Computational Study of the Rovibrational Spectrum of (CO₂)₂

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Abstract

An interpolating moving least squares method is used to fit ab initio points to obtain an intermolecular potential energy surface (PES) for (CO₂)₂. The surface is used in conjunction with the symmetry-adapted Lanczos algorithm to compute rovibrational transition frequencies. The PES has four equivalent minima separated by barriers high enough that tunneling splittings are very small. The lowest energy pathway connecting the minima is a disrotatory channel. The calculations enable us to assign a combination band observed by Dehghany et al. [Mol. Phys. **108**, 2195(2010)].

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I. INTRODUCTION

By using an exact ro-vibrational variational method for the intermolecular coordinates and a high-level *ab initio* potential energy surface (PES), it is possible to compute accurate spectra of Van der Waals dimers. [1–8] In this paper, we apply the same techniques to determine rovibrational energy levels for $(\text{CO}_2)_2$. The spectra of Van der Waals dimers reveal information about interactions between molecules.[9–14] In the case of CO_2 there is currently heightened interest due to it being implicated in climate change. Non-bonded interactions of CO_2 are of particular interest due to efforts to selectively separate it (on the industrial scale) from flue gas (CO_2 containing mixtures combined mainly with N_2). Calculating rovibrational spectra of Van der Waals dimers is difficult because they often have several stable structures and undergo large amplitude motion. Standard models based on harmonic oscillators and rigid rotors work poorly. It is sometimes also difficult to fit spectra to effective Hamiltonian models. Because it is often sufficient to focus only on the inter-molecular coordinates, typically only a few thousand high-level *ab initio* calculations are required to make an excellent PES, which permits one to compute numerically exact levels. Using the Lanczos algorithm makes solution of the rovibrational Schroedinger equation straightforward even when more than a million basis functions are required.

Many dimers with identical monomers have slipped parallel equilibrium configurations and their dynamics are dominated by a disrotatory path between different minima. [1, 2, 4] This applies to $(\text{CO}_2)_2$ as well. The CO_2 monomers do not have a dipole in their equilibrium configuration, and the weakly bound dimer exhibits large amplitude vibrational motion. There is important coupling between two of the inter-monomer coordinates (stretch and bend). Because the equilibrium configuration is slipped parallel and the monomers are identical and symmetric there are four equivalent minima. There are several previous theoretical papers on CO_2 dimer. Bukowski *et al.*[15] constructed an *ab initio* 4D intermolecular potential energy surface (PES) using many-body symmetry-adapted perturbation theory (SAPT). Subsequently, Chen and Light[16] used a sequential diagonalization truncation method to compute vibrational levels on this PES with a spherical harmonics type basis for the angles and discrete variable representation (DVR)[17] basis for the inter-monomer stretch coordinates (the same type of basis we shall use in this paper). Lee, Chen, and

Light later computed the same vibrational levels using a direct product DVR basis for all of the coordinates. They observed some problems due to singularities.[18] Kalugina *et al.*[19] recently computed a 4D PES at the explicitly correlated CCSD(T)-F12b level using a triple zeta AVTZ basis set and used it to compute some of the (only) A_1^+ vibrational levels with the BOUND program.[20] In this paper, we construct a highly accurate 4D PES using the (AE)-CCSD(T*)-F12b/CVQZ-F12 method which employs a larger (quadruple zeta) basis than Kalugina *et al.* and correlates all electrons including the core. (T*) denotes scaling of the perturbative triples contribution. Rovibrational levels on this PES are computed using the same type of basis as that of Chen and Light[16] and an iterative eigensolver.

$(\text{CO}_2)_2$ has four inter-molecular modes: geared (disrotatory) bend (B_u), anti-geared (conrotatory) bend (A_g), out-of-plane torsion (A_u), and van der Waals stretch (A_g). The labels are those of the C_{2h} point group symmetry. Rovibrational levels of inter-molecular states are reported in this paper. Unfortunately, there are no direct observations, in the Terahertz region, of transitions between rovibrational levels associated with the inter-molecular levels. There are, however, many experimental studies that measure transitions among pure intra-molecular states. [21–26] Recently Moazzen-Ahmadi, McKellar and co-workers[27] observed a combination band of $(\text{CO}_2)_2$ in the ν_3 fundamental region. Because the intra-molecular coordinates are not included in our calculations we cannot directly calculate combination bands. From experimental combination bands we can indirectly obtain “experimental” inter-molecular frequencies by taking the difference between the frequency of the combination and intra-molecular band centers. The errors of the inter-molecular frequencies thus obtained are usually very small (on the order of 0.1 cm^{-1}) because of the typically small coupling between the intra-molecular and inter-molecular coordinates. The authors of Ref. 27 were unable to assign the combination band. In this paper we propose an assignment.

II. COORDINATES AND BASIS FUNCTIONS

The vibrational coordinates used to represent the PES and calculate the rovibrational levels are $r_0, r_1, r_2, \theta_1, \theta_2, \phi_2$. See Fig. 1. They have also been used in previous studies. The $\vec{r}_0$ vector points from the center-of-mass of the one CO_2 monomer, whose two O-atoms are denoted 1 and 2, to the center-of-mass of the other CO_2 monomer, whose two O-atoms are

denoted 3 and 4. The $\vec{r}_1$ and $\vec{r}_2$ vectors point along the monomers. θ_1 and θ_2 are the angles between $\vec{r}_0$ and $\vec{r}_1$ or $\vec{r}_2$, respectively. ϕ_2 is the dihedral angle between the two normal vectors $\vec{r}_0 \times \vec{r}_1$ and $\vec{r}_0 \times \vec{r}_2$. r_1 and r_2 , the lengths of $\vec{r}_1$ and $\vec{r}_2$, are fixed at values consistent with rotational constants of CO₂. The three rotational coordinates are the Euler angles specifying 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 KEO is well known. [28–31]

Each of the basis functions we use is a product of a parity adapted bend-rotation function and potential optimized discrete variable representation [32, 33] (PODVR) functions for the stretches,

$$f_{\alpha 0}(r_0)u_{l_1 l_2 m_2 K}^{JMP}(\theta_1, \theta_2, \phi_2; \alpha, \beta, \gamma) . \quad (1)$$

The parity adapted (PA) bend-rotation function $u_{l_1 l_2 m_2 K}^{JMP}$ is a linear combination of primitive functions that are products of an associated Legendre function for θ_1 , a spherical harmonic for (θ_2, ϕ_2) , and a Wigner function for the Euler angles (α, β, γ) . $P = 0$ is even parity and $P = 1$ is odd parity. More information about the basis can be found in Refs. 34 and 35.

III. THE POTENTIAL ENERGY SURFACE

The 4D intermolecular potential for (CO₂)₂ is represented analytically by interpolating 1276 high-level ab initio data points using the same interpolating moving least squares (IMLS) method used previously for several other VdW dimers including CO₂-CS₂, (CO)₂, (NNO)₂, and (OCS)₂. [1–5] Due to the higher symmetry of (CO₂)₂, slightly fewer points were necessary than for the other systems. The same coordinates, fitting basis, distance metric etc. were used here. The range of inter-monomer center-of-mass distance was $r_0 = [2.8, 15.0]$ Å, and the energy range includes the global minimum well depth of about 520 cm⁻¹ and repulsive energies up to 2100 cm⁻¹, both with respect to the separated monomers asymptote. To avoid placing expensive high quality data in even higher energy locations, a low-level guide surface was constructed from 480 symmetry unique points. The points were distributed using a Sobol sequence biased to sample the short range region more densely. For the high-level PES, 1000 points were initially distributed, again via a biased Sobol sequence, but subject to exclusion based on the guide surface. Generations of 24 automatically determined points were then added until the estimated RMS fitting error was reduced below

1 cm⁻¹.

IV. ELECTRONIC STRUCTURE THEORY

The monomers were held rigid in a collinear geometry with the CO bond distance fixed at a value consistent with the experimental rotational constant: $r_{CO} = 1.16209$ Å.[36, 37] The MOLPRO electronic structure package was used for all of the calculations reported here.[38] The low-level guide surface was computed at the explicitly correlated CCSD(T)-F12a/VDZ-F12 level, while for the high level PES, the (AE)-CCSD(T*)-F12b/CVQZ-F12 method was used. As described in the MOLPRO manual,(T*) refers to a scaling of the triples contribution based on the ratio of the MP2-F12/MP2 contributions. All electrons were correlated and the special basis set developed for that purpose by Peterson was used.[39] The T_1 diagnostic was roughly 0.018 at all geometries in both data sets.

V. PROPERTIES OF THE SURFACE

A contour plot of the PES is given in Fig. 2. It has four equivalent slipped parallel global minima. The minimum energy geometry is given in Table I. There are four symmetrically equivalent minima because flipping each of the two monomers brings one from one minimum to another minimum. There is also a T-shaped saddle point at -427 cm⁻¹. In the PES contour plot of Fig. 2, we added two green contours to reveal that the T-shape structure is a saddle point, rather than a local minimum.

The shape at the minimum is similar to that previously obtained by Bukowski *et al.*[15] with symmetry-adapted perturbation theory (SAPT), but our PES has a significantly deeper well depth -520 cm⁻¹. The well depth on the PES of Bukowski *et al.*[15] is only -484 cm⁻¹ (see Table I).

McMahon and Lane[40] have performed single-point optimizations with the CCSD(T)-F12b method and very large basis sets. Their results should be highly accurate and are in excellent agreement with ours, and in poor agreement with the SAPT values of Bukowski *et al.*[15]. The recent PES of Kalugina *et al.*[19], at the CCSD(T)-F12b/AVTZ level, has a well depth of -515 cm⁻¹, quite close to our value, although they use a smaller basis and do not include core-correlation.

The PES in figure 2 is plotted in extended angles which make it easier to visualize the dynamics for planar structures. For each pair $(\tilde{\theta}_1, \tilde{\theta}_2)$, r_0 takes the value that minimizes the potential. The extended angles $(\tilde{\theta}_1, \tilde{\theta}_2)$ are defined in Ref. 3. Their ranges are $[-\pi, +\pi]$, extended from the range $[0, \pi]$ for (θ_1, θ_2) . Each point on the physical PES appears twice in figure 2. In the figure, one can clearly see a disrotatory cycle. One way to trace the cycle is to follow it along the channel from G_1 to G_2 to G_3 and then to leave the plot at the top and re-enter it at the bottom proceeding to G_4 , and then to leave the plot at the right and to re-enter at the left and continue back to G_1 . The maximum energy between equivalent minima (e.g. between G_1 to G_2) is -427 cm^{-1} corresponding to a T-shaped structure along the disrotatory cycle. This means that the barrier to move along the disrotatory channel is less than 100 cm^{-1} . The disrotatory cycle is the lowest energy pathway connecting the four equivalent minima. Tunneling may also occur along a conrotatory path (e.g. between G_1 to G_7 (a copy of G_3), with a C_{2v} saddle point, but the barrier is much higher. In principle, it is possible to get from G_1 to G_2 along an out-of-plane torsional path. However, a fully relaxed scan of the torsional coordinate allows one of the monomers to simply relax towards the planar T-shaped structure for which the torsional angle ϕ_2 is undefined, thus merging with the planar disrotatory path. There is also a disrotatory cycle connecting the four minima G_i ($i = 5, 6, 7, 8$), but it is just a copy of the first cycle.

VI. SYMMETRY

The molecular symmetry group[41] of $(\text{CO}_2)_2$, excluding the infeasible operations that break a monomer bond, is G_{16} . $G_{16} = \{E, E^*\} \otimes G_8$, and we use $G_8 = \{E, (12)\} \otimes \{E, (34)\} \otimes \{E, (13)(24)\}$. Instead of $(13)(24)$ one could also choose (1324) . The same G_{16} group was used by us to study Ar_4 . [42] Previously, G_{16} was used by Dyke [43] in his pioneering study of $(\text{H}_2\text{O})_2$. We take the character table for G_8 from Dyke's paper, reproduced here in Table II, but we change the definition of Dyke's symmetry labels. We label states that are symmetric/antisymmetric with respect to $(13)(24)$ with A/B , whereas Dyke used A/B for symmetry with respect to (1324) . We make this change because $(13)(24)$ can be simply interpreted as exchanging vector $\vec{r}_1$ with vector $\vec{r}_2$, while $(1324) = [(12)] [(13)(24)]$ flips vector $\vec{r}_1$ after applying the $(13)(24)$ operation. Following Dyke, we label states that are

symmetric (antisymmetric) with respect to both (12) and (34) with 1(2). Because Chen and Light[16, 18]) use the symmetry labels of Dyke their A_2/B_2 states correspond to our B_2/A_2 states.

When computing the spectrum, we reduce the cost of the calculation by exploiting symmetry. To do so we must know how the three operations (12), (34), and (13)(24), from which all operations in G_8 can be constructed, affect the PA basis functions $u_{l_1 l_2 m_2 K}^{JMP}$. This is given in Table 4 of Ref. 42. Note for $J > 0$, (13)(24) affects $K = 0$ and $K > 0$ functions differently. The effect of the projection operators, derived from the G_8 character table (Table II), on the basis functions is given in Table III for the non-PA basis. For the PA basis the effect can be derived using the equations of Table 4 of Ref. 42. From Table 4 of Ref. 42, we deduce that basis functions with l_1 even and l_2 even transform like A_1 or B_1 ; basis functions with l_1 odd and l_2 odd transform like A_2 or B_2 ; basis functions with l_1 (l_2) even and l_2 (l_1) odd transform like E . We can therefore do separate calculations for the three cases: (i) $l_1 = \text{even}$ and $l_2 = \text{even}$; (ii) $l_1 = \text{odd}$ and $l_2 = \text{odd}$; and (iii) $l_1 = \text{even}$ and $l_2 = \text{odd}$. We distinguish between A_1 and B_1 states of case (i) by using the symmetry-adapted Lanczos method (SAL). [44–46] Similarly for case (ii) we determine A_2 and B_2 levels. All levels obtained in case (iii) are of E symmetry.

There are four equivalent slipped parallel equilibrium structures of $(\text{CO}_2)_2$. Each has point group C_{2h} symmetry. In the high barrier limit, each structure has its own set of wavefunctions and all four sets are degenerate. and can be classified using the point group C_{2h} . We use the PES of section III and G_{16} and our wavefunctions are therefore not strictly degenerate and labelled by G_{16} irreps. Chen and Light[16, 18], following the work of Dyke, derived the correspondence between the irreducible representations of C_{2h} and those of G_{16} by linking the symmetry operations of C_{2h} and G_{16} . Each irrep of C_{2h} corresponds to three irreps of G_{16}

$$\begin{aligned}
A_g &= A_1^+ \oplus A_2^+ \oplus E^+ \\
A_u &= A_1^- \oplus A_2^- \oplus E^- \\
B_g &= B_1^- \oplus B_2^- \oplus E^- \\
B_u &= B_1^+ \oplus B_2^+ \oplus E^+
\end{aligned} \tag{2}$$

We find that the tunneling splitting are small, and therefore we can use Eq. (2) to find the

C_{2v} irrep that corresponds to each G_{16} irrep.

A. Averaging the potential over symmetry-related points

Because of the highly peaked nature of the weight functions used to make the IMLS PES, depending on how the method is applied, potential values at symmetrically equivalent points may not be precisely equal. For $(\text{CO}_2)_2$, every point has seven symmetrically equivalent points that can be generated by applying G_8 operations (there would be 15 points if inversion symmetry were considered). In order to obtain accurate tunneling splittings the PES must be precisely symmetric with respect to those operations. Otherwise, small symmetry errors will cause small spurious splittings which could be confused with tunneling splittings, which are also small. When nothing is done to ensure precise symmetry of the PES, eigenvalues of the tridiagonal matrix built by the SAL are not copied as its size increases. This is due to the fact that the Hamiltonian does not perfectly commute with the projection operators. [44] One can symmetrize by averaging values computed from a single interpolated PES. It is also possible to use inter-atomic coordinates and permutation invariant functions.[47, 48] Another option is to map calls to the PES into one symmetry unique subspace. (When this is done it is best to still place expansions at the symmetry equivalent locations to ensure correct and smooth behavior at the subspace boundaries.) In this paper we average values computed on a single interpolated PES. For each point at which we evaluate the PES, symmetrically equivalent points are determined by applying the operations in the A_1 projection operator for G_8 , $P^{A_1} = (1/8)[1 + (13)(24)][1 + (12)][1 + (34)]$. This requires knowing how (12), (34), and (13)(24) affect the dynamical coordinates. This is given in Table 4 of Ref. 42. However, the averaging is complicated by the fact that only half $([0, \pi])$ of the quadrature grid for ϕ_2 is stored, due to inversion symmetry. Symmetry partners obtained by applying the permutation operations (12) and (34) are not on the stored portion of the grid. (12) affects the vibrational angles as follows, $(12)(\theta_1, \theta_2, \phi_2) \rightarrow (\pi - \theta_1, \theta_2, \pi + \phi_2)$. The new point is not in the stored set because $\phi_2 > \pi$. This can be remedied by using the terms in $P = (1/8)[1 + (13)(24)][1 + (12)^*][1 + (34)^*]$ to generate symmetrical equivalent points. This is acceptable because inversion does not change the potential. It does, however, bring points back into the stored set owing to the fact that, e.g., $(12)^*(\theta_1, \theta_2, \phi_2) \rightarrow (\pi - \theta_1, \theta_2, \pi - \phi_2)$.

The averaging leads to a new requirement that the number of ϕ_2 Fourier quadrature points, N_{ϕ_2} , be even. Since if N_{ϕ_2} is odd and ϕ_2 is one of the quadrature points, $\pi - \phi_2$ is not. This would be fine if we did not average.

VII. CALCULATION DETAILS

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. Eigenvalues are obtained with the symmetry adapted Lanczos (SAL) algorithm. [44–46] The required matrix-vector products are evaluated by doing sums sequentially. [17, 30, 49–51] A ceiling is applied to the potential to reduce the spectral range of the Hamiltonian matrix. [51] Details are explained in previous papers. [1, 2]. The calculations were done using the RV4 code[52]. The masses used to compute the reduced mass associated with r_0 , are 15.9949146221,[53] and 12 u for O, and C, respectively. The rotational constant for the monomers is : 0.39022 cm^{-1} [36] which is the experimentally determined ground state value.

Four basis sets are specified in Table IV. Basis I is chosen as the final basis to calculate the levels presented in this paper. It has 203 000 even parity basis functions, before restricting the evenness and oddness of l_1 and l_2 indices. Convergence tests have been performed. Basis II has a larger PODVR basis for r_0 . Basis III has more angular functions. Our convergence tests show that most of our presented levels are converged to within 0.001 cm^{-1} . In the chosen Basis I, $l_x = m_x = 44$ are used. This is larger than the basis of Chen and Light ($l_x = 27$ and $m_x = 14$) [16] and of Kalugina ($l_x = m_x = 26$)[19]. Unlike Chen and Light and also Kalugina we can afford to use a large basis because we are using an iterative eigensolver.

VIII. CO₂ DIMER : RESULTS

A. Rovibrational levels

Vibrational levels are presented in Table VII and Table VIII. $J = 1$ levels are presented in Table IX and Table X. $J = 2$ and $J = 3$ levels are presented in Supplementary Material (SM). Each level is split into three sublevels (four states because one level is degenerate), forming a 3-level subfork structure. Of the three sublevels, the E level is always between a

“1” level and a “2” level. This is reminiscent of the subfork structure of $(\text{H}_2\text{O})_2$. Tunneling splits and shifts the levels, as in the case of $(\text{H}_2\text{O})_2$. Tunneling along the disrotatory path is most facile. Tunneling splittings are nevertheless small for levels below 50 cm^{-1} . For example, the tunneling splittings are smaller than 0.0001 cm^{-1} for the ground state and first excited vibrational state, which is a geared state. Splittings are small because the monomers are heavy. The states are assigned by looking at wavefunction cuts and probability density plots that are functions of one or two coordinates. For example, Fig. 3 shows a progression of geared excited states, from the ground state to $3v_g$ state. We use the same contour interval, so that one can appreciate that the probability density peaks decrease as the vibrational excitation increases. The anti-geared state has a higher frequency. It is shown in Fig. 4. The nodal patterns of the geared and anti-geared states are consistent with the definition of the geared coordinate $\delta\theta_1 + \delta\theta_2$ for $\phi_2 = \pi$ and the anti-geared coordinate $\delta\theta_1 - \delta\theta_2$ for $\phi_2 = \pi$. Fig. 5 shows that the $2v_g$ state has some stretch character which is similar to the stretch state v_s . Both states have the same symmetry and are close in energy. Fig. 6 shows a clear T-shaped A_1^+ state, but its A_2^+ tunneling partner state is not a clean T-shaped state and there is an unusually large tunneling splitting (5.56 cm^{-1}) between the two states. This indicates that wavefunction details are sensitive to the quality of the PES due to strong couplings.

There are small but significant differences between our $J = 0$ inter-molecular vibrational levels and those of Chen and Light; see Table V. For example, there is a 1 cm^{-1} difference for the fundamental v_g level. Differences are larger for higher energy levels, e.g., the difference is 6 cm^{-1} for $3v_g$ level. This must mean that the new PES is increasingly different further from the equilibrium geometry. In the $3v_g$ case the difference has important consequences when assigning experimental transitions (see the next section). The difference (5 cm^{-1}) for the stretch fundamental is larger than the difference for the bending and torsion fundamentals. The v_a state, at 92.23 cm^{-1} , is the highest of the four vibrational fundamentals. Its energy is close to Chen and Light’s value which is 90 cm^{-1} . This state is the 12th A_1^+ state in our calculation and the 14th A_1^+ state in Chen and Light’s calculation. Differences between the two sets of levels increase with increasing energy.

Kalugina *et al.*[19] recently computed only A_1^+ vibrational levels using a PES that is also high level and has a similar well depth. However, we see differences as large as 3.4 cm^{-1}

for the lowest four A_1^+ levels. See the last column of Table V. They used the BOUND program.[20] Their calculation might not be fully converged. Kalugina et al. discussed a level at 32 ± 2 and re-assigned it as the first excited A_1^+ level (accidentally the same as the $2\nu_g$ band we discuss in the next section) as if it were an experimental band. In fact, this level was derived by Jucks et al. [23] by diagonalizing FG, where the harmonic force constants are derived from centrifugal distortion constants. Thus, this level is not reliable and should not be compared with the variational calculations.

To facilitate comparison with experiment, we derive the three rotational constants for each vibrational state from the three $J = 1$ levels and report some of them in Table VI. It would be possible to obtain the rotational constants and centrifugal distortion constants by fitting to higher J levels, but this is not done since usually this leads to only small changes in the rotational constants. The calculated rotational constants we report are for E levels because they are in the middle of the 3-level subfork and representative of the three tunneling split levels. Note that only $A_1^\pm$ rovibrational states are Pauli allowed because C and O are bosons.

B. Assignment of the experimental combination band at 2382.28 cm^{-1}

In general, theory and experiment agree well. However, the accuracy of the calculations of Chen and Light[16] is not sufficient to assign the combination band Dehghany *et al.*[27] observed at 2382.28 cm^{-1} . The ν_3 monomer vibration is the CO_2 antisymmetric stretch. There are two $(\text{CO}_2)_2$ vibrations related to ν_3 of the two monomers: one is the in-phase (A_g) combination and the other is out-of-phase (B_u) combination. Only the out-of-phase fundamental band is infra-red allowed by symmetry and the band center of the fundamental is observed to be 2350.77 cm^{-1} . By assuming that the splitting between the dimer bands can be estimated with a 2×2 matrix model [54], Dehghany *et al.* propose that the forbidden in-phase band center is at 2346.76 cm^{-1} [27] The symmetry of the combination band of Dehghany et al. is deduced to be B_u . Dehghany et al. propose that it is either a combination of the 31.5 cm^{-1} A_g inter-molecular state and the B_u intramolecular mode at 2350.77 cm^{-1} or a combination of the 35.5 cm^{-1} B_u inter-molecular state and the forbidden A_g intramolecular mode at 2346.76 cm^{-1} . Unfortunately, on the basis of Chen and Light's calculation[16] it

is not possible to identify one option as being more likely because the error is 2.0 in one case and 3.8 cm^{-1} in the other. The intermolecular level could be either Chen and Light's A_g state at 29.45 cm^{-1} ($2v_g$) or their B_u state at 39.30 cm^{-1} ($3v_g$), where v_g is the geared in-plane bending vibration.

Our calculation does enable us to identify one option as more likely. Also in our case, there are two candidates for the inter-molecular level: the A_g state at 32.34 cm^{-1} ($2v_g$) and the B_u state at 45.32 cm^{-1} ($3v_g$). According to our calculations the Dehghany et al. combination band involves the A_g state at 32.34 cm^{-1} ($2v_g$). There are three reasons supporting our assignment. First, because our $3v_g$ state is much higher than that of Chen and Light, the discrepancies with experiment are now 0.8 and 9.8 cm^{-1} , which clearly favours the ($2v_g$) assignment. Second, if the observed combination band did involve the $3v_g$ intermolecular state then this band would be accompanied by a stronger combination band involving the v_g state which has the same symmetry and is 25 cm^{-1} to the red (simply because transitions to $v = 3$ are much weaker than transitions to $v = 1$). Such a v_g band is not observed. Third, the calculated rotational constants of the $2v_g$ state agree much better with experiment than those of $3v_g$ (See Table VI). We note in passing that the A constant of nv_g states changes erratically. For v_g it is 10% lower than that of the ground state, for $2v_g$ it is larger than that of the ground state and for $3v_g$ it is smaller than that of $2v_g$. The magnitude of the A constant reflects the distance of the O atoms from the principle a -axis. Therefore, the variation of A constant implies that during the course of the geared vibration, some O atoms move towards the a -axis and some move away.

We have recently learned that other combination bands have been observed in new experiments[55]. Of these new bands, the v_g and v_a bands are in good agreement with our calculations, another new band agrees with our 93.5 cm^{-1} band. All of these bands are perturbed. Analysis of all these bands is on-going.

IX. CONCLUSION

Using an accurate 4D PES for $(\text{CO}_2)_2$, we have computed rovibrational energy levels with a large basis and the Lanczos algorithm. The PES is obtained from (AE)-CCSD(T*)-F12b/CVQZ-F12 ab initio data and an IMLS interpolation method. Energy levels are com-

puted with the computer program RV4[52]. Calculations of this kind, with rigid monomers, are straightforward, despite the huge rovibrational basis sets. Our calculation is more accurate than that of Ref. 16 which uses a lower-quality SAPT PES. The only experimental combination band at 2382.28 cm^{-1} was observed by Dehghany *et al.*. By comparing with the previous calculation[16] they determined that it involves either the $2\nu_g$ (A_g) state or $3\nu_g$ (B_u) state. Errors are, respectively, 2.0 and 3.8 cm^{-1} . According to our calculations, the same states are possible but the errors are 0.8 and 9.8 cm^{-1} for the contending assignments and therefore we conclude that the experimental band is a combination of the $2\nu_g$ (A_g) state and the allowed out-of-phase monomer ν_3 vibration. Many vibrational states are assigned based on probability density plots. Tunneling splittings between states localized in the four equivalent wells are very small (about 0.0001 cm^{-1}) for levels below 50 cm^{-1} , but they become as large as 5.56 cm^{-1} for a T-shaped state near 65 cm^{-1} . Our computed higher rovibrational levels will be useful for the on-going analysis of the new experimental combination bands of this complex.

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TABLE I. Shape of CO₂ dimer at stationary points on the IMLS PES. “PES(IMLS)” is obtained from our IMLS surface fitted to points at the (AE)-CCSD(T*)-F12b/CVQZ-F12 level. Ref. 15 is based on SAPT calculations. Ref. 19 is based on CCSD(T)-F12b calculations. “Optimized” is the single-point optimization of McMahon and Lane[40].

	Slipped-parallel				T-shaped			
	PES(IMLS)	PES[15]	PES[19]	Optimized[40] ^a	PES(IMLS)	PES[15]	PES[19]	Optimized[40] ^b
r_0 (Bohr)	6.644	6.69	6.67	6.629	7.811	7.82	7.81	5.597+ r_{CO}
θ (deg)	58.75	59.0	58.7	58.86	90	90	90	90
V (cm ⁻¹)	-520.2	-484	-514.9	-521	-427.3	-412	-429.6	-430
r_{CO} (Bohr)	2.196024							

^a Obtained with the CCSD(T)-F12b method in the CP CBS VTZ-F12/VQZ-F12 limit.

^b Obtained with the CCSD(T)-F12b method in the CP CBS AVQZ/AV5Z limit.

TABLE II. Character table of G_8

This work	Dyke[43]	E	(12)	(13)(24)	(12)(34)	(1324)
			(34)	(14)(23)		(1423)
A_1	A_1	1	1	1	1	1
B_1	B_1	1	1	-1	1	-1
A_2	B_2	1	-1	1	1	-1
B_2	A_2	1	-1	-1	1	1
E	E	2	0	0	-2	0

The G_{16} symmetry labels are obtained by adding a +/- superscript (corresponding to even/odd parity respectively) to the G_8 symmetry labels.

TABLE III. Definition of symmetry labels and effect of G_8 projection operators on the primitive basis functions. The effect of the projection operators on the PA functions is more complicated, due to the fact that (13)(24) affects $K = 0$ and $K > 0$ functions differently. The symmetry labels and projection operators for permutation inversion group $G_{16} = \{E, E^*\} \otimes G_8$ can be easily obtained from this table.

Sym	evenness, oddness (l_1, l_2)	Projection operator
A_1	(e, e)	$P^{A_1} = (1/8)[1 + (-1)^{J+l_1+l_2}][1 + (-1)^{l_1}][1 + (-1)^{l_2}]$
B_1	(e, e)	$P^{B_1} = (1/8)[1 - (-1)^{J+l_1+l_2}][1 + (-1)^{l_1}][1 + (-1)^{l_2}]$
A_2	(o, o)	$P^{A_2} = (1/8)[1 + (-1)^{J+l_1+l_2}][1 - (-1)^{l_1}][1 - (-1)^{l_2}]$
B_2	(o, o)	$P^{B_2} = (1/8)[1 - (-1)^{J+l_1+l_2}][1 - (-1)^{l_1}][1 - (-1)^{l_2}]$
E_a	(e, o)	$P^{E_a} = (1/4)[1 + (-1)^{l_1}][1 - (-1)^{l_2}]$
E_b	(o, e)	$P^{E_b} = (1/4)[1 - (-1)^{l_1}][1 + (-1)^{l_2}]$

TABLE IV. Basis set parameters. N_{r_0} is the number of PODVR basis for r_0 coordinate. l_x and m_x are the maximum values of l and m indices of the spherical harmonic basis. N_θ and N_ϕ are the numbers of θ and ϕ quadrature points. N_{bas} is the number of even-parity basis functions. N_{quad} is the number of quadrature points retained under the ceiling value of 2099 cm^{-1} . “ratio” is the ratio of N_{quad} to the total number of quadrature points. 1K = 1 thousand, 1 M = 1 million.

Basis	N_{r_0}	$l_x = m_x$	N_θ	N_ϕ	N_{bas}	N_{quad}	ratio
Basis I	25	44	45	90	203K	1.981M	0.851
Basis II	28	44	45	90	227K	2.257M	0.865
Basis III	25	50	52	104	293K	3.047M	0.851

TABLE V. Some of the low-lying inter-molecular vibrational levels of $(\text{CO}_2)_2$ (in cm^{-1}). The zero-point energy is $-423.1954 \text{ cm}^{-1}$). Levels split by tunneling are presented as only one level since the splitting is small (no larger than 0.01 cm^{-1} except for the v_a level for which the splitting is 0.11 cm^{-1}).

assignment	This paper	Chen & Light[16]	Kalugina <i>et al</i> [19]
$v_g(B_u)$	20.64	19.69	N.A.
$v_t(A_u)$	24.44	22.62	N.A.
$2v_g(A_g)$	32.34	29.45	30.46
$v_g + v_t(B_g)$	43.27	41.01	N.A.
$3v_g(B_u)$	45.31	39.30	N.A.
$v_s(A_g)$	46.07	40.84	43.18
$2v_t(A_g)$	48.20	44.35	44.75
$2v_g + v_t(A_u)$	54.72	49.91	N.A.
...	...	...	...
$v_a(A_g)$	92.23	90	N.A.

TABLE VI. Rotational constants (in cm^{-1}) of $(\text{CO}_2)_2$ inter-molecular vibration states derived from $J = 1$ levels and comparison with experiment. Experimental values for the ground state and the $2v_g$ state are in bold under the line with the theoretical values. The experimental data are from Dehghany *et al.*[27]

vibration	vib. level	A	B	C
G.S.	0.00	0.3016	0.0535	0.0453
		0.3003	0.0536	0.0453
$v_g(B_u)$	20.64	0.2740	0.0495	0.0440
$v_t(A_u)$	24.44	0.3418	0.0545	0.0455
$2v_g(A_g)$	32.34	0.3068	0.0500	0.0432
		0.3081	0.0497	0.0429
$v_g + v_t(B_g)$	43.27	0.2279	0.0463	0.0442
$3v_g(B_u)$	45.31	0.3025	0.0477	0.0420
$v_s(A_g)$	46.07	0.3421	0.0514	0.0435
$2v_t(A_g)$	48.20	0.3787	0.0551	0.0456
$2v_g + v_t(A_u)$	54.72	0.3219	0.0499	0.0432

TABLE VII. All even parity vibrational levels (in cm^{-1}) of $(\text{CO}_2)_2$ up to 100 cm^{-1} . Note that only A_1^+ states are Pauli allowed.

A_1^+	A_2^+	B_1^+	B_2^+	E^+
A_g	A_g	B_u	B_u	$A_g + B_u$
0.0000	0.0000	20.6418	20.6418	0.0000
32.3420	32.3423	45.3087	45.3208	20.6418
46.0735	46.0785	61.4763	63.4725	32.3422
48.1994	48.1998	65.7434	65.7883	45.3147
57.4297	57.8248	68.2593	72.4947	46.0760
64.9448	70.5041	75.3510	79.6808	48.1996
75.2104	76.8553	85.3747	86.8043	57.6095
76.9696	78.7049	87.5942	93.7471	62.2308
83.5689	88.5994	93.4846		65.7307
88.0423	90.2291	98.9598		66.6722
89.6992	91.4941			71.7255
92.2251	92.3381			75.2862
93.7250	95.1756			76.9160
95.2609	97.1728			79.0691
				84.9692
				86.3317
				88.4784
				90.4405
				92.1961
				92.3465
				93.6824
				95.2860
				98.5337
				99.0619

TABLE VIII. All odd parity vibrational levels (in cm^{-1}) of $(\text{CO}_2)_2$ up to 100 cm^{-1} . Note that only A_1^- states are Pauli allowed.

A_1^-	A_2^-	B_1^-	B_2^-	E^-
A_u	A_u	B_g	B_g	$A_u + B_g$
24.4420	24.4420	43.2686	43.2685	24.4420
54.7231	54.7192	66.7574	66.6284	43.2685
68.3148	68.2559	82.3376	77.6873	54.7211
70.8020	70.7640	86.6742	86.2089	66.6909
77.6089	75.5880	93.5168	89.0543	68.2871
90.1234	83.1864		96.2035	70.7835
97.0911	95.3687			76.1258
	98.0099			79.9268
				85.5669
				87.0125
				92.3347
				95.7861
				97.5172

TABLE IX. All even parity $J = 1$ levels (in cm^{-1}) of $(\text{CO}_2)_2$ up to 70 cm^{-1} . Note that only A_1^+ and B_1^+ states are Pauli allowed.

A_1^+	A_2^+	B_1^+	B_2^+	E^+
A_g	A_g	B_u	B_u	$A_g + B_u$
0.3551	0.3551	20.9652	20.9652	0.3551
32.6991	32.6989	24.5420	24.5420	20.9652
43.3591	43.3590	24.8293	24.8293	24.5420
43.5407	43.5407	45.6708	45.6592	24.8293
46.4719	46.4672	54.8162	54.8123	32.6990
48.6336	48.6332	55.0845	55.0879	43.3590
58.1723	57.7903	63.8180	61.8724	43.5407
66.8457	65.3399	66.0395	66.0085	45.6649
66.9926	66.7184	68.4089	68.3099	46.4696
	67.1214	68.6460	68.4139	48.6334
			68.9237	54.8143
				55.0862
				57.9648
				62.6116
				66.0012
				66.7781
				66.9526
				67.1065
				68.3828
				68.6878

TABLE X. All odd parity $J = 1$ levels (in cm^{-1}) of $(\text{CO}_2)_2$ up to 70 cm^{-1} . Note that only A_1^- and B_1^- states are Pauli allowed.

A_1^-	A_2^-	B_1^-	B_2^-	E^-
A_u	A_u	B_g	B_g	$A_u + B_g$
20.7352	20.7352	0.0988	0.0988	0.0988
20.9597	20.9597	0.3469	0.3469	0.3469
24.8383	24.8383	32.4352	32.4355	20.7352
45.3984	45.4105	32.6923	32.6920	20.9597
45.6650	45.6535	43.5427	43.5428	24.8383
55.0913	55.0947	46.1685	46.1734	32.4354
61.5583	61.8676	46.4639	46.4594	32.6921
63.8129	63.5589	48.3001	48.3005	43.5428
65.8330	65.8771	48.6240	48.6236	45.4044
66.0393	66.0076	57.5167	57.7831	45.6592
68.3217	68.3822	58.1666	57.9145	46.1710
68.6752	68.9168	65.0254	65.3357	46.4617
		66.9972	67.1274	48.3003
				48.6238
				55.0930
				57.6966
				57.9595
				62.3139
				62.6069
				65.8204
				65.9998
				66.7526
				66.9517
				67.1106
				68.6949

FIG. 1. Vibrational coordinates for $(\text{CO}_2)_2$.

FIG. 2. PES contours as a function of the extended angles $(\tilde{\theta}_1, \tilde{\theta}_2)$, obtained by minimizing with respect to r_0 . 8 potential minima are marked with G_i . The contour interval is 50 cm^{-1} except for the blue contour at $E = 0$ and the two green contours at $E = -430$ and -427 cm^{-1} . The green contours show that the T-shape structure is a saddle point, rather than a local minimum. The wriggles of the $E = 0$ blue contour are due to the jump of r_0 between a local minima and r_0 at infinity. $\phi_2 = \pi$ in the squares with corners at $[-\pi, -\pi]$ and $[+\pi, +\pi]$.

FIG. 3. Probability densities of the ground state(A_1^+) (a), $v_g(B_1^+)$ (b), $2v_g(A_1^+)$ (c), and $3v_g(B_1^+)$ (d) states. The contour interval is 0.2.

FIG. 4. Probability densities of the anti-gear state $v_g(A_1^+)$, the 12th A_1^+ state. The contour interval is 0.2.

FIG. 5. Probability densities of the $2v_g(A_1^+)$ (a), and $v_s(A_1^+)$ (b) states. This shows that the $2v_g$ state is not a pure bend state, but has r_0 stretch character. The contour interval is 0.004.

FIG. 6. Probability densities of the T-shape state at 6th (A_1^+) state (a). Perhaps surprisingly, its tunneling partner, the 6th A_2^+ state (b) is not a clean T-shape state. The tunneling splitting of 5.56 cm^{-1} between the two states is unusually large. The contour interval is 0.4 for both states. The amplitude of the T-shape in (a) is so large that we have to use a larger contour interval.