Vibrations of the carbon dioxide dimer

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Fully coupled four-dimensional quantum-mechanical calculations are presented for intermolecular vibrational states of rigid carbon dioxide dimer for $J=0$. The Hamiltonian operator is given in collision coordinates. The Hamiltonian matrix elements are evaluated using symmetrized products of spherical harmonics for angles and a potential optimized discrete variable representation (PO-DVR) for the intermolecular distance. The lowest ten or so states of each symmetry are reported for the potential energy surface (PES) given by Bukowski et al. [J. Chem. Phys. 110, 3785 (1999)]. Due to symmetries, there is no interconversion tunneling splitting for the ground state. Our calculations show that there is no tunneling shift of the ground state within our computation precision (0.01 cm$^{-1}$). Analysis of the wave functions shows that only the ground states of each symmetry are nearly harmonic. The van der Waals frequencies and symmetry adapted force constants are found and compared to available experimental values. Strong coupling between the stretching coordinates and the bending coordinates are found for vibrationally excited states. The interconversion tunneling shifts are discussed for the vibrationally excited states. © 2000 American Institute of Physics. [S0021-9606(00)00911-9]

I. INTRODUCTION

Weakly bound van der Waals dimers may be used for experimental determination of two body interaction forces. Accurate description of the intermolecular interaction and the dynamical behavior of such dimers is of fundamental importance towards detailed understanding of the bulk properties of various condensed phase materials, and provides deeper insight to various important chemical and biological reactions. According to the nature of the intermolecular interaction, van der Waals dimers can be sorted into several different types. The hydrogen bonded dimers, like (HX)$_2$ (X can be F, Cl, etc.) and (H$_2$O)$_2$, where a hydrogen-bond can be formed between two monomers, are the most strongly bonded. The dipole bound dimers are formed by two monomers with permanent dipole moments. The quadrupole bound dimers where the lowest nonvanishing multipole moment of the monomers is the quadrupole, like (CO$_2$)$_2$, (C$_2$H$_2$)$_2$, etc. are usually very weakly bound. Most of these dimers were subject to extensive experimental and theoretical studies in the last few decades. Structure determination has been one of the essential tasks in the early stages. For hydrogen-bonded or strong dipole bond dimers, the structure determinations were relatively simple and not ambiguous. When it comes to some weakly bound dimers such as quadrupole bound dimers or dimers of weak dipoles such as (CO$_2$)$_2$, the structures were sometimes abnormal and incurred much debate. It is worthwhile to mention the simple model proposed by Buckingham and Fowler\textsuperscript{1} where distributed multipoles combined with hard spheres were employed to describe the intermolecular electrostatic interactions. The model was shown to be capable of predicting qualitatively correct structures for most van der Waals complexes including (CO$_2$)$_2$. Group theory analysis especially by the permutation-inversion (PI) group\textsuperscript{2} has turned out to be very useful in studying these weakly bound complexes. The PI symmetry of (CO$_2$)$_2$ is the same as water dimer and nitrogen dimer, for which a fair amount of work has been carried out by Dyke,\textsuperscript{3} Metropoulos,\textsuperscript{4} and Tennyson.\textsuperscript{5}

Among the family of van der Waals dimers, quadrupole bound dimers are of particular interest. The very weak intermolecular interaction between monomers allows large amplitude intermolecular vibrations. The shapes of the interaction potentials are often anharmonic and involve couplings among various degrees of freedom. Despite the numerous investigations devoted to these very weakly bound van der Waals dimers, many questions are still unclear to us. We have posed several of them below. Can we describe the intermolecular vibrations as normal modes? What is the coupling between the various vibrational modes? How strong is the anharmonicity of the vibrational modes? Are tunneling effects observable?

In the present study, we have chosen carbon dioxide dimer to study the above questions due to its importance in our environment and in many supercritical chemical processes. A further reason is the wealth of experimental information available to us. Since its discovery by Leckeuby and Robbins,\textsuperscript{6} (CO$_2$)$_2$ has attracted extensive attention both experimentally and theoretically. Early works have been focused on the determination of the equilibrium structure.\textsuperscript{7–14} Many attempts were made to resolve the ambiguity between two conflicting configurations, namely, the slipped parallel structure and the T-shaped structure. Finally Jucks et al.\textsuperscript{15,16} finished the debate by showing the equilibrium structure is slipped parallel with $C_{2h}$ symmetry, and the T-shaped structure with $C_{2v}$ is a transition state. They also made estimates for two intermolecular vibrational normal modes, the sym-

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metric intermolecular stretch (32 cm\(^{-1}\)) and symmetric in-plane bending (90 cm\(^{-1}\)). As in other homo-molecular dimers such as water dimer and (HX)\(_2\), permutation of the identical nuclei in (CO\(_2\))\(_2\) should split or shift the vibrational energy levels. As will be discussed later, the boson symmetry of both \(^{12}\)C and \(^{16}\)O make tunneling splittings forbidden in the \(J=0\) states. Thus no tunneling effects have been observed experimentally. Little is known about the possible tunneling path or tunneling barrier heights. Many intermolecular potential energy surfaces (PES) have been proposed. They are either made to fit to some kind of experimental data or based on \textit{ab initio} calculations. Among these potentials, the PES recently published by Bukowski et al.\(^{15}\) is believed to be the best and is used in our present study. The fact that the equilibrium structure and the transition state are at different radial separations and with different orientations and very weak interaction between monomers make the intermolecular vibrational motion very interesting. No accurate calculations of the vibrations on this PES have been carried out. It is the purpose of the current study to try to understand the dynamics on this PES and to attempt to evaluate the potential by comparing our results with appropriate experimental values.

In the present work we use the sequential diagonalization truncation method to diagonalize the \(J=0\) Hamiltonian. The PI group \((G_{16})\) is used to partition the bases into irreducible symmetry blocks to reduce the size of the problem. Nuclear spin statistics requires that only \(A_1^+\) states exist for \(J=0\). However, the calculated states for other symmetries help us to interpret the interconversion tunneling dynamics, i.e., instead of observing the shifting of the energy levels induced by tunneling motions, the staggering pattern can be studied explicitly by analyzing the virtual energy spectrum generated from our calculations. In addition, some of the missing states like \(A_2^+\) correspond to vibrational fundamentals, hence the calculations can be useful in studying the intermolecular vibrations. This will be discussed in Secs. III and VI.

This article is organized as follows. In Sec. II, the Hamiltonian, basis functions, and diagonalization procedures are described. In Sec. III, the PI symmetry and point group symmetry are discussed in detail. In Sec. IV, the potential energy surface and numerical integration of the potential matrix elements are discussed. Section V shows the convergence of the calculation. Discussions of intermolecular vibrations and tunneling effects are given in Sec. VI.

II. METHODS

The calculations were performed in Jacobi molecule–molecule collision coordinates (see Fig. 1), with the monomers held rigid. The body fixed \(z\) axis lies along the vector \(\mathbf{R}\) which connects the carbon atom of each monomer. \(\theta_i\) is the bending angle between the \(z\) axis and the O–C–O axis of monomer \(i\). \(\phi\) is the out-of-plane torsional angle. The \(J=0\) Hamiltonian for the intermolecular motion of rigid (CO\(_2\))\(_2\) can be written as

\[
H = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + H_{\text{ang}},
\]

\[
H_{\text{ang}} = B_z(j_1^2 + j_2^2) + \frac{j_2^2}{2\mu R^2} + V,
\]

where \(j_i\)'s are the monomer angular momentum operators, \(B_z\) is the monomer rotation constant, and \(\mathbf{j} = j_1 + j_2\).

The suitable angular basis for \(H_{\text{ang}}\) in Eq. (1) is the coupled angular momentum basis

\[
|j_1 j_2 j\rangle = \sum_m \langle j_1 m j_2 \bar{m}|j0\rangle Y_{j_1 m}(\omega_1) Y_{j_2 \bar{m}}(\omega_2),
\]

where \(Y_{jm}(\omega)\) is a spherical harmonic, \(\langle j_1 m j_2 \bar{m}|j0\rangle\) is a Clebsch–Gordan coefficient and \(\bar{m} = -m\). We note that the calculation will be made easy only when the potential \(V\) can be represented with only moderate number of terms in the following expansion:

\[
V(R, \theta_1, \theta_2, \phi) = \sum_{l_1, l_2, l} v_{l_1 l_2}(R) |l_1 l_2 l\rangle.
\]

However, the (CO\(_2\))\(_2\) potential we used is not readily expandable in the above form, and it has to be numerically integrated to obtain the potential matrix elements. Under these circumstances, we found that by using the uncoupled basis

\[
|j_1 j_2 m\rangle = Y_{j_1 m}(\omega_1) Y_{j_2 \bar{m}}(\omega_2),
\]

the potential matrix element evaluation time can be greatly reduced. An angular basis is defined by \(j_1^{\text{max}} = j_2^{\text{max}} = J^{\text{max}}\) and \(m^{\text{max}}(\leq J^{\text{max}})\). In order to converge the calculation, one needs to use a basis with \(J^{\text{max}}\) up to 27 and \(m^{\text{max}}\) up to 14.

The angular matrix elements over the angular momentum operators can be calculated analytically

\[
\langle j'_1 j'_2 m'|j_1 j_2 m\rangle = \delta_{j_1'j_1} \delta_{j_2'j_2} \delta_{mm'} (j_1(j_1 + 1) + j_2(j_2 + 2 - 2m^2) \delta_{mm'} + C_{j_1 m}^* C_{j_2 \bar{m}} \delta_{m+1,m'}) + C_{j_1 m} C_{j_2 \bar{m}}^* \delta_{m-1,m'}.
\]
where $C_{jm}^{j+m} = \sqrt{(j+m)(j\pm m+1)}$.

A potential optimized DVR (PODVR)\(^{18}\) was used for the $R$ coordinate. The PODVR basis was constructed by first determining the minimum potential energy (as a function of the three angles) for a large set of $R$ values. This potential energy curve was then fitted approximately by a Morse potential and a large 1D (one-dimensional) basis was diagonalized to yield accurate eigenfunctions in this potential. Using a subset of these eigenfunctions, the $R$ coordinate was then diagonalized to provide the PODVR points as eigenvalues and the PODVR-finite basis representation (FBR) transformation. A thirteen point DVR was used in the final calculations.

The total Hamiltonian matrix was diagonalized in two steps with sequential diagonalization truncation method.\(^{19–22}\) At each DVR point for $R$, the three-dimensional angular part of the Hamiltonian matrix ($H_{\text{ang}}$) was diagonalized in a basis of symmetry adapted combinations of the primitive basis functions and then truncated. The truncated 3D (three-dimensional) Hamiltonian matrices at each $R$ are then combined with the kinetic energy operator in $R$ to form a reduced 4D (four-dimensional) Hamiltonian matrix for final diagonalization.

### III. SYMMETRY

#### A. Permutation-inversion (PI) symmetry

The permutation inversion symmetry of the carbon dioxide dimer can be characterized using the $G_{16}$ group.\(^{3–5,23}\) The group has eight nondegenerate representations ($A_1^+, B_1^+, A_2^+, B_2^+, A_2^-, B_2^-$) and two doubly degenerate representations ($E^+, E^-$). Metropoulos\(^4\) and J. Tennyson et al.\(^{5,23}\) have shown how to construct the symmetry adapted basis functions for this symmetry group using space-fixed and body-fixed coordinates, respectively. In our calculation, body-fixed coordinates are used. The actions of the permutation-inversion operations on the body-fixed coordinates were given by J. Tennyson et al.\(^{5,23}\) To reduce the effort in the potential matrix element evaluation, we chose to use products of spherical harmonics [Eq. (4)] rather than the coupled spherical harmonics as primitive basis functions. The transformation properties of the primitive basis functions are derived using the properties of spherical harmonics and are given in Table I. The symmetry adapted basis functions are constructed using the character table provided by Dyke\(^5\) and using the projection operator\(^24\)

$$\phi_{\text{sym}} = N_{\text{norm}} \sum_R \chi_{\text{sym}}(\hat{R}) \hat{R}. \quad (7)$$

#### B. Point group symmetry of the vibrational levels

If (CO$_2$)$_2$ has no geometric symmetry, there will be 16 nonsuperimposible, isoenergetic conformations. But the various experiments\(^{14–16}\) suggested that the equilibrium configuration is of $C_{2h}$ symmetry. In this case, there are only four nonsuperimposible structures for (CO$_2$)$_2$, and in the high barrier limit, each of the four distinct configurations has its own vibration–rotation wave function, degenerate with those of the other configurations. In addition, these wave functions can be classified by their symmetry with respect to the point group $C_{2h}$. To find out the correspondence between irreducible representation of $C_{2h}$ group and that of the $G_{16}$ group, we followed Dyke’s analysis.\(^3\) First we find for each $C_{2h}$ symmetry operation the corresponding $G_{16}$ group operations that have the same effect on the Cartesian displacement coordinates. Note that the $C_{2h}$ point group operation only operates on the vibrational displacements, while the $G_{16}$ operations permute the identical nuclei, but have no effect on the vibrational displacements. Table III shows the correspondence...
dence of the symmetry operations. By comparing the character table of $C_{2h}^{24}$ against the character table of $G_{16}$ the following relations were found:

$$
\Gamma A_g = A_1^+ \otimes B_2^+ \otimes E^+,
$$
$$
\Gamma A_u = A_1^- \otimes B_2^- \otimes E^-,
$$
$$
\Gamma B_g = A_2^- \otimes B_1^- \otimes E^-,
$$
$$
\Gamma B_u = A_2^+ \otimes B_1^+ \otimes E^+.
$$

(9)

It can be seen that each ro-vibrational state will split into four sublevels according to its symmetry under $C_{2h}$ symmetry. The ground vibrational state with $J=0$ is of $A_g$ symmetry, and can be represented as a direct sum of $A_1^+$, $B_2^+$, and $E^+$ irreducible $G_{16}$ representations.

C. Symmetry of the ro-vibrational states

The rotational part of the ro-vibrational wave function can be described by using symmetrized wigner rotation functions as follows:

$$
\psi^\pm = \frac{1}{\sqrt{2(1+\delta_{K0})}} (|JKM\rangle \pm (-)^J |K\bar{R}M\rangle),
$$

(10)

where $|JKM\rangle = \sqrt{((2J+1)\pi)^{-1/2}} D_{MK}^{L*}(\alpha, \beta, 0)$ and $D_{MK}^{L*}$ is wigner rotation function. For $J$ even or odd, $\psi^+$ belongs to $A_1^+$ or $B_1^-$, respectively, and $\psi^-$ belongs to $B_1^+$ or $A_1^+$, respectively. Note that $\psi^-$ only exists for $K \neq 0$. According to boson statistics, ro-vibrational states must be totally symmetric with respect to the exchange of identical nucleii, i.e., $A_1^+$. The overall symmetry of the ro-vibrational states is determined by the direct product of the rotational symmetry and the vibrational symmetry, i.e., $\Gamma_{vib-rot} = \Gamma_{vib} \otimes \Gamma_{rot}$. Thus the allowed vibrational states for $J=0$ are $A_1^+$. Even for rotationally excited states, only $A_1^+$ and $B_1^-$ are allowed. The discussions in previous section [Eq. (9)] show that, without restrictions of boson statistics, each vibrational state will split into four sublevels (we denote these four sublevels as a sublevel group) due to tunneling motions. It would be possible to measure the tunneling splittings if any two different levels of the same sublevel group could show up. However the four allowed vibrational states all belong to different sublevel groups. Thus the study of the rotationally excited states will not give additional information about tunneling splittings.

IV. POTENTIAL ENERGY SURFACES

The $(CO_2)_2$ potential energy surface (PES) was provided by Bukowski et al. This potential was computed using the many-body symmetry-adapted perturbation theory (SAPT) and a large 5s3p2d1f basis set including bond functions. An accurate analytical fit was obtained in a form of an angular expansion incorporating the asymptotic coefficients computed ab initio at the level consistent with the applied SAPT theory. It follows from the potential that the minimum energy ($-484$ cm$^{-1}$) configuration is of slipped parallel geometry with $R=3.54$ Å, $\theta=59.0^\circ$, and a saddle point ($-412$ cm$^{-1}$) which is T-shaped at $R=4.14$ Å. The potential is given as a function of collision coordinates. Numerical integration is required to construct the potential matrix elements over the angular basis at a given value of $R$. To prevent repeated computation or extra work, the integrations were done for each symmetrized basis set separately. Since the calculations were performed symmetry by symmetry, $\langle j_1'j_2'm's'|V|j_1j_2ms\rangle_R$ or $\langle j_1'j_2'm's'|V|j_1j_2ms\rangle_R$ was pre-computed prior to the 3D calculations for each singly or doubly degenerate symmetry block, respectively. The numerical integrals were evaluated with Gauss–Legendre quadrature in $(\theta_1, \theta_2)$ and Gauss–Chebyshev quadrature in $\phi$. The number of quadrature points used were $(29, 29, 16)$ for $(\theta_1, \theta_2, \phi)$, respectively. It should be noted that, although not implemented in the present calculation, the potential integration might be further simplified by integrating over a primitive grid covering the unique portion of the PES and then multiplying by a factor to account for the PI symmetries.

V. RESULTS AND CONVERGENCE

In the present study, the $J=0$ Hamiltonian was diagonalized. The reduced mass $\mu = 21.995$ amu, and the monomer rotational constant $B_1 = 0.3902$ cm$^{-1}$ were used in the calculations. The final calculations were performed for a variational basis with $J_{max} = 27$, $m_{max} = 14$. Thirteen PODVR points were used for the $R$ coordinate. The 3D angular basis sizes were ~900 for singly degenerate representations, and 1600 for doubly degenerate representations. Next we shall inspect the dependence of the accuracy and convergence on various factors. We will show for each convergence parameter the changes in the energies of the lowest ten levels (for the symmetry noted) compared with the most accurate calculation done for the parameter in question.
We first examined the accuracy of the angular quadratures using a basis with $J_{\text{max}} = 27$, $m_{\text{max}} = 14$ and 4 PODVR points. By increasing the number of quadrature points along angles and observing the change of the final results, we estimate that the errors are within $\pm 0.01$ wave number (Table IV) when the number of quadrature points along $\theta_1$ is greater than 29, and the results are invariant to the number of quadrature points in $\phi$ up to the third decimal place when $N_\phi \geq 16$. The effect of the number of PO-DVR points was evaluated for the $E^-$ state. The calculation was done with 13 and then 14 PO-DVR points and the differences for the lowest 10 states are shown in Fig. 2. For these states the rms (root-mean-square) error is about 0.004 cm$^{-1}$. The lowest states differ only by 0.0002 cm$^{-1}$. The dependence of the accuracy on $J_{\text{max}}$ and $m_{\text{max}}$ was also checked for lowest 10 $E^-$ states. The calculations for $m_{\text{max}} = 14$ and for $m_{\text{max}} = 15$ show the $m_{\text{max}} = 14$ is sufficient to converge the calculation to the third decimal place. Table IV shows that $J_{\text{max}} = 27$ will converge the lowest 10 $E^-$ states within $\pm 0.01$ cm$^{-1}$. Overall, we believe our calculations yield the correct energies of the lowest ten states of each symmetry for the given PES within $\pm 0.02$ cm$^{-1}$ ($\pm 0.01$ cm$^{-1}$ for lowest five states).

The calculations were carried out on a Sun Enterprise 450 machine (250 MHz). Each doubly degenerate symmetry required about 4 min CPU time per DVR point for subsequent sequential diagonalization and about 80 min to finish the four-dimensional calculation. The lowest ten energy levels for each symmetry calculated from the aforementioned PES are presented in Table V.

### VI. DISCUSSION

The carbon dioxide dimer has four intermolecular vibrational normal modes

$$\Gamma_{\text{vib}} = 2A_g + A_u + B_u.$$  \hfill (11)

The four symmetry coordinates are qualitatively depicted in Fig. 3. We note that both van der Waals stretch and in-plane symmetric bending are of $A_g$ symmetry. Thus the $A_g$ normal mode coordinates cannot be derived merely through symme-

![FIG. 2](image1.png)

**FIG. 2.** Variation of 10 lowest $E^-$ states with the number of PO-DVR points in $R(N_R)$. $\Delta E = E(N_R = 13) - E(N_R = 14)$.

![FIG. 3](image2.png)

**FIG. 3.** The four intermolecular vibrational modes of (CO$_2$)$_2$. (a) Symmetric van der Waals stretch ($A_g$), (b) symmetric in-plane bend ($A_u$), (c) out-of-plane torsion ($A_u$), and (d) antisymmetric in-plane bend ($B_u$).

### TABLE V. The lowest ten energy levels (in cm$^{-1}$) calculated for $J=0$.

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try analysis. In order to find the accurate representations of the normal mode coordinates, \( F - G \) matrix analysis\(^{26} \) is performed for the Bukowski et al. PES. Diagonalization of the matrix product \( GF \) gives normal mode frequencies and the transformation matrix from original coordinates to normal mode coordinates. The details of this analysis are given in the Appendix. The normal mode frequencies are identical with those given by Bukowski et al.\(^{17} \) and are given in Table VI, and the normal mode coordinates are given by (the units for the coordinates are described in the Appendix),

\[
S_1 = \Delta \phi, \\
S_2 = \frac{1}{\sqrt{2}}(\Delta \theta_1 - \Delta \theta_2), \\
S_3 = 0.926\Delta R - 0.267(\Delta \theta_1 + \Delta \theta_2), \\
S_4 = 0.520\Delta R + 0.604(\Delta \theta_1 + \Delta \theta_2).
\]

The \( S_1 \) is the out-of-plane torsion motion of \( A_u \) symmetry, the \( S_2 \) corresponds to the antisymmetric in-plane bend of \( B_u \) symmetry, the \( S_3 \) and \( S_4 \) are mixtures of intermolecular stretch and symmetric in-plane bend, both with \( A_g \) symmetry. The \( S_3 \) is mostly stretch motion and the \( S_4 \) gets more contribution from symmetric in-plane bending motion. Following Nxumalo et al.,\(^{27} \) the frequencies corresponding to \( S_1, S_2, S_3, \) and \( S_4 \) are labeled by \( \nu_7, \nu_{12}, \nu_5, \) and \( \nu_4, \) respectively. The zero point energy calculated with these normal mode frequencies is 96.9 cm\(^{-1} \). Our calculation shows the zero point energy is 91.9 cm\(^{-1} \). This difference should indicate that the anharmonicities exist for the ground state though the effect is quite small.

The analysis of the ro-vibrational wave function enables us to understand the (de)localized nature of the ro-vibrational states. We have taken suitable two-dimensional cuts through the full 4D wave functions. Instead of using \( \theta_1, \theta_2, \) we have chosen \( \theta^+ = \theta_1 + \theta_2 \) and \( \theta^- = \theta_1 - \theta_2 \) as coordinates to make the 2D cuts because these coordinates are more closely related to the normal modes. Figure 4 shows that the ground \( A_1^+ \) state is localized around the equilibrium structure (\( R = 3.54 \) Å, \( \theta^+ = 59.0^\circ, \) and \( \phi = 0^\circ \) or \( 360^\circ \)). Figures 5 and 6 show the wave functions of the lowest \( A_g^2 \) and \( A_1^+ \) states. They correspond to the antisymmetric in-plane bending fundamental (\( \nu_{12} \)) and out-of-plane torsion fundamental (\( \nu_7 \)), respectively. Figure 7 shows the third excited \( A_1^+ \) state. The plots show that the wave functions extend to a wide region in the four-dimensional space. Although there apparently exists mixing between the stretching coordinate and the antisymmetric in-plane bending coordinate, most of the excitation goes to the stretching coordinate. Therefore, this state can be identified as the stretch fundamental (\( \nu_3 \)). The probability distribution of the wave functions in \( R \) (Fig. 8) also confirms this assignment as the curve corresponding to third excited state of \( A_1^+ \) clearly shows one node along the \( R \) coordinate. The symmetric in-plane bending is even more difficult to identify because it involves much higher energy excitation. We found that the fourteenth excited state of the \( A_1^+ \) symmetry is most likely to be the symmetric in-plane bending fundamental (Fig. 9). Overall, we were able to estimate all the fundamental frequencies based on our calculations. They are listed in Table VI together with the experimental frequencies estimated by Jucks et al.\(^{16} \) and results from the normal mode analysis from the PES used in the calculation.\(^{17} \) It should be noted that all our calculated frequencies are well below those obtained from normal mode analysis, which indicates that the normal mode model is insufficient to describe the intermolecular vibrations due to the anharmonicities. The zero point energy predicted from our fundamental frequencies (87 cm\(^{-1} \)) is smaller than the calculated zero point energy (91.9 cm\(^{-1} \)). The difference is due to the anharmonicities in the vibrational motions, because our frequencies are obtained by analyzing the excited vibrational states and should reflect the properties of excited vibrational

<table>
<thead>
<tr>
<th>( \text{cm}^{-1} )</th>
<th>Ours</th>
<th>Expt</th>
<th>Normal mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g, ) symmetric bend (( \nu_5 ))</td>
<td>90</td>
<td>90</td>
<td>100.0</td>
</tr>
<tr>
<td>( A_u, ) symmetric stretch (( \nu_2 ))</td>
<td>41</td>
<td>32</td>
<td>42.8</td>
</tr>
<tr>
<td>( A_u, ) out of plane torsion (( \nu_3 ))</td>
<td>23</td>
<td>24.9</td>
<td>26.2</td>
</tr>
<tr>
<td>( B_u, ) antisymmetric bend (( \nu_{12} ))</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIG. 4. Two-dimensional cuts through \( J = 0 \) wave function of the ground \( A_1^+ \) state.
states. The comparisons of the frequencies between our calculation and the normal mode analysis also show that the in-plane bending motions ($\nu_4$ and $\nu_{12}$) are probably more anharmonic. This analysis also indicates that the intermolecular vibrations are complicated by the coupling between different normal modes as for the third $A_1^2$ state shown in Fig. 7. Our calculated frequencies for the PES agrees quite well with the Jucks et al. results for the symmetric in-plane bending motion. In their paper, Jucks et al. also calculated the symmetry adapted force constants in symmetry coordinates, namely, $S_s^+=\delta R$ and $S_b^+ = \sqrt{2}(\delta \varphi_1 + \delta \varphi_2)$. The vibrational fundamentals obtained above allow the evaluation of these quantities and they are calculated and compared with Jucks et al. results (Table VII). These quantities agree quite well. The lack of experimental information, however, makes it difficult for us to evaluate the given potential precisely.

The energy spectrum is plotted in Fig. 10. Also plotted are the harmonic oscillator levels. The harmonic oscillator levels are combinations of the four fundamental frequencies obtained by performing normal mode analysis on the potential and are given by Bukowski et al. The difference of the calculated spectrum from the harmonic oscillator levels shows the anharmonicities of the intermolecular vibrations and, for higher levels, tunneling splittings.

Since we have data on all symmetries, we can evaluate the level shifts which correspond to the symmetry allowed subset of the tunneling states. The group theory analysis (Sec. III B) told us that each ro-vibrational energy level is a composite of four sublevels [Eq. (9)]. This is consistent with our computational results. The lowest energy for each singly degenerate representation and the lowest two levels of each doubly degenerate representation of our calculation can be classified into four groups, $\{A_1^+, B_2^+, E^-\}$, $\{A_2^+, B_1^+, E^-\}$, $\{A_1^-, B_2^-, E^-\}$, and $\{A_2^-, B_1^-, E^-\}$. Among them, only vibrational states with $A_1^+$ symmetry are permitted for the ground rotational state. As has been shown in the previous experimental studies, because of the large reduced masses, the interconversion tunneling shifts are effectively quenched for the lowest levels. Our calculations also show there are no tunneling shifts for the ground state within our computational precision ($\pm 0.01 \text{ cm}^{-1}$). When the dimer is vibrationally excited, it possesses enough energy to penetrate the tunneling barrier such that the tunneling shifts can be observed for excited vibrational states. In Fig. 10, the virtual tunneling splittings for the excited vibrational states have been magnified on the right. Without the restrictions of boson symmetry, each vibrational state would split into three sublevels. The three sublevels are nearly evenly spaced, i.e.,

---

FIG. 5. Two-dimensional cuts through $J=0$ wave function of the ground $A_1^2$ state.

FIG. 6. Two-dimensional cuts through $J=0$ wave function of the ground $A_1^1$ state.
which may imply there exists only one tunneling pathway low enough in energy to be seen. For the third excited $A_1^+$ state, the fifth excited $E^+$ state and the third excited $B_2^+$ state, $h \approx 0.15$ cm$^{-1}$. And for the fourth excited $A_1^+$ state, the sixth excited $E^+$ state and the fourth excited $B_2^+$ state, $h \approx 0.06$ cm$^{-1}$. Although the latter set of states possess higher energies, it has less tunneling. The analysis of the 2D wave function cuts shows the third excited $A_1^+$ state is excited with one quantum of $\nu_5$ (Fig. 7) and the fourth excited $A_1^+$ state is excited with two quanta of $\nu_7$ (Fig. 12). This implies that the tunneling motion tends to occur within the plane, and out-of-plane torsion ($\nu_7$) motion is less correlated with the tunneling pathway than the stretch motion ($\nu_5$). The most probable tunneling pathway between two slipped parallel minima ought to be the geared in-plane bending of the two monomers via the T-shaped transition state. The T-shaped transition state is about 72 cm$^{-1}$ above the minimum configuration. But as has been shown for acetylene dimer, the actual tunneling pathway may not follow the potential minimum path for kinetic reasons. Instead for (C$_2$H$_2$)$_2$ the tunneling motion corresponds to only the internal rotation, with the center-of-mass distance between monomers remaining fixed. So the actual tunneling barrier may be much higher than 72.0 cm$^{-1}$ (about a couple of hundred wave numbers) for the ground state.

\begin{equation}
E_{B_2^+} - E_{E^+} = E_{E^+} - E_{A_1^+} = h, \tag{13}
\end{equation}

excited with two quanta of $\nu_5$ (Fig. 12). This implies that the tunneling motion tends to occur within the plane, and out-of-plane torsion ($\nu_7$) motion is less correlated with the tunneling pathway than the stretch motion ($\nu_5$).

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(0,3,0,0)  
(1,2,0,0)  
(2,1,0,0)  
(3,0,0,0)  
(0,1,1,0)  
(1,0,1,0)

FIG. 10. The energy diagrams. The levels on the left are those given by the harmonic oscillator model where the labels are \( (\nu_x, \nu_y, \nu_z, \nu_R) \). The levels in the middle are calculated levels for \( J=0 \). The levels on the right are magnified (\( \times 5 \)) spectral lines to show the tunneling splittings. Note that only the \( A^+_1 \) levels exist for \( J=0 \).

the wave function spans a larger region of space and the intermonomer distance may become larger; the real barrier is effectively lowered to allow the tunneling to occur. The excitation of the out-of-plane torsion affects the intermonomer separation less than the excitation of the stretch mode which in turn results in smaller tunneling splittings. We note that the eigenspectrum plotted in Fig. 10 is not the real spectrum one will see in experiment. Boson statistics will remove most of the states and we are only left with \( A^+_1 \) states. The tunneling splittings we see in Fig. 10 becomes tunneling shifts instead. However, the tunneling dynamics is more evident in this virtual spectrum.

Finally, natural orbital expansion analysis \(^{22}\) is used to study the separability of the stretching coordinate from the angular coordinates. In our calculations, the eigenfunctions are given in the following form:

\[
\psi(R, \Omega) = \sum_{i,j_1,j_2,m} C_{i,j_1,j_2,m} \chi_i(R) |j_1,j_2,m\rangle,
\]

where \( \Omega \) represents the angular coordinates and \( \chi_i(R) \)'s are DVR basis functions. In this form, the mixing of \( R \) coordinate with the angular coordinates can be easily evaluated. Assuming the natural expansion of the eigenfunction is given by by

\[
\psi(R, \Omega) = \sum_q d_q F_q(R) G_q(\Omega).
\]

The set of \( d_q \)'s show the separability of \( R \) coordinate from the other coordinates. If \( d_1 \to 1 \), then \( R \) is completely uncoupled from the other coordinates. For a given state, the density kernel \( P \) for the coordinate \( R \) is given by

\[
P(R,R') = \sum_{i,i'} A_{i,i'} \chi^*_i(R') \chi_i(R)
\]

\[
= \sum_q d_q^2 F_q^*(R') F_q(R),
\]

where \( A_{i,i'} \) is given by

\[
A_{i,i'} = \sum_{j_1,j_2,m} C_{i,j_1,j_2,m} C_{i',j_1,j_2,m}.
\]

Diagonalization of \( A \) matrix yields the set of \( \{d_q^2\} \), the population of each natural orbital in \( R \) for the vibrational state in question. The entropy of mixing is calculated as

\[
S = \sum_q -d_q^2 \ln d_q^2.
\]

In the case of perfect separation, \( S \to 0 \). Figure 11 shows the entropy of mixing for the lowest ten \( A^+_1 \) states. Most of the states shown in the figure have quite large entropy of mixing, indicating that the dimer is very loosely bound and the intermolecular motion is very floppy. For the ground state, \( S = 0.08 \), which is consistent with the previous analysis that the ground state is quite localized and harmonic. The fourth \( A^+_1 \) state has better separability than the other excited states. This implies that the out-of-plane torsion is less coupled with the other degrees of freedom since this state has been shown to be solely \( \nu_7 \) excited.

VII. CONCLUSIONS

We have found the intermolecular bound states of carbon dioxide dimer by performing fully coupled four-dimensional quantum calculation for a recently developed PES. The resulting eigenvalues and eigenfunctions have enabled us to study the intermolecular vibrations and the interconversion tunneling motion. We found that the tunneling
motion is effectively quenched for the ground vibrational states due to the high effective tunneling barrier as well as the high reduced mass of the dimer. The analysis of the tunneling splittings for the vibrationally excited states has revealed that the tunneling motion tends to occur within the molecular plane and that the out-of-plane motion contributes little to the interconversion tunneling. Through the analysis of the wave functions, we were able to find the intermolecular vibrational frequencies that are comparable with the experimental values and the normal mode analysis results. These, together with a natural orbital expansion analysis on the eigenfunctions, shows that, except for the ground state, the intermolecular vibrational motions are highly anharmonic and that the intermolecular stretch is closely coupled with the in-plane bending motion.

**ACKNOWLEDGMENTS**

We acknowledge partial support of this research by the NSF CHE-9877086. We also would like to thank Dr. R. Bukowski for providing the potential energy subroutines.

**APPENDIX**

The $F$ matrix is given by $F_{ij} = \partial^2 V / \partial x_i \partial x_j$, evaluated at the potential minimum, with $x_1 = R$, $x_2 = \theta_1$, $x_3 = \theta_2$, and $x_4 = \phi$.

$$
\begin{pmatrix}
2252.10 & 1838.00 & 1838.00 & 0.00 \\
1838.00 & 4527.29 & 3646.00 & 0.00 \\
1838.00 & 3646.00 & 4527.29 & 0.00 \\
0.00 & 0.00 & 0.00 & 291.21
\end{pmatrix}
$$

where the units are cm$^{-1}$ for energy, Å for length, and radian for angles. The $G$ matrix elements are given by

$$
\begin{align*}
G_{RR} &= \frac{1}{\mu}, & G_{\theta\theta} &= 2B + \frac{1}{\mu R^2}, \\
G_{\phi\phi} &= \frac{4B}{\sin^2 \theta}, & G_{\theta\theta} &= \frac{1}{\mu R^2},
\end{align*}
$$

where $R$ and $\theta$ take the values at the minimum configuration. So the $G$ matrix is given as

$$
\begin{pmatrix}
1.533 & 0.000 & 0.000 & 0.000 \\
0.000 & 0.903 & 0.123 & 0.000 \\
0.000 & 0.123 & 0.903 & 0.000 \\
0.000 & 0.000 & 0.000 & 2.123
\end{pmatrix}
$$

The right eigenvectors of the matrix product $GF$ are

$$
\begin{pmatrix}
0.551 & 1.108 & 0.000 & 0.000 \\
0.604 & -0.319 & -0.625 & 0.000 \\
0.604 & -0.319 & 0.625 & 0.000 \\
0.000 & 0.000 & 0.000 & 1.000
\end{pmatrix}
$$

and the normal mode frequencies, which are the square roots of the eigenvalues, are 100.0, 42.8, 26.2, and 24.9 (cm$^{-1}$), respectively.