute very accurate spectra of Van der Waals dimers.⁹⁻¹⁶ In this paper, we apply the same techniques to determine energy levels and rotational constants for $\text{CO}_2\text{-C}_2\text{H}_2$ and $\text{CO}_2\text{-C}_2\text{D}_2$. Many acetylene containing complexes have been investigated experimentally in the gas phase. $\text{CO}_2\text{-C}_2\text{H}_2$ is a dimer composed of two different nonpolar molecules containing conjugated triple bonds. Although there are several *ab initio* studies of the equilibrium geometry¹⁷⁻¹⁹ we compute the first PES. It has two equivalent wells. Many dimers with identical linear monomers have slipped-parallel equilibrium configurations and their dynamics are dominated by a disrotatory path between different minima.^{9-12,20} The CO_2 dimer is a good example. Motion along a low-energy disrotatory path connects equivalent slipped-parallel minima and motion along a conrotatory coordinate, which also connects equivalent minima, is impeded by a large barrier (a PES plot is shown in Figure 7 of a recent fitting methods review).²¹ $\text{CO}_2\text{-C}_2\text{H}_2$ is quite different. There is no disrotatory path between different minima. This is due to the fact that the two monomers are centrosymmetric and the two equivalent equilibrium structures are planar with the monomers being parallel and at 90° to the inter-monomer axis, i.e. the structure is not slipped parallel. In contrast, the $\text{CO}_2\text{-CS}_2$ dimer¹³ with slipped-parallel minima has both dis- and conrotatory paths connecting equivalent minima, with the conrotatory coordinate being the lower path. For $\text{CO}_2\text{-CS}_2$ the torsional coordinate provides an even lower out-of-plane path passing through what turns out to be a cross-shaped global minimum. For $\text{CO}_2\text{-C}_2\text{H}_2$, torsion also connects equivalent minima, but no cross-shaped minimum is found on the PES.

It is remarkable how difficult it has been to correctly anticipate the relevant minima and the paths between them for Van der Waals dimers. Previous studies conducted before high-level calculations were routine, often identified surprising new isomers, or failed to confirm the presumed global minimum. One hopes that a close look at the electronic structure of the monomers, and the corresponding dimer PESs can yield some transferable insight.

There are a number of previous papers on $\text{CO}_2\text{-C}_2\text{H}_2$. Several groups have measured fundamental frequencies of the monomers.^{19,22,23} and others have obtained frequencies of inter-monomer vibrational states from combination bands by subtracting the corresponding intramolecular band centre. For example, in 2011 Lauzin *et al.*²⁴ determined the torsional frequency of $\text{CO}_2\text{-C}_2\text{H}_2$ by measuring a band that combined it with the CO_2 ν_3 fundamental. Inter-monomer vibrational frequencies derived from the combination bands are expected to have errors smaller than about 0.1 cm^{-1} for many dimers due to the small cross anhar-

monicity between the monomer vibrational modes and inter-monomer vibrational modes. For a planar configuration, the four inter-monomer vibrational modes of a dimer with two linear monomers are the Van der Waals stretch, the torsion and the in-plane disrotatory and conrotatory bends. In 2014, Rezaei *et al.*²⁵ measured the IR spectra of several bands of CO₂-C₂H₂ and CO₂-C₂D₂²⁵ and derived three new inter-monomer vibration frequencies: an in-plane bend of CO₂-C₂H₂, an in-plane bend and the torsion of CO₂-C₂D₂. Since the two in-plane bend levels (disrotatory bend and conrotatory bend) have the same symmetry (because both monomers are symmetric), Rezaei *et al.* cannot use symmetry arguments to determine whether the bend they observe is disrotatory or conrotatory. They tentatively assigned it as the disrotatory bend, based on low-level *ab initio* harmonic calculations of Ref. 17. Previous theoretical studies^{17,18,26} are not accurate enough to make reliable predictions. In this paper we confirm this assignment by examining wavefunction plots. In fact, the three inter-monomer frequencies of Rezaei *et al.* and the single inter-monomer frequency of Lauzin *et al.* are all in excellent agreement with the energies we report in this paper. This demonstrates the accuracy of the underlying PES and the variational method used to compute the energy levels. Note that what is called anti-gearred in Refs. 17 and 25 is here called disrotatory, because the two monomers are rotating in opposite directions and the motion that is called geared in Refs. 17 and 25 is here called conrotatory, because the two monomers are rotating in the same direction.

II. POTENTIAL ENERGY SURFACE

As was done for other dimers, the PES is made by using the interpolating moving least squares (IMLS) method to connect local fits using a weight function. The inter-monomer vibrational coordinates of any dimer composed of two linear monomers are: r_0 , r_1 , r_2 , θ_1 , θ_2 , and ϕ_2 . The vector $\vec{r}_1$ points along the CO₂ monomer, $\vec{r}_2$ points along the C₂H₂ monomer, and $\vec{r}_0$ is from the centre of mass of CO₂ to the centre of mass of C₂H₂. In this paper we fix the lengths of $\vec{r}_1$ and $\vec{r}_2$. It is a good approximation to consider only the inter-monomer coordinates because their frequencies are all much less than those of the intra-monomer coordinates. The CO bond length is fixed at 1.162086 Å;²⁷ the CH bond length is fixed at 1.06164 Å; and the CC bond length is fixed at 1.202958 Å following recommended parameters published in 2011.²⁸ These values for C₂H₂ are referred to as semi-empirical as they were obtained by a detailed analysis of experimental data for 10 isotopologues with some computed corrections. Similar values were obtained in a very recent analysis of experimental rotational constants.²⁹ The angle between $\vec{r}_1$ and $\vec{r}_0$ is θ_1 . The angle between $\vec{r}_2$ and $\vec{r}_0$ is θ_2 . The final coordinate, ϕ_2 , describes the out of plane torsional motion of the dimer. It is the angle between the two vectors normal to the $\vec{r}_0 \times \vec{r}_1$, and $\vec{r}_0 \times \vec{r}_2$ planes. See figure ??.

A. IMLS PES Fitting

The 4D CO₂-C₂H₂ potential is built using an interpolating moving least squares (IMLS) method which employs a weight function to interpolate between local fits done with basis expansions. The procedure has been described in detail previously,⁹ including recent review articles.^{21,30} A total of 1814 symmetry unique points were used to make the PES. The automated procedure that was developed to construct a 4D PES for other dimers was also used here.^{9,12,13} For each of the local fits, a fitting basis of 301 functions is used. Each

function is a product of a radial function and associated Legendre bend functions. The maximum value of the Legendre l index is $l_{max} = 6$ and the maximum radial power is 6. The range of inter-monomer center-of-mass distances is $r_0 = [2.5, 15.0]$ Å. In contrast to the procedure used for other dimers, the high-level surface was computed directly (without an initial low-level guide surface). Lacking the guide surface, a few of the highest energy points fell above the relevant energy range and were excluded from the fit. For the high-level surface, 1600 symmetry unique points were initially distributed according to a Sobol sequence³¹ subject to an exponential r_0 -dependent bias that favors points at $r_0 = 2.5$ Å over points at $r_0 = 15.0$ Å by a factor of about 20. Starting from the 1600 seed points, sets of 24 automatically determined points were added until the estimated root mean square (RMS) fitting error was reduced to 1.1 cm^{-1} . The estimated error is computed from differences between values obtained with the fitting basis with 301 functions and a basis that is one degree lower in both the radial basis (maximum radial power of 5) and the angular basis ($l_{max} = 5$), for a total of 171 functions. In addition, a small set of 288 high-level data (not included in the fit) were computed at randomly selected points and the RMS fitting error for those points was found to be 1.2 cm^{-1} .

B. Electronic Structure Theory

Electronic structure considerations for global PESs were recently detailed in a review article including an example application involving the construction of a 4D PES for two rigid linear fragments as is the case for $\text{CO}_2\text{-C}_2\text{H}_2$.³⁰ The Molpro electronic structure package was used to perform the single reference (AE)-CCSD(T*)-F12b calculations reported here.³² The (T*) indicates that the perturbative triples contribution is scaled (based on the ratio of correlation energy captured at the MP2-F12/MP2 levels). Tests indicate that the scaling brought the triples contribution closer to the CBS limit. No multireference character was anticipated, and the T_1 diagnostic was recorded and found to be below 0.019 for all of the geometries in the dataset (which is to be expected for the non-bonded interaction between two closed-shell species). Here we use the explicitly correlated F12 method^{33,34}, without CBS extrapolation, and Peterson’s specialized CVTZ-F12 basis³⁵ set correlating all electrons.

C. Properties of the Surface

The surface has two symmetrically equivalent minima. The shape at the bottom of one of the wells is shown in figure ???. The well depth is 750.816 cm^{-1} . Bone and Handy¹⁷ computed a well depth of only 568 cm^{-1} using the MP2 method and a TZ2P basis set. Although their calculation is not as accurate as ours, their equilibrium r_0 value of 6.109 bohr is fairly close to our value of 6.045 bohr. Bone and Handy also reported a collinear local minimum with an energy of -358 cm^{-1} , which is not found on our higher-level surface.

Figure ?? is a 2D contour plot of the $\text{CO}_2\text{-C}_2\text{H}_2$ PES. It is obtained by minimizing the 4D PES with respect to r_0 for all planar configurations. The plot is in extended coordinates.¹¹

It is made by plotting $\tilde{V}_q$ in quadrant q , where

$$\begin{aligned}
\tilde{V}_I(\tilde{\theta}_1, \tilde{\theta}_2) &\equiv V(\tilde{\theta}_1, \tilde{\theta}_2, \pi) && \text{for quadrant I} \\
\tilde{V}_{II}(\tilde{\theta}_1, \tilde{\theta}_2) &\equiv V(-\tilde{\theta}_1, \tilde{\theta}_2, 0) && \text{for quadrant II} \\
\tilde{V}_{III}(\tilde{\theta}_1, \tilde{\theta}_2) &\equiv V(-\tilde{\theta}_1, -\tilde{\theta}_2, \pi) && \text{for quadrant III} \\
\tilde{V}_{IV}(\tilde{\theta}_1, \tilde{\theta}_2) &\equiv V(\tilde{\theta}_1, -\tilde{\theta}_2, 0) && \text{for quadrant IV} ,
\end{aligned} \tag{2.1}$$

and the PES on the right side of these equations is in terms of the dynamical coordinates, $V(\theta_1, \theta_2, \phi_2)$. The ranges of $(\tilde{\theta}_1, \tilde{\theta}_2)$ in quadrants I to IV are $([0, \pi], [0, \pi])$, $([-\pi, 0], [0, \pi])$, $([-\pi, 0], [-\pi, 0])$, and $([0, \pi], [-\pi, 0])$, respectively. In the top right and bottom left corners of the plot $\phi_2 = \pi$, In the top left and bottom right corners of the plot $\phi_2 = 0$, The extended coordinates are discussed and defined in Ref. 11.

Because Fig ?? is in extended coordinates there are four minima, only two of which are physical. If the left side is the physical half then G2 is a copy of G1 (obtained from it by rotating the molecule about $\vec{r}_0$ by π) and G3 is a copy of G4 (obtained from it by rotating the molecule). Unlike previous monomers we have studied there is no disrotatory minimum energy path (MEP) connecting physical minima. There is a disrotatory path that connects G1 and the linear configuration at the centre of Fig ?. There is a very shallow well slightly before the linear configuration. The highest potential value along the path is at 344.8 cm^{-1} . There is a copy of this disrotatory path from G2 to the centre of the figure. The tunnelling splitting, due to the two wells on the left side is expected to be small. There is a minimum energy path (MEP) along the torsion coordinate, but the barrier is high. The in-plane path between the two wells is a vertical line on the figure. It crosses a barrier that is high and wide. The disrotatory minimum energy path (MEP) that connects G1 and the linear configuration at the centre is the left half of Fig ?. There is no conrotatory path between the minima, and motion along the conrotatory coordinate is significantly more hindered. One therefore expects the disrotatory bend to have a lower frequency than the conrotatory bend. An out-of-plane torsional path (plotted in Fig ?) connects the minima. Remarkably, the barrier height along the torsional path, (347.2 cm^{-1}), is nearly identical to the barrier to linearity. The monomers prefer to maintain their parallel arrangement along the torsional path and no cross-shaped minimum is found on the PES.

It is interesting to compare the $\text{CO}_2\text{-C}_2\text{H}_2$ PES with that of $\text{CO}_2\text{-CS}_2$ ¹³. $\text{CO}_2\text{-CS}_2$ has four planar slipped parallel wells connected by both dis- and conrotatory paths, with the conrotatory path being significantly lower. In fact for $\text{CO}_2\text{-CS}_2$ (as mentioned in the introduction), the torsional coordinate provides an even lower path, passing through the cross-shaped global minimum. If in the equilibrium structure of $\text{CO}_2\text{-CS}_2$, the angles between $\vec{r}_0$ and $\vec{r}_2$ and between $\vec{r}_0$ and $\vec{r}_1$ were both 90° , then it would also have two wells. This explains why there are four wells for $\text{CO}_2\text{-CS}_2$ and only two wells for $\text{CO}_2\text{-C}_2\text{H}_2$, the consequence of which is that each level of $\text{CO}_2\text{-C}_2\text{H}_2$ is split into two, rather than four as seen for $\text{CO}_2\text{-CS}_2$.

III. CALCULATING ROVIBRATIONAL ENERGIES

To compute energy levels we use a spherical-harmonic type angular basis. Matrix elements of the kinetic energy operator are exact. Potential matrix elements are calculated with Gauss quadrature by doing sums sequentially.³⁶⁻³⁸ Eigenvalues are obtained with the symmetry adapted Lanczos (SAL) algorithm.³⁹⁻⁴¹ Details are explained in previous papers.^{9,10}

Rovibrational levels have been computed with Lanczos methods for many years.⁴² In addition to the vibrational coordinates of figure ??, we have Euler angles that specify the orientation of a body-fixed frame attached such that the z axis is along $\vec{r}_0$ and the x axis is along the vector $\vec{r}_0 \times \vec{r}_1 \times \vec{r}_0$. The masses used for each atom are: 15.99491461957 amu for O, 12 amu for C, 1.00782503223 amu for H, and 2.01410177812 amu for D. al constants for the monomers are: 0.39021894, 0.84784720, and 1.17664632 for CO₂, C₂D₂, and C₂H₂ respectively.^{13,43} These are experimentally determined ground state values⁴³ and are very close to a slightly more recent value.⁴⁴

For the stretch coordinate we use a potential optimised discrete variable representation with 20 functions defined in the range [4, 20] bohr and computed in a sine basis.^{38,45,46} To test convergence levels we also computed with 120 sine discrete variable representation functions. Energy level difference are less than .0001 cm⁻¹. Max l_1 , l_2 , and m_2 quantum numbers for the angular basis are 44, 45 Gauss-Legendre quadrature points, 90 trapezoid points were used.

The molecular symmetry group⁴⁷ of the Hamiltonian is G_8 , composed of the operations $\{E, \sigma_O, \sigma_{CH}, \sigma_O \sigma_{CH}\} \otimes \{E, E^*\}$. σ_O flips CO₂ (vector $\vec{r}_1$), σ_{CH} flips C₂H₂ (vector $\vec{r}_2$). There are eight irreducible representations which we label +ee, +eo, +oe, +oo, -ee, -eo, -oe, -oo. +/− label even and odd parities. e/o label states symmetric or antisymmetric with respect to σ_O and σ_{CH} , respectively. The point group for the equilibrium structure is C_{2v} . The point group is isomorphic to G_4 , a sub-group of G_8 obtained by discarding σ_O and σ_{CH} which are unfeasible because they require overcoming high barriers. All the levels are calculated using the G_8 group and have the G_8 irreducible representation (irrep) labels. To find the C_{2v} irreps, one can use the relation between the irreps of C_{2v} and those of the G_8 given in Table I. It is straightforward to separately calculate levels with even and parity by using a parity-adapted basis. The size of the even parity basis is 627900. Within a parity block we calculate ee, eo, oe, and oo levels by using the SAL. The projection operators are easily obtained by knowing that basis functions are symmetric (anti-symmetric) with respect to permutation of the O atoms if l_1 is even (odd)⁴⁸ and symmetric(anti-symmetric) with respect to simultaneous permutation of the C and H atoms in acetylene if l_2 is even (odd)⁴⁸.

IV. RESULTS

A. Energies and labels for J=0

Table II lists the lowest $J = 0$ eigenvalues for each irrep of CO₂-C₂H₂. Table III lists the lowest $J = 0$ eigenvalues for each irrep of CO₂-C₂D₂. There are four inter-monomer vibrational modes. In previous papers^{10,12} we have labelled them: v_t for the torsion, v_g for the geared bend, v_a for the anti-geared bend, and v_r for the Van der Waals stretch.^{10,11} Each state was assigned either on the basis of its probability density or its wavefunction cut. See Refs 10 and 11 for more details. Bone and Handy and also Rezaei et al. label the disrotatory bend as anti-geared.¹⁷ We label it as geared because the two monomers are rotating in opposite directions, but to avoid confusion we shall use the terms disrotatory (v_{dis}) and conrotatory (v_{con}). In this paper, the vibrational modes are denoted by ($v_t, v_{dis}, v_{con}, v_r$).

Our results agree well with experimental data. In 1989, Muentner⁴⁹, using harmonic approximations, obtained torsion frequency values of 41.3 cm⁻¹ for CO₂-C₂D₂ and 45 cm⁻¹ for CO₂-C₂H₂, from the eQq constant and a stretch harmonic frequency value of 75 cm⁻¹

for CO₂-C₂H₂ from the D_J centrifugal constant, all of which are derived from a molecular beam electric resonance spectroscopy experiment. Muentert estimated that the errors are a few cm⁻¹. These three numbers compare reasonably well with our calculated values of 39.70, 44.32 and 70.07 cm⁻¹, suggesting these vibrational modes are harmonic-like. The experimental CO₂-C₂H₂ torsion frequency was determined to be 44.39(1) cm⁻¹ by Lauzin *et al.*²⁴ in 2011 from a combination band involving the CO₂ ν_3 fundamental, and to be 44.31(1) cm⁻¹ by Didriche *et al.*⁵⁰ in 2012 from a combination band involving the C₂H₂ $\nu_1 + \nu_3$ fundamental. In 2014, Rezaei *et al.* measured the IR spectra of several bands of CO₂-C₂H₂ and CO₂-C₂D₂²⁵ and derived three inter-monomer vibrational frequencies. From a combination band with the CO₂ ν_3 fundamental, they obtain a torsion frequency for CO₂-C₂D₂ at 39.9(5) cm⁻¹. From a combination band with the asymmetric stretch of C₂D₂, they obtain 39.961(1) cm⁻¹ for the torsion frequency. From a combination band with the CO₂ ν_3 fundamental, they obtain an in-plane bend for CO₂-C₂D₂ at 54.5(5) cm⁻¹. From a combination band with the CO₂ ν_3 fundamental, they obtain an in-plane bend for CO₂-C₂H₂ at 61.408(1) cm⁻¹. The two torsion frequencies would be identical if there were no coupling between the intra- and inter-monomer coordinates. These numbers are in excellent agreement with our results with errors smaller than 0.5 cm⁻¹!. See Table ??.

The two in-plane bending states of CO₂-C₂H₂ have frequencies of 60.84 and 85.66 cm⁻¹. They both have the same symmetry, +eo, for the lower tunneling component. This makes it very hard for experimentalists to assign the two bending modes. To assign the two in-plane bending modes to disrotatory or conrotatory motion, we first plotted the probability density (PD) $P(\theta_1, \theta_2)$, but then discovered that the PD plot is similar for both states (see Fig. ??c and ??c). It is therefore necessary to look at wavefunction cuts. Consider first, the disrotatory case. The corresponding cuts are in Fig. ??a and Fig. ??b. In the $\phi_2 = 0^\circ$ well the disrotatory coordinate is $Q_{\text{dis}} = \delta\theta_1 - \delta\theta_2$ and disrotatory motion is along a line from top left to bottom right. The disrotatory motion is shown in the inset. In the $\phi_2 = 180^\circ$ well the disrotatory coordinate is $Q_{\text{dis}} = \delta\theta_1 + \delta\theta_2$ and disrotatory motion is along a line from bottom left to top right. The disrotatory motion is shown in the inset. Both the wavefunction plots reveal the disrotatory nature of the vibration. However, because $P(\theta_1, \theta_2)$ by definition contains contributions from both $\phi_2 = 0$ and $\phi_2 = 180^\circ$ it is a superposition and therefore the disrotatory nature of the vibration cannot be recognized. The wavefunction plots confirm that the vibration of the state at 60.84 cm⁻¹ is disrotatory. A similar analysis confirms that the vibration of the state at 85.66 cm⁻¹ is conrotatory. Bone and Handy's MP2/DZP results are 66 and 93 cm⁻¹. They are in fairly good agreement with our results even though they use a lower level ab initio method and a harmonic approximation. Bone and Handy's normal mode coordinate picture (their Fig. 7) nicely confirms our wavefunction cut analysis of the two modes. When the masses of the two monomers are very different, the two in-plane bending mode have local character. If the two bending states were pure θ_1 and θ_2 vibrations then the symmetry of the two bending states would be clear: the θ_1 bend is clearly +oe and the θ_2 bend is clearly +eo.

The G_8 symmetries of the vibrational levels are known from our calculations. The corresponding C_{2v} symmetries can be found from the correlation in Table I. The symmetry of the vibrational levels can also be understood by examining the symmetry property of the vibrational coordinates in C_{2v} group. According to Ref. 48, the symmetry operations affect the angles in the following way

$$\sigma_O \sigma_{CH}(\theta_1, \theta_2, \phi_2, \alpha, \beta, \gamma) = (\pi - \theta_1, \pi - \theta_2, \phi_2, \alpha, \beta, \gamma) . \quad (4.1)$$

From this equation we can derive the symmetries of vibrational coordinates that describe the disrotatory and conrotatory bends and the torsion. The disrotatory bend coordinate is $Q_{\text{dis}} = \delta\theta_1 - \delta\theta_2(\phi_2 = 0)$ and $Q_{\text{dis}} = \delta\theta_1 + \delta\theta_2(\phi_2 = \pi)$. See Fig. ??a and Fig. ??b. The conrotatory bend coordinate is $Q_{\text{con}} = \delta\theta_1 + \delta\theta_2(\phi_2 = 0)$ and $Q_{\text{con}} = \delta\theta_1 - \delta\theta_2(\phi_2 = \pi)$. See Fig. ??a and Fig. ??b. The torsion coordinate is $Q_t = \phi_2$. Therefore,

$$\begin{aligned}\sigma_O\sigma_{CH}Q_{\text{dis}} &= -Q_{\text{dis}} & E^*Q_{\text{dis}} &= +Q_{\text{dis}} \\ \sigma_O\sigma_{CH}Q_{\text{con}} &= -Q_{\text{con}} & E^*Q_{\text{con}} &= +Q_{\text{con}} \\ \sigma_O\sigma_{CH}Q_t &= +Q_t & E^*Q_t &= -Q_t\end{aligned}\tag{4.2}$$

Note that Q_{dis} and Q_{con} satisfy the above equations in both wells. According to the C_{2v} character table of Table I, which is based on the convention of Ref. 47, the symmetries of the disrotatory, conrotatory and torsion coordinates are therefore B_2 , B_2 and A_2 . Bone and Handy labelled them as B_1 , B_1 and B_2 , respectively, which are also adopted in Ref. 25. Bone and Handy have the wrong symmetry for the torsion.

In principle, tunnelling can occur between the two minima and split each level into a doublet. For the ground vibrational state, the lower component of the doublet is $+ee$ and, according to our calculation, the higher component is $+oo$. The tunnelling splittings are tiny because the barrier separating the two wells is high. It is for this reason that we report only the energy of the lower component. Why is the upper component $+oo$? A similar situation arises for $\text{CO}_2\text{-CS}_2$. In Ref. 13, it is explained that when irreps of the symmetry group are non-degenerate, the upper level of the lowest tunneling pair of a double well will always be odd with respect to all operations that interconvert the two wells. For $\text{CO}_2\text{-C}_2\text{H}_2$, both σ_O and σ_{CH} interconvert the two wells and therefore the symmetry of the higher component of the ground state tunneling doublet is $+oo$. If there were only one feasible operation that interconverts the wells then the symmetry of the higher component of the tunneling doublet would be the same as that of the tunnelling coordinate. This is often the case, e.g. NH_3 . For excited vibrational states, the symmetry of the higher component is a product of the symmetry of the lower component and oo . Many highly excited $J = 0$ states are also assigned. For some of them, assignment becomes difficult due to coupling.

B. $J > 0$ Energies and Rotational Constants

$J > 0$ levels have been computed for J up to 6. Table ?? lists the lowest $J = 1$ eigenvalues for each irrep of $\text{CO}_2\text{-C}_2\text{H}_2$. Table ?? lists the lowest $J = 1$ eigenvalues for each irrep of $\text{CO}_2\text{-C}_2\text{D}_2$. For each of the levels in the tables there is also a nearly degenerate tunnelling partner that we do not report. In each case, the partner's energy is about $.000001 \text{ cm}^{-1}$ higher. The symmetry of the missing partner is the product of the symmetry of the level we do report and $+oo$. Each $J > 0$ level is assigned a vibrational label. This is done by using the vibrational parent analysis (VPA) technique of Refs. 10,51. The VPA is done by expanding the rovibrational wavefunctions in terms of vibrational wavefunctions. Assigning vibrational labels to $J > 0$ states allows us to fit the rotational levels of a vibrational state and obtain spectroscopic constants which can be compared with those determined by fitting experimental data. Results for the ground state of $\text{CO}_2\text{-C}_2\text{H}_2$ and $\text{CO}_2\text{-C}_2\text{D}_2$ are given in Tables ?? and ?. Excellent agreement is obtained. For many higher vibrational states, three rotational constants can be simply derived from the three $J = 1$ levels; they are reported in Tables ?? and ?.

To the extent that a rovibrational wavefunction is well described by a product of vibrational (its vibrational parent) and rotational functions, it is possible to determine symmetries of rotational functions for each vibrational state, i.e., $\Gamma_{vr} = \Gamma_v \Gamma_r$. Having done the VPA and knowing the symmetries of the vibrational wavefunctions we can therefore determine the symmetries of the rotational factors. Assuming that the levels are in the order $1_{01}, 1_{11}, 1_{10}$, from lowest to highest we find that their symmetries are (in the same order) $-ee, -oe, +oe$ for the lower component of the tunneling doublet. See Tables ?? and ?. It is straightforward to show that this is consistent with what one obtains from “the asymmetric top symmetry rule” of Ref. 47. First, identify the principal axes of an equilibrium structure: the a -axis is the C_2 axis, b -axis is on the molecular plane and c -axis is perpendicular to the plane. Second, find equivalent rotations for each of the C_{2v} operations given in Table I⁴⁷. Last, determining transformation properties of $|JK_aM\rangle$ and $|JK_cM\rangle$ shows that the symmetry of rotational levels depend on the evenness and oddness of K_a, K_c . The results are shown in the last column Table I, from which we find that, for example for $J = 1$, the C_{2v} symmetries of $1_{01}, 1_{11}, 1_{10}$ are A_2, B_1 and B_2 .

V. CONCLUSION

An accurate PES has been made for $\text{CO}_2\text{-C}_2\text{H}_2$ and used to compute low-lying energy levels of the complex. The PES is obtained from (AE)-CCSD(T*)-F12b/CVTZ-F12 ab initio data and an IMLS interpolation method. Energy levels are computed using the Lanczos algorithm. The sums required to evaluate matrix-vector products are done sequentially. Calculations of this kind, with rigid monomers, are straightforward, despite the huge vibrational basis sets. The computer program will be published shortly.⁵² As was the case for other Van der Waals dimers, agreement between experiment and theory is excellent. From our results we are able to confirm the tentative assignment of the in-plane bending level, observed by Rezaei et al., to the disrotatory bend. This is possible because we computed wavefunctions. For $\text{CO}_2\text{-C}_2\text{H}_2$ there are only two (identical) wells. Dimers with either non centrosymmetric monomers or different monomers with slipped-parallel structures have more than two wells. Here, because the two wells are identical, probability distribution plots superimpose two different distributions and therefore are not useful. Vibrational parent analysis enables us to obtain rotational constants. In $\text{CO}_2\text{-C}_2\text{H}_2$ there are no low-lying paths between the minima. In part this is due to the parallel C_{2v} equilibrium structure.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation (CHE-1300945 to RD) and the Natural Sciences and Engineering Research Council (to TC). This article in honour of Bob Le Roy whose infectious enthusiasm and attention to detail in the field of spectroscopy and PES development continues to inspire us.

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Table I. Character table for point group C_{2v} and permutation inversion group G_4 ⁴⁷. The G_4 and C_{2v} symmetry operations are given at the first line and the second lines, respectively. ip is in-plane and op is out-of-plane. The third line is the equivalent rotation.

C_{2v}	G_8	E E R^0	$\sigma_O\sigma_{CH}$ C_2 R_a^π	E^* $\sigma_v(\text{ip})$ R_c^π	$\sigma_O\sigma_{CH}^*$ $\sigma_v(\text{op})$ R_b^π	vib. mode	K_a, K_c
A_1	$+ee, +oo$	+1	+1	+1	+1	v_r	ee
A_2	$-ee, -oo$	+1	+1	-1	-1	v_t	eo
B_1	$-eo, -oe$	+1	-1	-1	+1		oo
B_2	$+eo, +oe$	+1	-1	+1	-1	$v_{\text{dis}}, v_{\text{con}}$	oe

Table II. $J=0$ levels (in cm^{-1}) of $\text{CO}_2\text{-C}_2\text{H}_2$, ZPE = $-608.94109 \text{ cm}^{-1}$.

State	Symmetry	State	Symmetry
0.0000(0,0,0,0)	(+ee)	44.3173(1,0,0,0)	(-ee)
60.8423(0,1,0,0)	(+eo)	103.5958(1,1,0,0)	(-eo)
70.0737(0,0,0,1)	(+ee)	112.5787(1,0,0,1)	(-oo)
85.6620(0,0,1,0)	(+eo)	128.1236(3,0,0,0)	(-oo)
87.1194(2,0,0,0)	(+ee)	128.3947(1,0,1,0)	(-eo)
120.8228(0,2,0,0)	(+ee)	162.1504(1,2,0,0)	(-oo)
122.3369(0,3,0,1)	(+eo)	163.6471(1,0,1,1)	(-oe)
136.3516(0,0,0,2)	(+ee)	176.8748(1,0,0,2)	(-oo)
141.6604(0,1,1,0)	(+ee)	183.2030(1,2,1,0)	(-ee)
144.8834(2,1,0,0)	(+eo)	184.2679(3,1,0,0)	(-oe)
151.3515(0,1,1,1)	(+eo)	191.1274(3,0,0,1)	(-oo)
153.0568(2,0,0,1)	(+ee)	192.2123(1,0,1,1)	(-eo)
167.3225(4,0,0,0)	(+ee)	204.6483(5,0,0,0)	(-oo)
167.5648(0,0,2,0)	(+ee)	208.6573(3,0,1,0)	(-eo)
169.4847(2,0,1,0)	(+eo)	208.8851(1,0,2,0)	(-oo)
173.0989(0,3,0,1)	(+eo)	213.6706(1,3,0,1)	(-eo)

Table III. $J=0$ levels (in cm^{-1}) of $\text{CO}_2\text{-C}_2\text{D}_2$, ZPE = $-617.4977 \text{ cm}^{-1}$

State	Symmetry	State	Symmetry
0.0000 (0,0,0,0)	(+ee)	39.6978 (1,0,0,0)	(-ee)
54.6368 (0,1,0,0)	(+eo)	93.0498 (1,1,0,0)	(-eo)
68.6306 (0,0,0,1)	(+ee)	106.4515 (1,0,0,1)	(-ee)
78.4187 (2,0,0,0)	(+ee)	115.9420 (3,0,0,0)	(-ee)
82.5565 (0,0,1,0)	(+eo)	120.7901 (1,1,0,0)	(-eo)
110.1640 (0,2,0,0)	(+ee)	147.4557 (1,2,0,0)	(-ee)
115.6716 (0,1,0,1)	(+eo)	152.7262 (1,1,0,1)	(-eo)
130.4836 (2,1,0,0)	(+eo)	166.5284 (3,1,0,0)	(-oe)
131.3484 (0,2,0,1)	(+ee)	168.0173 (1,0,0,2)	(-oo)
133.9687 (0,0,0,2)	(+ee)	170.4734 (1,1,1,0)	(-oo)
142.7339 (2,0,0,1)	(+ee)	177.2984 (5,0,0,0)	(-oo)
146.7104 (0,0,1,1)	(+eo)	183.1105 (1,0,1,1)	(-eo)
152.3913 (4,0,0,0)	(+ee)	187.7045 (5,0,0,0)	(-oo)
157.9455 (2,0,1,0)	(+oe)	193.8245 (3,0,1,0)	(-eo)
161.6909 (0,0,2,0)	(+ee)	198.5388 (1,0,2,0)	(-oo)

Table IV. The four calculated inter-monomer vibrational frequencies (in cm^{-1}). The disrotatory and conrotatory bends are called anti-gearred and geared, respectively, by Bone and Handy.¹⁷

description	mode	CO ₂ -C ₂ H ₂	CO ₂ -C ₂ D ₂
torsion	v_t	44.32	39.70
disrotatory bend	v_{dis}	60.84	54.64
conrotatory bend	v_{con}	85.66	82.56
stretch	v_r	70.07	68.63

Table V. Comparison between the observed and calculated inter-monomer vibrational frequencies (in cm^{-1}).

Molecule	mode	obs.	cal.
CO ₂ -C ₂ H ₂ ²⁵	v_{dis}	61.408(1)	60.84
CO ₂ -C ₂ D ₂ ²⁵	v_{dis}	54.5(5)	54.64
CO ₂ -C ₂ H ₂ ²⁴	v_t	44.39(1)	44.32
CO ₂ -C ₂ H ₂ ⁵⁰	v_t	44.31(1)	44.32
CO ₂ -C ₂ D ₂ ²⁵	v_t	39.961(1)	39.70
CO ₂ -C ₂ D ₂ ²⁵	v_t	39.9(5)	39.70

Table VI. $J = 1$ levels (in cm^{-1}) of CO₂-C₂H₂.

$J = 0(v_t, v_a, v_g, v_r)$	1 ₀₁ (sym)	1 ₁₁ (sym)	1 ₁₀ (sym)	A	B	C
0.0000 (0,0,0,0)(+ee)	0.1688(-ee)	0.3684(-oe)	0.3922(+oe)	0.2959	0.0963	0.0724
44.3173 (1,0,0,0)(-ee)	44.4832(+ee)	44.6856(+oe)	44.7068(-oe)	0.2959	0.0936	0.0724
60.8423 (0,1,0,0)(+eo)	61.0076(-eo)	61.2119(-oo)	61.2363(+oo)	0.2992	0.0949	0.0704
70.0737 (0,0,0,1)(+ee)	70.2369(-ee)	70.4407(-oe)	70.4636(+oe)	0.2969	0.0930	0.0702
85.6620 (0,0,1,0)(+eo)	85.8281(-eo)	86.0559(-oo)	86.03271(+oo)	0.2993	0.0715	0.0947
87.1194 (2,0,0,0)(+ee)	87.2825(-ee)	87.4876(-oe)	87.5061(+oe)	0.2959	0.0908	0.0723
103.5958 (1,1,0,0)(-eo)	103.7592(+eo)	103.9654(+oo)	103.9879(-oo)	0.2991	0.0930	0.0705
112.5787 (1,0,0,1)(-oo)	112.7382(+oo)	112.9457(+eo)	112.9648(-eo)	0.2967	0.0893	0.0702
120.8228 (0,2,0,0)(+ee)	120.9834(-ee)	121.1937(-oe)	121.2178(+oe)	0.3026	0.0924	0.0683
122.3369 (0,3,0,1)(+eo)	122.4974(-eo)	122.7067(-oo)	122.7309(+oo)	0.3016	0.0923	0.0682
128.1236 (3,0,0,0)(-oo)	128.2839(+oo)	128.4914(+eo)	128.5077(-eo)	0.2958	0.0883	0.0720
128.3947 (1,0,1,0)(-eo)	128.5580(+eo)	128.7654(+oo)	128.7853(-oo)	0.2990	0.0916	0.0717

Table VII. $J = 1$ levels (in cm^{-1}) of $\text{CO}_2\text{-C}_2\text{D}_2$.

$J = 0(v_t, v_a, v_g, v_r)$	$1_{01}(\text{sym})$	$1_{11}(\text{sym})$	$1_{10}(\text{sym})$	A	B	C
0.0000 (0,0,0,0)(+ee)	0.1608(-ee)	0.3384(-oe)	0.3621(+oe)	0.2698	0.0923	0.0685
39.6978 (1,0,0,0)(-ee)	39.8558(+ee)	40.0361(+oe)	40.0571(-oe)	0.2698	0.0895	0.0685
54.6361 (0,1,0,0)(+eo)	54.7945(-eo)	54.9758(-oo)	55.0003(+oo)	0.2727	0.0914	0.0669
68.6306 (0,0,0,1)(+ee)	68.7863(-ee)	68.9679(-oe)	68.9906(+oe)	0.2708	0.0893	0.0665
78.4187 (2,0,0,0)(+ee)	78.5736(-ee)	78.7570(-oe)	78.7750(+oe)	0.2698	0.0864	0.0685
82.5565 (0,0,1,0)(+eo)	82.7149(-eo)	82.8970(-oo)	82.9200(+oo)	0.2728	0.0907	0.0677
93.0498 (1,1,0,0)(-eo)	93.2068(+eo)	93.3894(+oo)	93.4125(-oo)	0.2727	0.0900	0.0670
106.4515 (1,0,0,1)(-ee)	106.6039(+ee)	106.7887(+oe)	106.8077(-oe)	0.2705	0.0857	0.0667
110.1640 (0,2,0,0)(+ee)	110.3188(-ee)	110.5049(-oe)	110.5292(+oe)	0.2756	0.0896	0.0652
115.6716 (0,1,0,1)(+eo)	115.8241(-eo)	116.0114(-oo)	116.0260(+oo)	0.2709	0.0835	0.0689
115.9420 (3,0,0,0)(-oo)	116.1033(+oo)	116.2803(+eo)	116.2965(-eo)	0.2657	0.0888	0.0725
120.7901 (1,0,1,0)(-eo)	120.9452(+eo)	121.1306(+oo)	121.1502(-oo)	0.2727	0.0874	0.0677

Table VIII. Comparison with experiment for $\text{CO}_2\text{-C}_2\text{H}_2$.

Parameter	Lauzin et al. ²⁴	This Work
A	0.295813(17)	0.29583(82)
B	0.0954378(9)	0.0963(12)
C	0.0719343(9)	0.0724(11)
Δ_K	$-5.66(94) \times 10^{-6}$	$3.81(1100) \times 10^{-6}$
Δ_{JK}	$2.08(18) \times 10^{-6}$	$-8.13(1370) \times 10^{-6}$
Δ_J	$2.68(17) \times 10^{-7}$	$8.52(332) \times 10^{-7}$
δ_K	$-4.86(44) \times 10^{-6}$	$12.14(6652) \times 10^{-6}$
δ_J	$1.01(10) \times 10^{-8}$	$-1.01(3048) \times 10^{-7}$

Table IX. Comparison with experiment for $\text{CO}_2\text{-C}_2\text{D}_2$

Parameter	Rezaei et al. ²⁵	This Work
A	0.269846(18)	0.2698459(49)
B	0.0915008(75)	0.0922548(74)
C	0.0680829(62)	0.0685289(69)
Δ_K	$-5.6(10) \times 10^{-6}$	$-1.59(39) \times 10^{-6}$
Δ_{JK}	$3.35(38) \times 10^{-6}$	$1.38(51) \times 10^{-6}$
Δ_J	$2.77(52) \times 10^{-7}$	$3.2(1) \times 10^{-7}$
δ_J	$2.19(27) \times 10^{-7}$	$0.8(2) \times 10^{-7}$

Figure 1. $\text{CO}_2\text{-C}_2\text{H}_2$ coordinates, O is red, C is grey, and H is yellow.

Figure 2. Parallel orientation of $\text{CO}_2\text{-C}_2\text{H}_2$

Figure 3. PES contour plot as a function of extended angle coordinates. Obtained by minimizing with respect to r_0 . ϕ_2 is constrained such that the molecule is planar. Labeled contours are placed every 100 cm^{-1}

Figure 4. Wavefunction contours for the fundamental disrotatory bending state of $\text{CO}_2\text{-C}_2\text{H}_2$ with energy 60.84 cm^{-1} . Plot a) has ϕ_2 constrained to be 0° while b) has ϕ_2 constrained to be 180° , c) is the probability density plot. All three panels are for +eo. The corresponding +oe panels look identical.

Figure 5. Wavefunction contours for the fundamental conrotatory bending state of $\text{CO}_2\text{-C}_2\text{H}_2$ with energy 85.66 cm^{-1} . Plot a) has ϕ_2 constrained to be 0° while b) has ϕ_2 constrained to be 180° , c) is the probability density plot. All three panels are for +eo. The corresponding +oe panels look identical.

Figure 6. Wavefunction contours for the fundamental anti-gearred bending state of $\text{CO}_2\text{-C}_2\text{D}_2$ with energy 54.64 cm^{-1} . Plot a) has ϕ_2 constrained to be 0° while b) has ϕ_2 constrained to be 180° , c) is the probability density plot, made from the two above plots. All three panels are for +eo. The corresponding -eo panels look identical.

Figure 7. Wavefunction contours for the fundamental geared bending state of $\text{CO}_2\text{-C}_2\text{D}_2$ with energy 82.56 cm^{-1} . Plot a) has ϕ_2 constrained to be 0° while b) has ϕ_2 constrained to be 180° , c) is the probability density plot. All three panels are for +eo. The corresponding +oe panels look identical.

Figure 8. The left half of this plot is the minimum energy planar disrotatory path connecting the physical minimum labeled G1 and the linear configuration at the centre of Fig. 3. The right half is the path from the linear configuration to G2, which is a copy of G1 (see text). The highest point is at 47° and is 344.8 cm⁻¹.

Figure 9. The minimum energy out-of-plane torsional path connecting physical minima labeled G1 and G4 in Fig 3 is plotted. Since all geometries along the path (except the minima) are non-planar, the path is not represented in Fig 3. The maximum barrier height (at 90 degrees) is 347.2 cm^{-1} .