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CO Dimer: New Potential Energy Surface and Rovibrational Calculations

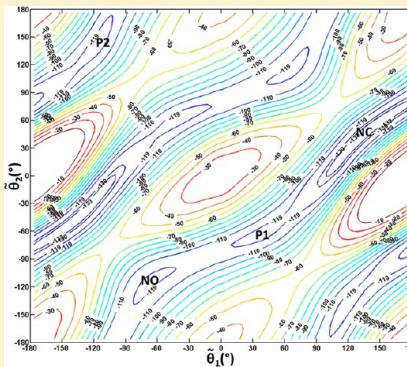
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Supporting Information

ABSTRACT: The spectrum of CO dimer was investigated by solving the rovibrational Schrödinger equation on a new potential energy surface constructed from coupled-cluster ab initio points. The Schrödinger equation was solved with a Lanczos algorithm. Several 4D (rigid monomer) global ab initio potential energy surfaces (PESs) were made using a previously reported interpolating moving least-squares (IMLS) fitting procedure specialized to describe the interaction of two linear fragments. The potential has two nonpolar minima giving rise to a complicated set of energy level stacks, which are very sensitive to the shapes and relative depths of the two wells. Although the CO dimer has defied previous attempts at an accurate purely ab initio description our best surface yields results in good agreement with experiment. Root-mean-square (rms) fitting errors of less than 0.1 cm^{-1} were obtained for each of the fits using 2226 ab initio data at different levels. This allowed direct assessment of the quality of various levels of ab initio theory for prediction of spectra. Our tests indicate that standard CCSD(T) is slow to converge the interaction energy even when sextuple zeta bases as large as ACV6Z are used. The explicitly correlated CCSD(T)-F12b method was found to recover significantly more correlation energy (from singles and doubles) at the CBS limit. Correlation of the core–electrons was found to be important for this system. The best PES was obtained by extrapolation of calculations at the CCSD(T)(AE)-F12b/CVnZ-F12 ($n = 3, 4$) levels. The calculated energy levels were compared to $105 J \leq 10$ levels from experiment. The rms error for 68 levels with $J \leq 6$ is only 0.29 cm^{-1} . The calculated energy levels were assigned stack labels using several tools. New stacks were found. One of them, stack y_1 , has an energy lower than many previously known stacks and may be observable.



I. INTRODUCTION

The CO dimer has intrigued spectroscopists for many years. It has long been understood that the rovibrational levels can be organized into stacks associated with a given symmetry and a value of K , the quantum number for the projection of the angular momentum along the axis joining the two CO monomers. Some of the lowest stacks can be unambiguously associated with one of the two shallow wells on the PES (potential energy surface). At higher energies, the wave functions delocalize, and the stacks cannot be separated into two clearly distinguishable groups.^{1–7}

To compute the rovibrational spectrum of CO dimer, one assumes that it is sufficient because the CO stretch frequencies are much higher than the intermolecular frequencies, to solve a Schrödinger equation with four vibrational coordinates specifying the shape of the dimer and three Euler angles specifying the orientation of the dimer. One way to solve this Schrödinger equation is to expand the potential in terms of coupled angular functions so that all matrix elements of the potential can be determined analytically. Several calculations have been done with this approach.⁸ An alternative is to use quadrature. This has the advantage of obviating the expansion and its associated error. Quadrature can be used with the Lanczos algorithm to calculate a spectrum without computing individual potential

matrix elements. It is only necessary to evaluate matrix-vector products, and this can be done by evaluating sums sequentially.^{9–18} The CO dimer is weakly bound, and it is therefore necessary to use basis functions that span the entire configuration space of the molecule. This is easily done if one uses the polar-type coordinates commonly referred to as polyspherical coordinates.¹⁹ Owing to the fact that it is not necessary to store the Hamiltonian matrix, it is straightforward to increase the number of basis functions and the number of quadrature points to ensure that the energy levels are converged. The accuracy of spectrum obtained from the Lanczos calculation is limited only by the quality of the PES.

To make a good PES for CO dimer, one needs both a very accurate ab initio method and an excellent fitting procedure. The spectrum is very sensitive to the relative depths and the shapes of the two wells. There was some debate in the literature between 1999 and 2001 regarding the accuracy of CCSD(T) for this system.^{20–22} A SAPT based diagrammatic analysis of

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correlation contributions revealed that fifth-order terms neglected in CCSD(T) (for any system) might be particularly relevant for $(CO)_2$.²⁰ It was not determined at that time what the practical limitations would be for the accuracy of a CCSD(T)-based PES at the complete basis limit. If a consensus was reached, it was that electron correlation is very important in this system and that describing it requires large bases. In 2003, Vissers et al., nevertheless, constructed a CCSD(T)-based ab initio PES producing fairly good agreement with experiment.²³ In 2005, Vissers et al. revisited the system producing a DFT-SAPT based PES.⁸ Whereas on the CCSD(T) PES the order of the a and c stacks did not agree with experimental results because the difference in depths of the two wells was not large enough, on the DFT-SAPT PES, the order was correct but the depth difference was too large. This motivated the development of an empirically adjusted hybrid PES. It was made by mixing CCSD(T) and DFT-SAPT surfaces and choosing the mixture so that the gap between the lowest two energy levels nearly precisely agrees with experimental results.

In this article, we use CBS extrapolated CCSD(T)-F12b/CVnZ-F12 ab initio methods and also test the correlation of all electrons. Our results confirm the importance of high-order correlation as well as large basis sets. As discussed in more detail below, the perturbative triples (T) contribute roughly 1/3 of the well depths. We also note the slow convergence of standard CCSD(T) with basis set and clearly benefit in this regard from the more recently developed explicitly correlated F12 methods. Our surface is built using an interpolated moving least-squares (IMLS) fitting (interpolation) method, which is flexible and enables us to obtain an excellent fit with a small number of points. An root-mean-square (rms) fitting error of less than 0.1 cm⁻¹ was obtained using 2226 points. The negligible fitting errors obtained for this system allow direct evaluation of the performance of different basis set levels and the effects of core–electron correlation. The best surfaces of this article are comparable in accuracy to the hybrid surface of Vissers et al.,⁸ but they are pure ab initio surfaces: they contain no empirical adjustments. Even the distribution of ab initio points is determined by the fitting program.

II. POTENTIAL ENERGY SURFACES

A. IMLS Fitting. Different types of fitting/interpolation methods are used to obtain PESs.^{24–33} We use an interpolating moving least-squares approach that has been shown to be very accurate for van der Waals molecules.^{34–36} The four dimensional (4D) intermolecular (CO_2) potentials are each built from 2226 high-level ab initio energy points and are

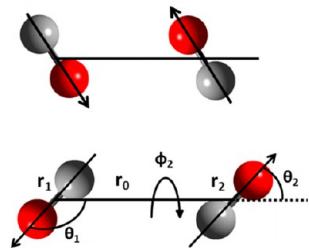


Figure 1. Coordinates used to define dimer geometries. Length of r_0 , center-of-mass separation, angles of CO vectors (r_1 and r_2) with respect to r_0 (θ_1 and θ_2), and torsional angle from r_1 to r_2 around r_0 (ϕ_2). The local (O-in) (upper) and global (C-in) (lower) nonpolar shapes are shown.

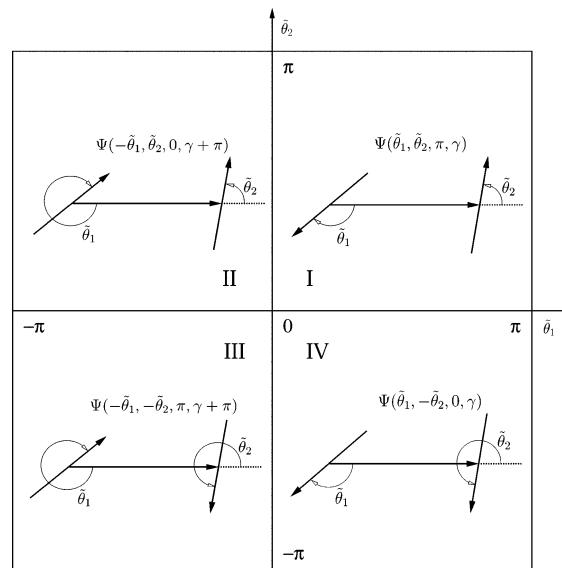


Figure 2. Definition of the extended angles $(\tilde{\theta}_1, \tilde{\theta}_2)$. In our convention, monomer 1 is left of monomer 2, and the positive directions for $\tilde{\theta}_1$ and $\tilde{\theta}_2$ are clockwise and counter-clockwise, respectively. The extended angles are defined: $\tilde{\theta}_1 = \theta_1$ and $\tilde{\theta}_2 = \theta_2$ (quadrant I); $\tilde{\theta}_1 = -\theta_1$ and $\tilde{\theta}_2 = \theta_2$ (quadrant II); $\tilde{\theta}_1 = -\theta_1$ and $\tilde{\theta}_2 = -\theta_2$ (quadrant III); $\tilde{\theta}_1 = \theta_1$ and $\tilde{\theta}_2 = -\theta_2$ (quadrant IV). The rovibrational wave functions $\Psi(\tilde{\theta}_1, \tilde{\theta}_2, \gamma)$, plotted in Figures 8–11, are obtained, in each of the four quadrants, from the computed wave functions $\Psi(\tilde{\theta}_1, \tilde{\theta}_2, \phi_2, \gamma)$ as indicated in this figure.

Table 1. Geometric Parameters for Local O-in-Minimum Isomer of CO Dimer (Rigid Monomers); Distances Are in Angstroms and Angles Are in Degrees. The Energy of the Local Minimum is -119.5479 cm⁻¹

coordinate ^a	local minimum				
	Val. TZ ^b	Val. QZ ^b	AE TZ ^c	AE QZ ^c	CBS(AE) ^d
r_0	3.6337	3.6288	3.6443	3.6282	3.6277
θ_1	64.48	65.19	64.09	65.19	65.21
θ_2	115.52	114.81	115.91	114.81	114.79
ϕ_2	180.00	180.00	180.00	180.00	180.00

^aSee Figure 1 (upper). ^bCCSD(T)-F12b/VnZ-F12 ($n = 3$ “TZ” or 4 “QZ”) with valence electrons correlated. ^cCCSD(T)-F12b/CVnZ-F12 ($n = 3$ “TZ” or 4 “QZ”) with all electrons correlated. ^dCBS extrapolation of all-electron calculations using CVTZ-F12 and CVQZ-F12 bases, optimized on the fitted IMLS PES CBS_PL. Monomer bond distances were frozen at $R_{CO} = 1.1282$ Å.

represented analytically with an interpolating moving least-squares (IMLS) method using a weight function to interpolate between local fitting basis expansions. The same specialized and automated procedure that was developed to construct 4D PESs for $(NNO)_2$ and $(OCS)_2$ was employed here.^{34,36} Jacobi type coordinates (see Figure 1) and a fitting basis of 301 functions composed of products of radial functions with associated Legendre bend functions was used at each data point. The maximum value of the Legendre l index is $l_{max} = 6$, and the maximal radial power is also 6. The previously described distance metric, interpolative weight function, and SVD-based dynamic conditioning procedure were also used.³⁴ For $(CO)_2$, the range of intermonomer center-of-mass distances was $r_0 = [2.64, 15.0]$ Å. The fitted energy range includes all stable isomers and extends from the global minimum (with a well depth of ~ 135 cm⁻¹) to 3.0 kcal/mol (~ 1050 cm⁻¹) above the

Table 2. Geometric Parameters for Global C-in-Minimum Isomer of CO Dimer (Rigid Monomers); Distances Are in Angstroms and Angles Are in Degrees. The Energy of the Global Minimum is $-135.1448 \text{ cm}^{-1}$

coordinate ^a	global minimum				
	Val. TZ ^b	Val. QZ ^b	AE TZ ^c	AE QZ ^c	CBS(AE) ^d
r_0	4.3433	4.3338	4.3447	4.3309	4.3306
θ_1	134.44	134.52	134.42	134.54	134.58
θ_2	45.56	45.48	45.58	45.46	45.42
φ_2	180.00	180.00	180.00	180.00	180.00

^aSee Figure 1 (lower). ^bCCSD(T)-F12b/VnZ-F12 ($n = 3$ "TZ" or 4 "QZ") with valence electrons correlated. ^cCCSD(T)-F12b/CVnZ-F12 ($n = 3$ "TZ" or 4 "QZ") with all electrons correlated. ^dCBS extrapolation of all-electron calculations using CVTZ-F12 and CVQZ-F12 bases, optimized on the fitted IMLS PES CBS_PL. Monomer bond distances were frozen at $R_{\text{CO}} = 1.1282 \text{ \AA}$.

separated monomers asymptote. To avoid computing and discarding costly high-level ab initio data in highly repulsive regions, an initial lower-level guide surface was constructed using a set of 1600 symmetry unique points distributed

according to a Sobol sequence. The points were distributed according to an exponential r_0 -dependent bias that favors points at $r_0 = 2.64 \text{ \AA}$ over points at $r_0 = 15.0 \text{ \AA}$ by a factor of ~ 20 (making the short-range repulsive region much more densely sampled). The guide surface was fit using the same IMLS scheme as the final high-level PESs, but with a smaller fitting basis of only 40 functions per local expansion. For the high-level PESs, 1500 initial seed points were distributed the same way, according to the exponentially radially biased Sobol sequence, but with high-energy regions excluded by the lower level guide surface. Starting from the 1500 seed points, sets of 48 automatically determined points were added in each of a series of iterations until the procedure was stopped at 2226 ab initio data. Our procedure to estimate the fitting error at each iteration has been described before, and remarkably for this system, the estimated rms fitting error is below 0.1 cm^{-1} with 2226 points. This estimate was confirmed to be accurate using a test set of 1152 randomly generated test points not included in the fit. This error is more than an order of magnitude smaller than the $1\text{--}2 \text{ cm}^{-1}$ rms fitting errors achieved by the same fitting method for $(\text{NNO})_2$ and $(\text{OCS})_2$ whose data sets include 1757 and 2914 data, respectively. We attribute this to

Table 3. Convergence Behavior of Individual Energy Components for the CO-Monomer, and Two Nonpolar Isomers (Local Minimum, O-in, Denoted NO), and the Global C-in Minimum Denoted NC; All Values are in Hartree^a

CCSD(T)-F12b		monomer		
n	reference	CCSD-F12 corr.	(T)	total
2	-112.78794954	-0.496634983	-0.01583488	-113.30042425
3	-112.79045422	-0.50953004	-0.01895233	-113.31893660
4	-112.79075814	-0.51220972	-0.01981689	-113.32278475
CCSD(T)		monomer		
n	HF	CCSD corr.	(T)	total
3	-112.78209430	-0.46929223	-0.01868284	-113.27006936
4	-112.78928716	-0.49648596	-0.01989151	-113.30566462
5	-112.79072980	-0.50539105	-0.02029467	-113.31641552
6	-112.79088180	-0.50784702	-0.02039638	-113.31912521
CCSD(T)-F12b		NO		
n	reference	CCSD-F12 corr.	(T)	total
2	-225.57577281	-0.99377259	-0.03178191	-226.60132732
3	-225.58077973	-1.01958965	-0.03802998	-226.63839937
4	-225.58138077	-1.02496247	-0.03976465	-226.64610789
CCSD(T)		NO		
n	HF	CCSD corr.	(T)	total
3	-225.56409437	-0.93919814	-0.03750170	-226.54079421
4	-225.57845762	-0.99355113	-0.03991876	-226.61192751
5	-225.58132393	-1.01135092	-0.04072563	-226.63340048
6	-225.58162681	-1.01625841	-0.04092920	-226.63881442
CCSD(T)-F12b		NC		
n	reference	CCSD-F12 corr.	(T)	total
2	-225.57554424	-0.99401882	-0.03180595	-226.60136901
3	-225.58055090	-1.01983131	-0.03805802	-226.63844024
4	-225.58115417	-1.02521501	-0.03979875	-226.64616793
CCSD(T)		NC		
n	HF	CCSD corr.	(T)	total
3	-225.56387504	-0.93946155	-0.03753300	-226.54086960
4	-225.57823696	-0.99380449	-0.03995168	-226.61199312
5	-225.58109834	-1.01159397	-0.04075877	-226.63345108
6	-225.58140077	-1.01650121	-0.04096252	-226.63886450

^aCCSD(T)-F12b(AE)/CVnZ-F12 and CCSD(T)(AE)/ACVnZ (see text for details).

Table 4. Convergence Behavior of Isomer Well Depths for the Two Nonpolar Isomers (Local Minimum, O-in, Denoted NO, and the Global C-in Minimum, Denoted NC); the Middle Column Lists Well-Depths Computed without the Triples (T) Correction, while the Rightmost Column Adds the (T) Correction^a

CCSD(T)-F12b		NO well depth (cm ⁻¹)	
<i>n</i>		CCSD-F12b	CCSD(T)-F12b
2		-80.5	-105.1
3		-88.0	-115.5
4		-89.4	-118.2
CCSD(T)		NO well depth (cm ⁻¹)	
<i>n</i>		CCSD	CCSD(T)
3		-114.0	-143.9
4		-101.5	-131.3
5		-95.1	-125.0
6		-93.8	-123.8
CCSD(T)-F12b		NC well depth (cm ⁻¹)	
<i>n</i>		CCSD-F12b	CCSD(T)-F12b
2		-84.3(-3.9)	-114.2(-9.1)
3		-90.8(-2.8)	-124.5(-9.0)
4		-95.1(-5.7)	-131.3(-13.1)
CCSD(T)		NC well depth (cm ⁻¹)	
<i>n</i>		CCSD	CCSD(T)
3		-123.7(-9.7)	-160.4(-16.5)
4		-108.7(-7.2)	-145.7(-14.4)
5		-98.9(-3.8)	-136.1(-11.1)
6		-97.5(-3.7)	-134.8(-11.0)

^aComparison is between explicitly correlated CCSD(T)-F12b(AE)/CVnZ-F12 and standard CCSD(T)(AE)/ACVnZ. Values in parentheses are the difference in well depths between the global and local minima.

the nearly spherical effective shape of the CO monomers, smaller energy range, and simpler topography with fewer minima than the other systems, which have longer more aspherical triatomic monomers. The use of an interpolative fitting strategy with negligible fitting errors permits meaningful assessment of different levels of ab initio theory. As discussed further below, our best PES has a difference in well depths between the global and local minima of 15.59 cm⁻¹ compared to a difference of 15.9 cm⁻¹ on the empirically adjusted hybrid PES of Vissers et al.⁸ The rovibrational energy level stacks in the (CO)₂ system are extremely sensitive to the shapes and relative depths of the two wells. According to our results, levels computed on two very high-level PESs with well depth differences that are as small as 3–5 cm⁻¹ differ significantly. Vissers et al. used a noninterpolative fitting strategy and report fitting errors of ~3 cm⁻¹ in the neighborhood of a spurious minimum (see Figure 3 of ref 8), making it harder to draw conclusions about the underlying methods (CCSD(T) and DFT-SAPT) included in their adjusted hybrid. Here, using an interpolative approach with high-fidelity to the data, we have separately fit PESs using different basis sets and CBS extrapolation schemes, and compared valence-only correlation with all-electron calculations. The PESs only took about 2–3 days each to generate using 48 cores running in parallel on a dedicated Linux based HPC cluster.

The coordinates chosen for fitting the PES and calculating the rovibrational levels and wave functions are defined in Figure 1. To facilitate understanding of the large amplitude motion,

the PES and wave functions are plotted in extended coordinates. They are defined in Figure 2. The extended coordinates are $\tilde{\theta}_1$ and $\tilde{\theta}_2$. They are defined in $[-\pi, \pi]$ and have a period of 2π . The $[-\pi, 0]$ range of the extended angle of Surin et al. coincides with the $[\pi, 2\pi]$ range of our extended theta. The advantage of the extended coordinates, as pointed out by Hougen and Ohashi,³⁷ is that the large amplitude but planar motion that links the two nonpolar isomers (the global minimum is at $\varphi_2 = \pi$) and the polar saddle points are easily recognized without exiting and re-entering the PES and wave function plots. The large amplitude motion is best understood in terms of the coordinate $X = (\tilde{\theta}_1 + \tilde{\theta}_2)/2$. A complete disrotatory cycle ($X = 0$ to 2π) can be traced on a 2-d potential plot in the extended coordinates (energy minimized with respect to other coordinates). See, for example, Figure 3 of ref 35. A disadvantage of the extended coordinates is that each molecular shape appears twice on the 2-d potential plot.

The extended coordinates for continuously examining the shape of the wave function are defined in Figure 2 and more details are given in section III.

B. Electronic Structure Theory. Masses of 15.9949146221 and 12 u were used for ¹⁶O and ¹²C, respectively. To facilitate comparison with the work of Vissers, the same rigid monomer CO distances were used: $R_{\text{CO}} = 2.132$ bohr (1.1282 Å) corresponding to $B_{\text{CO}} = 1.9317$ cm⁻¹.^{8,1} The size-consistent coupled-cluster CCSD(T) method was chosen to represent the vdW interaction between the two closed-shell CO monomers. The Molpro electronic structure code was used for all of the calculations reported here.³⁸ To assess the applicability of a single-reference method, the T₁-diagnostic was evaluated at various geometries, and all values were below 0.02, presumably indicating that the CCSD(T) single-reference method is appropriate for this system. Interestingly, however, calculations of 1D PECs (given in Supporting Information) for the monomer stretch found that a multireference description produced vibrational levels for the monomer in much better agreement with experiment than the highest affordable level of single-reference calculations. This is true even for the lowest few monomer vibrational levels, which are localized in a region of the potential with no obvious breakdown of the CCSD(T) method (e.g., at $R_{\text{CO}} = 1.3$ Å, the T₁-diagnostic is still only 0.025, and the leading reference coefficient in a multireference calculation is 0.93). Nevertheless, higher-order correlation is known to be important for the (CO)₂ vdW dimer interaction, so we settled on the CCSD(T) method (which includes triples perturbatively) for the rigid monomer PESs. On the basis of our experience with the (NNO)₂ and (OCS)₂ systems, we focus primarily on the explicitly correlated CCSD(T)-F12b method but also perform some benchmarks using standard CCSD(T). The experimental spectra involve states localized in two wells corresponding to nonpolar isomers (a local-O-in and the global-C-in minimum, see Figure 1). To test the severity of the rigid monomer approximation and the effects of core-correlation, optimized geometries were located for the two minima at the explicitly correlated CCSD(T)-F12b/VnZ-F12 ($n = 3, 4$) levels with only the valence electrons correlated, and also at the CCSD(T)-F12b/CVnZ-F12 ($n = 3, 4$) levels with all electrons correlated. The effect of CBS extrapolation was also explored using a fitted IMLS PES. In addition, fully relaxed geometries were located for the two dimer minima as well as for the isolated monomer (with all electrons correlated). As shown in Tables 1 and 2, the geometric parameters of the two isomers

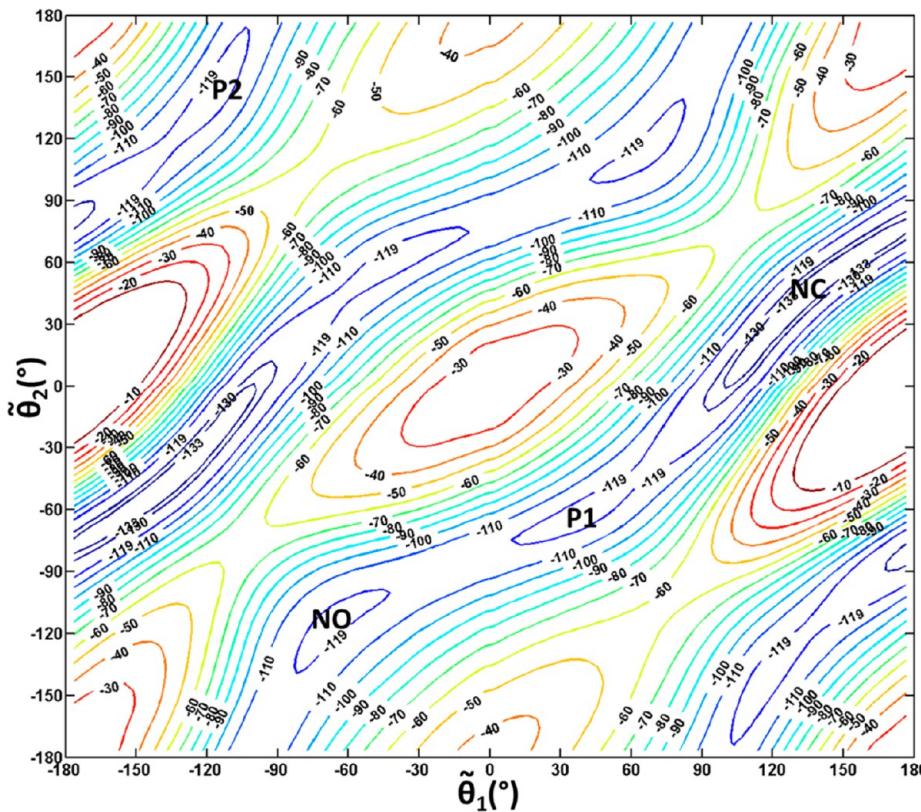


Figure 3. Plot of the IMLS PES fit to data at the CCSD(T)-F12b(AE)/CBS_PL level (see text). The coordinates are shown in Figures 1 and 2. Only planar geometries are shown. φ_2 is either π or 0 (see Figure 2). For each pair of angles, the intermonomer distance (r_0) is optimized to minimize the energy. The energy origin is chosen so that $V(r_0 = \infty) = 0$. A nearly barrierless disrotatory path starting at the global minimum NC passes through P1, arrives at NO, and continues through P2 arriving back at NC. NC, $E = -135.14 \text{ cm}^{-1}$; P1, $E = -121.06 \text{ cm}^{-1}$; NO, $E = -119.55 \text{ cm}^{-1}$.

do not depend strongly on basis set or core-correlation for these high-accuracy methods.

The largest variations are noted for the local minimum (O-in) structure (Table 1) where the trend with larger basis sets is toward shorter intermonomer distances (r_0), reaching 3.620 Å at the CBS limit in the all-electron calculations. Comparing our isomer structures to those reported by Vissers and co-workers for their empirically adjusted PES,¹ it is interesting to note that their global minimum (C-in) isomer is very similar to ours, but the O-in minimum differs significantly. For the global minimum, they report $r_0 = 4.33 \text{ \AA}$ and $\theta_1 = 134.2^\circ$ compared with $r_0 = 4.331 \text{ \AA}$ and $\theta_1 = 134.79^\circ$ from our CBS(AE) calculations (see Table 2). For the O-in minimum, they report $r_0 = 3.67 \text{ \AA}$ and $\theta_1 = 61^\circ$ compared with $r_0 = 3.620 \text{ \AA}$ and $\theta_1 = 65.18^\circ$ from our CBS(AE) calculations (see Table 1). Both coordinates differ significantly (there are only two independent coordinates for these C_{2h} structures). They adjusted their PES to match only the energy gap between the lowest levels of the a and c stacks.

The rigid monomer approximation appears to be particularly good in this system. The PESs were computed with the monomer bond distances frozen at $R_{\text{CO}} = 1.1282 \text{ \AA}$. The optimized bond distance for the isolated monomer at the CCSD(T)-F12b(AE)/CVQZ-F12 level is 1.1279 Å. Fully relaxed optimizations for the two dimer isomers at the same level produce monomer distances of $R_{\text{CO}} = 1.1277$ and 1.1280 Å in the global and local minima, respectively. The differences between the rigid and relaxed structures are orders of magnitude smaller than what has been noted in hydrogen-bonded systems such as $(\text{H}_2\text{O})_2$ and $(\text{NH}_3)_2$.

The geometries optimized at the CCSD(T)-F12b(AE)/CVQZ-F12 level were used to benchmark contributions to the interaction energy of each isomer. Table 3 shows how the reference, CCSD-F12b correlation energy, and triples (T) contributions converge with the basis set for CCSD(T)-F12b(AE)/CVnZ ($n = 2-4$). Also shown are the corresponding contributions for standard CCSD(T) and the ACVnZ ($n = 3-6$) basis series (HF, CCSD correlation, and (T) triples). The reference energy tabulated for the explicitly correlated F12b method is known as the new reference energy within the Molpro code and is the sum of the HF energy and a small F12 singles correction.

It is remarkable how much lower the total energy is with the F12b method compared with standard CCSD(T). This is true even when a sextuple-zeta basis is used for the standard CCSD(T) and only a quadruple- ζ basis is used for the CCSD(T)-F12b calculations. The difference comes from the singles and doubles correlation energy (as expected). Looking at the CCSD correlation energy (from standard CCSD) for any of the structures and comparing the ACV5Z and ACV6Z bases, that contribution appears to have nearly converged, yet the corresponding contribution from the explicitly correlated method (CCSD-F12b) is much larger. Not surprisingly, the reference (or HF) energies are quite well converged by the largest bases applied to each method. The triples contribution is not directly included in the F12 procedure, so similar contributions from (T) are obtained at each zeta level (standard CCSD(T) recovers the largest triples contribution with the sextuple-zeta basis). There is a rather large increase in the triples contribution going from double- to triple- ζ (in the

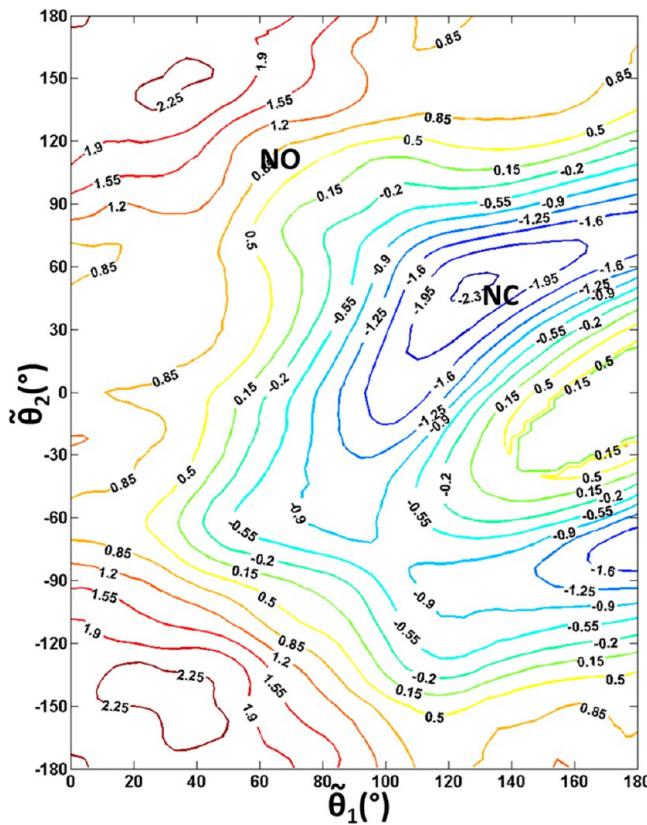


Figure 4. Effects of core-correlation. Same as that of the right side of Figure 3, but representing the difference between PESs with and without core-correlation at the CBS level (the CCSD(T)-F12b/CBS PES is subtracted from the CCSD(T)-F12b(AE)/CBS PES). With core-correlation, the NO well is raised slightly (positive difference), while NC is slightly deeper. Core-correlation also changes the shape of the NC well (making the walls slightly steeper). The difference at NC is -2.1 cm^{-1} .

F12b results), followed by smaller subsequent increases. It is clear that any CBS extrapolation scheme will arrive at much lower total energy when processing the F12b data.

Table 4 shows the well depths of the NO and NC isomers using the energy data in Table 3. The progression (with basis set) of each well depth and the difference between the two wells is shown for each method. The importance of higher-order correlation to the interaction energy has been discussed previously in the literature. In Table 4, the well depths are computed with and without the triples (T) contribution. Remarkably, adding the triples correction deepens the wells by between 30 and 40%. Our best PES (for predicting the rovibrational spectrum) includes CBS extrapolation and has a difference between wells of 15.59 cm^{-1} . The empirically adjusted PES of Vissers has a difference of 15.9 cm^{-1} .⁸ It is worth noting that the progression with basis set of standard CCSD(T) (listed in Table 4) appears to have nearly converged at the sextuple-zeta level, but would be less than 11 cm^{-1} at the CBS limit. In contrast, the explicitly correlated progression is 9.0 for triple- ζ and 13.1 for quadruple- ζ . Thus, depending on which CBS extrapolation scheme is chosen, a value very close to the empirical value of 15.9 (by Vissers) is obtained by extrapolating the F12 data.

The rigorousness of the various CBS extrapolation schemes in common use is questionable. Feller et al. have developed several CBS schemes and have even reported using the average

of five different methods stating that no particular scheme was more justified.³⁹ We fit a total of seven PESs, four of which use CBS extrapolation. The first three include only valence electron correlation, the first two of which are at the CCSD(T)-F12b/VnZ-F12 ($n = 3, 4$) levels, while the third estimates the CBS limit from the first two methods using the l^{-3} formula. Four PESs were made, which include correlation of the core-electrons (AE). The first is at the CCSD(T)-F12b(AE)/CVQZ-F12 level. Three more were made using CBS extrapolation. The first uses data from the CCSD(T)(AE)-F12b/CVnZ-F12 ($n = 3, 4$) levels and the l^{-3} formula (denoted CBS_L3), while the last two are made with CBS schemes that also include data at the double- ζ CCSD(T)(AE)-F12b/CVDZ-F12 level, the first applying Peterson's mixed Gaussian and exponential scheme (CBS_GE), and the last applying separate extrapolation of components of the energy using an optimized power law (CBS_PL).³⁹ Although explicitly correlated methods produce very well-converged data even at the double- ζ level, it is clear from the well depth data in Table 4 that the double- ζ F12 data is much further from the CBS limit than the triple and quadruple- ζ data. The double- ζ data was computed because the last two CBS schemes require data from three different zeta levels. The differences in well depths for the three all-electron CBS surfaces are 16.25 , 15.94 , and 15.59 cm^{-1} for the CBS_L3, CBS_GE, and CBS_PL PESs, respectively. All of these PESs are very similar. Perhaps fortuitously, by a small margin, the CBS_PL PES produced the best agreement with experimental rovibrational levels. This is despite the fact that the energy difference between wells is 15.94 cm^{-1} on the CBS_GE PES (very close to the empirically adjusted value of 15.9 cm^{-1} by Vissers). The shape of the wells is also clearly important, and as discussed above, our PESs place the local minimum in a significantly different location than their hybrid PES. Figure 3 shows the CBS_PL PES, which includes all-electron correlation. The main effects of core-correlation are appreciated by the difference plot shown in Figure 4. Core-correlation raises the energy of the local minimum (very slightly), while also tightening the global minimum well.

III. ROVIBRATIONAL CALCULATIONS

A. Kinetic Energy Operator and Basis Functions. The polyspherical coordinates defined in Figure 1 are used to compute the energy levels. The molecule-fixed (MF) frame is attached so that the z -axis is along \mathbf{r}_0 and the x -axis is along $\mathbf{r}_0 \times \mathbf{r}_1 \times \mathbf{r}_0$. The kinetic energy operator in these coordinates is well-known.^{19,40,41} We use a basis composed of products of discrete variable representation (DVR) functions^{42–45} for the stretch coordinate and parity-adapted rovibrational functions^{46,18} for the bend and rotational coordinates. The parity-adapted basis makes it possible to calculate even and odd parity levels separately. A complete product basis function is

$$f_{\alpha 0}(\mathbf{r}_0) u_{l_1 l_2 m_2 K}^{\text{JMP}}(\theta_1, \theta_2, \varphi_2; \alpha, \beta, \gamma) \quad (1)$$

where $f_{\alpha 0}(\mathbf{r}_0)$ is a DVR function, $u_{l_1 l_2 m_2 K}^{\text{JMP}}$ is a parity adapted rovibrational function, and α , β , and γ are Euler angles. $P = 0$ and 1 correspond to even and odd parity, respectively.

B. Symmetry Adapted Lanczos Eigensolver. Using a symmetry adapted variant^{47,48} of the Cullum and Willoughby⁴⁹ Lanczos method to compute the energy levels makes it possible to do a single calculation for each parity block to obtain both states that are symmetric and states that are antisymmetric with respect to permuting the two CO monomers. Eigenvalues are

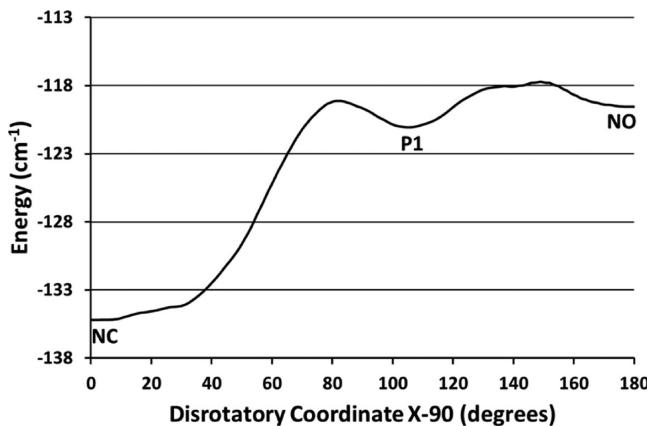


Figure 5. Disrotatory path starting at the global minimum NC (0 degrees displacement), passes through P (105 degrees displacement), and arrives at NO (180 degrees displacement). NC, $E = -135.14 \text{ cm}^{-1}$; P, $E = -121.06 \text{ cm}^{-1}$; NO, $E = -119.55 \text{ cm}^{-1}$ (see also Figure 2).

obtained by computing matrix-vector products. Similar techniques have been used to compute energy levels of many molecules.^{50,14,10,43} The full permutation-inversion (PI) symmetry group for the Hamiltonian we use is G_4 , composed of operations where σ_{ex} permutes monomer 1 with monomer 2. A/B label symmetric and antisymmetric irreducible representations (irreps) with respect to σ_{ex} and \pm label even and odd parities. There are four PI irreps: (A+, B+, A-, B-). Only A+ and A- states are allowed for $^{12}\text{C}^{16}\text{O}$ dimer due to nuclear spin statistics. To use the symmetry-adapted Lanczos algorithm within each parity block to obtain the A states, one must apply

projection operators. Kinetic energy matrix-elements are given in refs 39 and 40. Potential matrix-vector products are evaluated by using quadrature and doing sums sequentially, as explained in ref 39. The wave functions are obtained from eigenvectors of the Hamiltonian matrix that are computed as described previously.⁵¹

C. Calculation Parameters. The bases for the rovibrational calculations have been tested to ensure good convergence. The rovibrational levels we report are computed with an angular basis having $l_{\max} = m_{\max} = 14$ (the same l_{\max} for l_1 and l_2) together with 16 Gauss-Legendre quadrature points for θ_1 and θ_2 and 32 equally spaced trapezoid points in the range $[0, 2\pi]$ for φ_2 , with the first point zero. For r_0 , we use 80 sine DVR functions in the range [6.0 bohr, 28.0 bohr]. Convergence errors for vibrational levels calculated with this basis are all smaller than 0.003 cm^{-1} up to 32 cm^{-1} above the zero-point energy (ZPE). The convergence errors are obtained by comparing with levels calculated using a larger benchmark basis and quadrature grid, for which $l_{\max} = m_{\max} = 18$, $n_\theta = 20$, $n_{\varphi_2} = 40$ and has 120 sine DVR functions in the range [6.0 bohr, 28.0 bohr]. As a comparison, Vissers et al. use $l_{\max} = m_{\max} = 10$ and 15 radial wave functions of a minimized 1-d r_0 potential.⁸ Given the two nearly isoenergetic isomers, it is prudent to use a large number of sine DVR functions, which, unlike eigenfunctions of a reference potential, are not biased toward one of the two isomers.

The vibrational even-parity basis size is 99 200, built from 1240 even-parity angular basis functions. We use a potential ceiling of 1200 cm^{-1} to reduce the spectral range.⁵³ The monomer rotational constant is taken to be the experimental ground state value of $1.9225125 \text{ cm}^{-1}$.^{52,53} Vissers et al. use $B = 1.9317 \text{ cm}^{-1}$ consistent with the equilibrium value of the bond

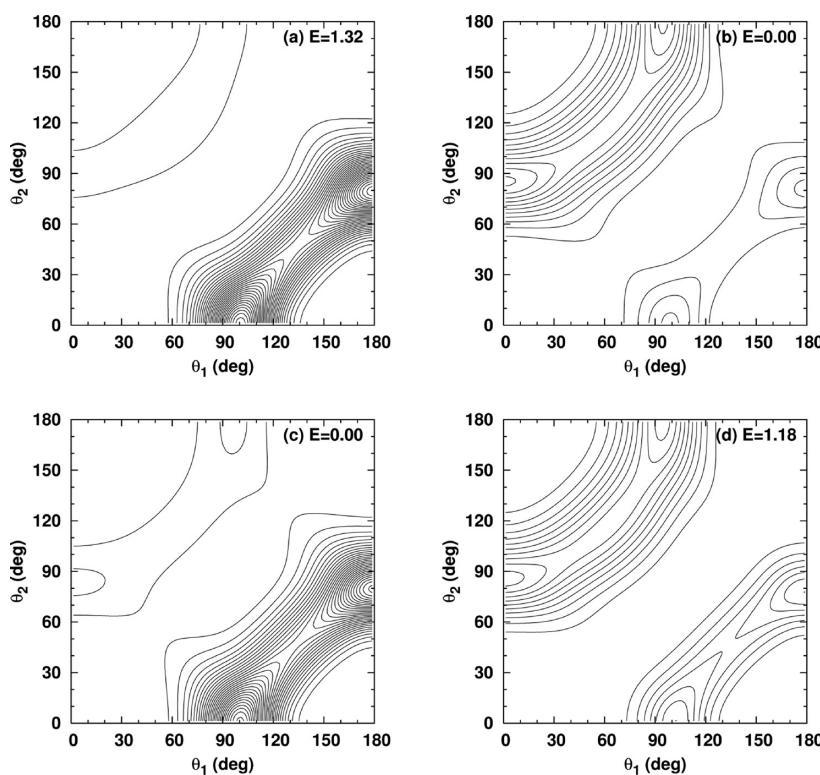


Figure 6. PD plots for the first two A+ vibrational states with $E_0 = 1.316 \text{ cm}^{-1}$ (a) and 0 cm^{-1} (b) relative to a ZPE of -81.101 cm^{-1} for PES CBS_val and with $E_0 = 0 \text{ cm}^{-1}$ (c) and 1.180 cm^{-1} (d) relative to a ZPE of -80.528 cm^{-1} for PES CBS_PL. The two left panels are the C-bonded isomer, and the two right panels are the O-bonded isomer. The contour interval is 0.05 for all PD plots.

Table 5. A+ Rovibrational Levels (in cm^{-1}) of CO Dimer^a

stack	E_0 (tw)	E_0 (expt)	Δ_1	Δ_2	K	c_1	c_2	$\langle B_0 \rangle$
l	9.964	10.088	-0.12	-0.07	2	0.98d		0.0626
<i>J</i> = 0, A+								
<i>a</i>	0.000	0.000			0	1.00s		0.0653
<i>c</i>	1.180	0.877	0.30	0.01	0	1.00s		0.0773
<i>m</i>	6.854	7.077	-0.22	-0.21	0	1.00s		0.0728
<i>r</i>	11.733	11.874	-0.14	-0.01	0	1.00s		0.0692
	18.089				0	1.00s		0.0732
<i>J</i> = 1, A+								
<i>b</i>	2.601	2.654	-0.05	-0.02	1	1.00p		0.0632
<i>d</i>	3.056	2.934	0.12	-0.10	1	1.00p		0.0802
<i>g</i>	8.368	8.644	-0.28	-0.23	1	1.00p		0.0723
<i>x</i> ₂	12.787				1	1.00p		0.0689
<i>x</i> ₅	17.683				0	0.91s	0.09p	0.0756
	18.110				1	0.92p	0.08s	0.0761
<i>J</i> = 2, A+								
<i>a</i>	0.379	0.382	0.00	0.00	0	1.00s		0.0648
<i>c</i>	1.621	1.311	0.31	0.00	0	0.99s		0.0777
<i>b</i>	2.842	2.893	-0.05	-0.02	1	0.99p		0.0629
<i>d</i>	3.351	3.227	0.12	-0.12	1	1.00p		0.0805
<i>m</i>	7.277	7.505	-0.23	-0.22	0	1.00s		0.0727
<i>n</i> ^c	8.145	8.400	-0.26	-0.25	2	1.00d		0.0824
<i>g</i>	8.622	8.896	-0.27	-0.24	1	0.99p		0.0722
<i>l</i>	9.599	9.725	-0.13	-0.06	2	0.99d		0.0625
<i>r</i>	12.126	12.267	-0.14	-0.02	0	1.00s		0.0692
<i>x</i> ₁	12.506				2	1.00d		0.0725
<i>x</i> ₂	13.048				1	1.00p		0.0690
<i>x</i> ₄	16.148				2	1.00d		0.0694
<i>J</i> = 3, A+								
<i>b</i>	3.212	3.261	-0.05	-0.01	1	1.00p		0.0626
<i>d</i>	3.837	3.711	0.13	-0.12	1	1.00p		0.0807
<i>n</i> ^c	8.618	8.870	-0.25	-0.25	2	0.99d		0.0823
<i>g</i>	9.049	9.328	-0.28	-0.24	1	0.98p		0.0721
<i>x</i> ₁	12.926				2	0.99d		0.0724
<i>x</i> ₂	13.441				1	0.99p		0.0690
<i>x</i> ₃	15.535				3	1.00f		0.0834
<i>x</i> ₄	16.536				2	0.99d		0.0694
<i>x</i> ₅	18.283				0	0.77s	0.22p	0.0756
	18.973				1	0.79p	0.20s	0.0757
<i>J</i> = 4, A+								
<i>a</i>	1.251	1.259	-0.01	0.00	0	1.00s		0.0640
<i>c</i>	2.658	2.340	0.32	-0.01	0	0.97s	0.03p	0.0782
<i>b</i>	3.684	3.725	-0.04	-0.02	1	0.98p		0.0625
<i>d</i>	4.411	4.283	0.13	-0.13	1	0.98p		0.0808
<i>m</i>	8.261	8.502	-0.24	-0.23	0	0.99s		0.0725
<i>n</i>	9.247	9.496	-0.25	-0.26	2	0.98d		0.0821
<i>g</i>	9.531	9.802	-0.27	-0.22	1	0.95p	0.04d	0.0720
<i>l</i>	10.450	10.571	-0.12	-0.07	2	0.96d	0.03p	0.0627
<i>r</i>	13.045	13.185	-0.14	-0.04	0	0.99s		0.0693
<i>x</i> ₁	13.485				2	0.97d		0.0722
<i>x</i> ₂	13.964				1	0.98p		0.0691
<i>x</i> ₃	16.177				3	0.99f		0.0833
<i>x</i> ₄	17.056				2	0.98d		0.0695
<i>J</i> = 5, A+								
<i>b</i>	4.302	4.345	-0.04	-0.01	1	1.00p		0.0623
<i>d</i>	5.250	5.115	0.14	-0.15	1	0.99p		0.0808
<i>n</i>	10.030	10.276	-0.25	-0.27	2	0.96d	0.04p	0.0816
<i>g</i>	10.268	10.548	-0.28	-0.23	1	0.91p	0.10d	0.0719
<i>l</i>	11.066	11.184	-0.12	-0.07	2	0.93d	0.07p	0.0631
<i>x</i> ₁	14.181				2	0.95d	0.04p	0.0720
<i>x</i> ₂	14.622				1	0.95p	0.03d	0.0693

Table 5. continued

stack	E_0 (tw)	E_0 (expt)	Δ_1	Δ_2	K	c_1	c_2	$\langle B_0 \rangle$
<i>l</i>	9.964	10.088	-0.12	-0.07	2	0.98d		0.0626
<i>J</i> = 5, A+								
<i>x</i> ₃	16.977				3	0.98f		0.0832
<i>x</i> ₄	17.705				2	0.97d	0.03p	0.0696
<i>x</i> ₅	19.457				0	0.71s	0.28p	0.0755
<i>J</i> = 6, A+								
<i>a</i>	2.603	2.607	0.00	0.00	0	0.99s		0.0631
<i>c</i>	4.295	3.979	0.32	-0.04	0	0.93s	0.07p	0.0783
<i>b</i>	5.003	5.025	-0.02	-0.02	1	0.93p	0.06s	0.0628
<i>d</i>	6.083	5.945	0.14	-0.16	1	0.97p		0.0808
<i>m</i>	9.800	10.062	-0.26	-0.25	0	0.99s		0.0722
<i>g</i> ^b	10.910	11.258	-0.35	-0.36	12	0.58p	0.40d	0.0738
<i>n</i> ^b	11.019	11.177	-0.16	-0.13	21	0.67d	0.32p	0.0793
<i>l</i>	11.795	11.908	-0.11	-0.09	2	0.91d	0.08p	0.0633
<i>r</i>	14.493	14.631	-0.14	-0.05	0	0.99s		0.0695
<i>x</i> ₁	15.011				2	0.92d	0.07p	0.0716
<i>x</i> ₂	15.407				1	0.94p	0.06d	0.0693
<i>x</i> ₃	17.936				3	0.97f		0.0831
<i>x</i> ₄	18.490				2	0.96d	0.03p	0.0697
<i>J</i> = 7, A+								
<i>b</i>	5.871	5.902	-0.03		1	0.99p		0.0620
<i>d</i>	7.291	7.144	0.15		1	0.98p		0.0807
<i>g</i>	11.938	12.218	-0.28		12	0.49p	0.40d	0.0716
<i>n</i>	12.126	12.355	-0.23		2	0.76d	0.23p	0.0802
<i>l</i>	12.683	12.805	-0.12		2	0.81d	0.18p	0.0643
<i>x</i> ₁	15.974				2	0.87d	0.11p	0.0712
<i>x</i> ₂	16.340				1	0.88p	0.10d	0.0697
<i>x</i> ₃	19.051				3	0.95f	0.04d	0.0829
<i>x</i> ₄	19.405				2	0.93d	0.04p	0.0699
<i>x</i> ₅	21.220				0	0.68s	0.30p	0.0752
<i>J</i> = 8, A+								
<i>a</i>	4.423	4.417	0.01		0	0.98s		0.0625
<i>c</i>	6.479	6.222	0.26		01	0.65s	0.35p	0.0738
<i>b</i>	6.858	6.808	0.05		10	0.66p	0.33s	0.0673
<i>d</i>	8.359				1	0.95p	0.03s	0.0805
<i>m</i>	11.884	12.172	-0.29		0	0.97s		0.0717
<i>g</i>	12.843	13.110	-0.27		1	0.73p	0.23d	0.0697
<i>n</i>	13.354	13.553	0.24		2	0.90d	0.08p	0.0811
<i>l</i>	13.650	13.758	-0.11		2	0.82d	0.16p	0.0649
<i>r</i>	16.472	16.609	-0.14		0	0.98s		0.0697
<i>x</i> ₁	17.062				2	0.80d	0.18p	0.0707
<i>x</i> ₂	17.392				1	0.83p	0.16d	0.0698
<i>J</i> = 9, A+								
<i>b</i>	7.915	7.934	-0.02		1	0.99p		0.0619
<i>d</i>	9.954				1	0.97p	0.03d	0.0804
<i>g</i>	14.128	14.386	-0.26		12	0.53p	0.46d	0.0673
<i>n</i>	14.777				2	0.83d	0.15p	0.0806
<i>l</i>	14.862	15.010	-0.15		2	0.65d	0.34p	0.0674
<i>x</i> ₁	18.275				2	0.70d	0.27p	0.0702
<i>x</i> ₂	18.613				1	0.71p	0.25d	0.0702
<i>J</i> = 10, A+								
<i>a</i>	6.706	6.685	0.02		0	0.97s	0.03p	0.0621
<i>b</i> ^d	8.898				1	0.87p	0.12s	0.0637
<i>c</i> ^d	9.555				0	0.86s	0.14p	0.0772
<i>d</i>	11.231				1	0.92p	0.05s	0.0801
<i>m</i>	14.500	14.816	-0.32		0	0.95s	0.04p	0.0712
<i>g</i>	15.225	15.473	-0.25		12	0.57p	0.37d	0.0677
<i>n</i>	16.006				21	0.62d	0.36p	0.0656
<i>l</i>	16.359				2	0.93d	0.03f	0.0817
<i>r</i>	18.990				0	0.97s	0.03p	0.0700

Table 5. continued

stack	E_0 (tw)	E_0 (expt)	Δ_1	Δ_2	K	c_1	c_2	$\langle B_0 \rangle$
<i>l</i>	9.964	10.088	-0.12	-0.07	2	0.98d		0.0626
<i>J</i> = 10, A+								
x_1	19.604				21	0.60d	0.38p	0.0696
x_2	19.935				12	0.62p	0.35d	0.0702

^a $\Delta_1 = E_0$ (tw) – E_0 (expt). $\Delta_2 = E_0$ (hybrid) – E_0 (expt). c_1 and c_2 are the two largest P_K^l which are followed by a letter (s, p, ...) designating K (0, 1 ...). The column K gives the K value of the leading one or two P_K^l . "tw" is "this work". "expt;" refers to the experimental results of ref 1. "hybrid" refers to the theoretical results of ref 1 on the hybrid PES. ^bThe assignment of g and n to these two calculated states is based on $\langle B_0 \rangle$. Their energy order is opposite to the experimental energy order. ^cNew experimental levels of Rezaie et al.⁵⁵ d_b(10) and c(10) level order is reversed. The assignment is supported by the distinct $\langle B_0 \rangle$ and K.

length of CO monomer.⁸ We have done test calculations with the latter B. The differences in the rovibrational energy levels are small (less than 0.01 cm⁻¹).

D. Results. D1. Assessment of ab Initio PESs. On CBS_PL, it is possible to clearly identify a vibrational wave function localized above the C-bonded global minimum (NC) and another partially localized above the O-bonded minimum (NO). Experimentally, the state localized in the global minimum is 0.88 cm⁻¹ lower. Energies of the two minima are very close and a disrotatory path with low barriers leads from the global to the local minimum; see Figure 5 for a plot of the minimum energy path (MEP) along the disrotatory coordinate X, defined as $X = (\tilde{\theta}_1 + \tilde{\theta}_2)/2$, on CBS_PL.

The gap between these localized states is an obvious measure of the accuracy of a CO dimer PES. Rovibrational states localized above the global minimum are called *a* states, and states localized above the local minimum are called *c* states (the names *a* and *c* are stack labels, see below). The empirical hybrid surface that is a linear combination of DFT-SAPT and CCSD(T) PESs is tuned to reproduce the 0.88 cm⁻¹ gap exactly.⁸ We find the order of the $J = 0$ *a* and *c* levels is incorrect on all our PESs without core-correlation, e.g., on CBS_val the gap is -1.32 cm⁻¹. On the surfaces with core correlation, the order is correct, e.g. on CBS_PL the gap is 1.18 cm⁻¹ indicating that core correlation is important for CO dimer. Probability density (PD) plots for the $J = 0$ *a* and *c* levels on CBS_val and CBS_PL are shown in Figure 6, whereas on the hybrid surface of Vissers et al. both the *a* state and the *c* state are localized. Figure 6 shows that on CBS_PL (and CBS_val) the *a* state is localized and the *c* state is partially localized with significant spill into the disrotatory valley and the global minimum. This is a key difference between the hybrid PES of Vissers et al. and CBS_PL. Overall, our best surface is CBS_PL. The overall quality of CBS_PL, considering rovibrational levels up to $J = 6$, is comparable to the hybrid surface of Vissers et al. (see below for more details). All results reported in subsequent sections are obtained with CBS_PL.

D2. Stacks of Rotational Levels. Following the practice initiated by Brookes and McKellar, CO dimer stacks are organized into stacks labeled by letters. Each stack is associated with a value of K, the component of the angular momentum along the intermonomer axis, and contains levels of one symmetry. Within a stack, levels are labeled by different J values. Sorting the calculated rovibrational levels into stacks makes it possible to compare with experimental results.

Because we use the SAL and a parity adapted basis, we separately compute A+ and A– states. For both types of states, we wish to form stacks. To sort the levels into stacks, we use four tools. First, we exploit the fact that energies of levels in a stack increase linearly with J. $E(J)$ vs J plots for two stacks may

cross at most once. When levels for all J values are assigned to stacks, the order of the stack labels is the same for low J values; crossings usually occur for larger J. K = 0 stacks are special (see section D3) because only half the J values are allowed. Second, we assign a K to each level by computing

$$P_K^l = \sum_{l_1 l_2 m_2, \alpha_0} d_{l_1 l_2 m_2, JK, \alpha_0}^2 \quad (2)$$

where $d_{l_1 l_2 m_2, JK, \alpha_0}$ ² are wave function expansion coefficients in the parity adapted basis of eq 1.⁵⁴ Because the Coriolis coupling is weak for this system, we find that for most of the levels, P_K^l is much larger for one K than for all others. Third, from the calculated rovibrational wave function, it is straightforward to compute $\langle B_0 \rangle$, the expectation value of operator $B(r_0) = 1/(2\mu_0 r_0^2)$ for each rovibrational level. Levels assigned to a given stack often have similar $\langle B_0 \rangle$. Fourth, wave functions of levels in a stack, evaluated at some value of the Euler angles, often have similar features. The fourth tool is used, however, only in a few ambiguous cases because examining wave functions is laborious.

Rovibrational levels on CBS_PL up to $J = 10$ and up to about $E = 19$ cm⁻¹ above the ZPE are listed in Tables 5 (A+ levels) and 6 (A– levels). For each level, the K assignment (based on the largest P_K^l), the two largest P_K^l and $\langle B_0 \rangle$ are reported. The stack assignment for each level, determined using the four tools discussed in the previous paragraph, is also presented. Using the stack assignments one can easily compare our levels with both those of Surin et al.¹ and the experimental levels. Assigning K to experimental stacks can be tricky because the dipole has nonzero components along the two in-plane principal axes (the *a* axis is almost parallel to the *z*-axis along vector \mathbf{r}_0). There are therefore no selection rules limiting transitions that can occur between K states. Experimental K assignments may be uncertain when lower-J levels within a stack are missing (e.g., *p*, *o*, and *u* stacks of A– symmetry). Overall, our calculated levels and those of Surin et al. are of comparable accuracy, when compared with experimental levels, implying that our ab initio PES is about as good as the hybrid empirical surface used by Surin et al. For the 68 experimental levels with $J \leq 6$, the root-mean-square deviation (rmsd) is 0.29 cm⁻¹ for CBS_PL and 0.26 cm⁻¹ for Surin et al. Levels with $J > 6$ on their hybrid surface are not available. Some CBS_PL states with $J > 6$ have errors larger than 1 cm⁻¹ presumably due to the inaccuracy of the PES.

Once we have sorted levels into stacks, it is possible to characterize a stack by fitting the levels to $E = E_0 + BJ(J + 1) - D_J^2(J + 1)^2$ to obtain an effective rotational constant and stack band center E_0 . The fitted *B* is interpreted as the rotational constant for rotation about the intermonomer axis. $\langle B_0 \rangle$ is typically larger than the fitted *B*. E_0 and *B* for the different stacks computed on CBS_PL are compared with those on the

Table 6. A– Rovibrational Levels (in cm⁻¹) of CO Dimer

stack	E_0 (tw)	E_0 (exptl)	Δ_1	Δ_2	K	c_1	c_2	$\langle B_0 \rangle$
<i>J</i> = 0, A–								
<i>y</i> ₁	11.500				0	1.00s		0.0800
<i>y</i> ₄	17.172				0	1.00s		0.0672
<i>J</i> = 1, A–								
<i>e</i>	3.487	3.859	−0.37	−0.19	0	1.00s		0.0672
<i>f</i>	5.093	5.150	−0.06	0.11	1	1.00p		0.0681
<i>j</i>	5.937	5.905	0.03	−0.03	0	1.00s		0.0710
<i>k</i>	7.125	7.012	0.11	0.11	1	1.00p		0.0712
<i>u</i>	12.935				0	0.98s		0.0719
<i>s</i>	13.101				1	0.98p		0.0740
<i>y</i> ₂	15.499				1	1.00p		0.0790
<i>J</i> = 2, A–								
<i>f</i>	5.361	5.428	−0.07	0.11	1	1.00p		0.0680
<i>k</i>	7.392	7.270	0.12	0.11	1	1.00p		0.0713
<i>p</i>	11.571				2	1.00d		0.0638
<i>y</i> ₁	11.957				0	0.98s	0.02p	0.0799
<i>o</i>	12.305				2	1.00d		0.0774
<i>s</i>	13.401				1	0.98p	0.02s	0.0741
<i>y</i> ₂	15.745				1	0.89p	0.11d	0.0783
<i>y</i> ₃	16.110				2	0.89d	0.11p	0.0736
<i>y</i> ₄	17.570				0	0.99s		0.0673
<i>J</i> = 3, A–								
<i>e</i>	4.121	4.497	−0.38	−0.18	0	0.99s		0.0670
<i>f</i>	5.743	5.836	−0.09	0.09	1	0.98p		0.0676
<i>j</i>	6.611	6.570	0.04	−0.04	0	0.99s		0.0712
<i>k</i>	7.808	7.675	0.13	0.11	1	1.00p		0.0715
<i>p</i>	11.934				2	1.00d		0.0637
<i>o</i>	12.750				2	1.00d		0.0774
<i>u</i>	13.593				0	0.94s	0.06p	0.0719
<i>s</i>	13.815	13.734	0.08	0.16	1	0.94p	0.05s	0.0737
<i>y</i> ₂	16.178				12	0.72p	0.27d	0.0774
<i>y</i> ₃	16.586				21	0.73d	0.27p	0.0745
<i>J</i> = 4, A–								
<i>f</i>	6.284	6.392	−0.11	0.10	1	1.00p		0.0673
<i>k</i>	8.341	8.187	0.15	0.10	1	0.99p		0.0718
<i>p</i>	12.417				2	0.99d		0.0637
<i>y</i> ₁	13.018				0	0.92s	0.07p	0.0794
<i>o</i>	13.342				2	0.99d		0.0773
<i>s</i>	14.438	14.411	0.03	0.12	1	0.92p	0.07s	0.0741
<i>y</i> ₂	16.663				12	0.69p	0.30d	0.0771
<i>y</i> ₃	17.173				21	0.69d	0.30p	0.0746
<i>y</i> ₄	18.498				0	0.96s	0.04p	0.0674
<i>J</i> = 5, A–								
<i>e</i>	5.258	5.644	−0.39	−0.16	0	0.98s		0.0665
<i>f</i>	6.900	7.047	−0.15	0.07	1	0.96p	0.04s	0.0669
<i>j</i>	7.828	7.774	0.05	−0.06	0	0.97s	0.03p	0.0715
<i>k</i>	9.045	8.880	0.17	0.08	1	0.99p		0.0720
<i>p</i>	13.024	13.681	−0.66	−0.22	2	0.99d		0.0636
<i>o</i> ^a	14.081	15.069	−0.99	−1.19	2	0.99d		0.0772
<i>u</i>	14.788				0	0.92s	0.08p	0.0719
<i>s</i> ^a	15.085	14.939	0.15	0.20	1	0.93p	0.06s	0.0734
<i>y</i> ₂	17.405		−0.14	−0.05	21	0.50d	0.49p	0.0761
<i>y</i> ₃	17.995				12	0.49p	0.49d	0.0757
<i>J</i> = 6, A–								
<i>f</i>	7.717	7.883	−0.17	0.08	1	1.00p		0.0664
<i>k</i>	9.845	9.649	0.20	0.08	1	0.98p		0.0724
<i>p</i>	13.747	14.562	−0.82	−0.38	2	0.98d		0.0636
<i>y</i> ₁	14.666				0	0.83s	0.15p	0.0788
<i>o</i>	14.968	16.050	−1.08	−1.31	2	0.98d		0.0771
<i>s</i>	16.072				1	0.83p	0.15s	0.0740
<i>y</i> ₂	18.139				12	0.55p	0.43d	0.0761

Table 6. continued

stack	E_0 (tw)	E_0 (exptl)	Δ_1	Δ_2	K	c_1	c_2	$\langle B_0 \rangle$
<i>J</i> = 6, A-								
<i>y</i> ₃	18.805				21	0.54d	0.44p	0.0750
<i>y</i> ₄	19.952				0	0.91s	0.08p	0.0676
<i>J</i> = 7, A-								
<i>e</i>	6.890	7.290	-0.40		0	0.97s	0.03s	0.0658
<i>f</i>	8.548	8.753	-0.21		1	0.94p	0.05s	0.0660
<i>j</i>	9.591	9.524	0.07		0	0.94s	0.06p	0.0718
<i>k</i>	10.846	10.649	0.20		1	0.98p	0.02s	0.0726
<i>p</i>	14.596	15.596	-1.00		2	0.98d		0.0634
<i>o</i> ^{a,b}	15.998	17.267	-1.27		2	0.98d		0.0769
<i>u</i> ^b	16.522	15.851	0.67		0	0.91s	0.08p	0.0717
<i>s</i> ^a	16.903	16.677	0.23		1	0.93p	0.06s	0.0730
<i>J</i> = 8, A-								
<i>f</i>	9.642	9.871	-0.23		1	0.99s		0.0654
<i>k</i>	11.921	11.682	0.24		1	0.96p	0.03s	0.0731
<i>p</i>	15.558	16.900	-1.34		2	0.98d		0.0634
<i>y</i> ₁	16.882				0	0.71s	0.25p	0.0779
<i>o</i>	17.177				2	0.95d		0.0768
<i>s</i>	18.304				1	0.71p	0.28s	0.0739
<i>J</i> = 9, A-								
<i>e</i>	9.005	9.419	-0.41		0	0.96s	0.04p	0.0651
<i>f</i>	10.672	10.931	-0.26		1	0.93p	0.06s	0.0651
<i>j</i>	11.906	11.821	0.09		0	0.92s	0.08p	0.0721
<i>k</i>	13.217				1	0.96p	0.03s	0.0731
<i>p</i>	16.651	18.288	-1.64		2	0.98d		0.0633
<i>o</i>	18.491				2	0.96d		0.0765
<i>u</i>	18.796				0	0.90s	0.09p	0.0715
<i>s</i>	19.262	18.950	0.31		1	0.93p	0.05s	0.0726
<i>J</i> = 10, A-								
<i>f</i>	12.040	12.016	0.02		1	0.99p		0.0644
<i>k</i>	14.578				1	0.95p	0.04s	0.0736
<i>p</i>	17.850				2	0.97d		0.0632
<i>y</i> ₁	19.641				01	0.57s	0.36p	0.0768
<i>o</i>	19.961				2	0.92d	0.05p	0.0764
<i>s</i>	21.130				10	0.56p	0.42s	0.0736

^aThe assignment of *o* and *s* to these two calculated states is based on $\langle B_0 \rangle$ and *K*. Their energy order is opposite to the experimental energy order.

^bThe assignment of *o*(7) and *u*(7) is based on $\langle B_0 \rangle$ and *K*. Their energy order is opposite to the experimental energy order.

hybrid surface and experimental values in Table 7. For some stacks, a sextic centrifugal constant *H* can be obtained with a small uncertainty, and in these cases, the corresponding term is included in the fit. For most stacks, the errors of E_0 and *B* on CBS_PL and the hybrid PES are similar. For the lowest four A+ stacks and lowest three A- stacks, the CBS_PL errors are larger. E_0 of stack *c* (A+) and stack *e* (A-) on CBS_PL have noticeably large errors, ca. 0.30 and 0.37 cm⁻¹, respectively, compared to experiment. However, *B* for these two stacks have small errors. This implies that the deficiencies of CBS_PL mostly affect vibrational levels. Therefore, CBS_PL could probably be improved by adjusting parameters to reduce these E_0 errors.

D3. Allowed *J* for *K* = 0 Stacks. All of the previously known experimental and calculated A+ (A-) *K* = 0 stacks have only even (odd) *J* levels. This makes it easy to distinguish *K* = 0 and *K* > 0 stacks. We have identified new *K* = 0 stacks (stacks *y*₁ and *y*₄ and stack *x*₅) for which the allowed *J* values have a different pattern. The new A+ (A-) *K* = 0 stacks have only odd (even) *J* levels. In this subsection, we explain the origin of *J* restrictions for *K* = 0 stacks. Only A+ and A- rovibrational states are allowed (both C and O are bosons with zero spin). Each

rovibrational wave function can be thought of as a sum of products of rotational and vibrational factors. The symmetry of a rovibrational wave function is the symmetry of the dominant term, which is a product of the symmetry of the rotational and vibrational factors. For CO dimer, the symmetry of the rotational factor is the symmetry of $|JKM\rangle$ at a planar antiparallel geometry (both the global and the local minima are a planar antiparallel), which can be determined as explained in Bunker and Jensen.⁵⁵ A planar antiparallel geometry has the C_{2h} symmetry, and for this geometry, σ_{ex} is equivalent to a rotation of the MF frame (defined in section IIIA) by π around its *y*-axis. Following Jensen and Bunker, this operation is denoted by $R_{\pi/2}^{\pi}$ (R_{α}^{π} means a rotation by π around an axis on the *x*-*y* plane and making an angle α with *x*-axis). The effect of $R_{\pi/2}^{\pi}$ on $|JKM\rangle$ is

$$R_{\pi/2}^{\pi}|JKM\rangle = (-1)^{J+K}|J\bar{K}M\rangle \quad (3)$$

where $\bar{K} \equiv -K$ (see eqs 12–47 of Bunker and Jensen⁵⁴). When *K* = 0, the symmetry of the rotational factor is therefore A only if *J* is even and B only if *J* is odd. Therefore, *K* = 0 stacks associated with an A vibrational state only have *J* even levels (e.g., stacks *a*, *c*, *m*, *r*, and *y*₁, *y*₄) and *K* = 0 stacks associated

Table 7. Experimental and Calculated Fitting Parameters (in cm^{-1}) of CO Dimer^a

stack	E_0			B			rmsd	J_{\max}	N
	exptl	hybrid	TW	exptl	hybrid	TW			
<i>a</i>	0.0			0.0637	0.0638	0.0631 ^b	7.9×10^{-4}	10	5
<i>c</i>	0.877	0.886	1.180	0.0722	0.0714	0.0731 ^b	1.5×10^{-4}	8	5
<i>b</i>	2.528	2.504	2.484	0.0614	0.0622	0.0596 ^b	6.1×10^{-3}	9	9
<i>d</i>	2.792	2.658	2.913	0.0740	0.0775	0.0744	3.3×10^{-2}	7	7
<i>m</i>	7.077	6.866	6.854	0.0715	0.0705	0.0705	6.1×10^{-5}	10	6
<i>n</i>	7.920	7.678	7.673	0.0786	0.0790	0.0782	8.8×10^{-3}	7	6
<i>g</i>	8.511	8.258	8.229	0.0664	0.0692	0.0669	5.3×10^{-2}	10	5
<i>l</i>	9.385	9.301	9.288	0.0582	0.0600	0.0600	3.3×10^{-2}	10	9
<i>r</i>	11.874	11.857	11.733	0.0655	0.0648	0.0656	2.7×10^{-4}	8	5
<i>x</i> ₁		12.083			0.0705		6.3×10^{-4}	10	9
<i>x</i> ₂		12.656			0.0653		2.3×10^{-3}	10	10
<i>x</i> ₃		14.571			0.0805		2.1×10^{-4}	7	5
<i>x</i> ₄		15.760			0.0646		6.9×10^{-4}	7	6
<i>x</i> ₅		17.556			0.0605		7.3×10^{-3}	7	4
<i>e</i>	3.731	3.542	3.360	0.0641	0.0647	0.0635	9.8×10^{-5}	9	5
<i>f</i>	5.029	5.134	4.951	0.0662	0.0665	0.0678 ^b	3.0×10^{-2}	10	10
<i>j</i>	5.773	5.747	5.802	0.0662	0.0648	0.0673 ^b	1.3×10^{-4}	9	5
<i>k</i>	6.874	6.990	6.992	0.0662	0.0653	0.0670 ^b	1.3×10^{-2}	10	10
<i>y</i> ₁		11.500			0.0764 ^b		2.0×10^{-4}	10	6
<i>o</i>	12.869	11.773	11.859	0.0674	0.0686	0.0743 ^b	1.7×10^{-3}	10	9
<i>s</i>	13.00	13.072	12.976	0.0655	0.0666	0.0688	2.9×10^{-2}	6	6
<i>p</i>	11.53	11.567	11.207	0.0697	0.0650	0.0606	2.0×10^{-3}	10	9
<i>u</i>		12.804	12.801		0.0657	0.0661	1.5×10^{-3}	9	5
<i>y</i> ₂		15.350			0.0683		2.5×10^{-2}	6	6
<i>y</i> ₃		15.609			0.0833		2.3×10^{-2}	6	5
<i>y</i> ₄		17.172			0.0664		8.6×10^{-5}	6	4

^aN is the number of fitted levels. “hybrid” refers to the theoretical results of ref 1 on the hybrid PES. TW means computed on PES CBS_PL. ^bFor these stacks, sextic centrifugal H parameter are also included in the fit.

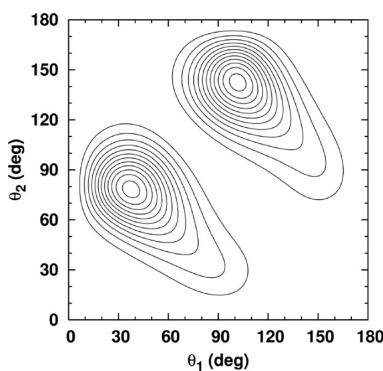


Figure 7. PD for the first $B-$ vibrational state showing localization in the polar region.

with a B vibrational state only have J odd levels (e.g., stacks *e*, *j*, *u*, and *x*₅). Stacks with $K > 0$ stacks have levels with even and odd J values.

Table 9. Assignment of Rotational Level Stacks of CO Dimer in Terms of v_g from Rezaie et al.^{55a}

	Γ_{tot}	$K = 0$	$K = 1$	$K = 2$
$v_g = 0$	A+	<i>a</i> [0]	<i>b</i> [0]	<i>l</i> [0]
$v_g = 0$	A+	<i>c</i> [2]	<i>d</i> [0]	<i>n</i> [0] ^b
$v_g = 1$	A-	<i>j</i> [4]	<i>k</i> [4]	<i>o</i> [4]
$v_g = 1$	A-	<i>e</i> [2]	<i>f</i> [2]	<i>p</i> [2]
$v_g = 2$	A+	<i>r</i> [6]	<i>x</i> ₂ [6]	<i>x</i> ₄ [6]
$v_g = 2$	A+	<i>m</i> [4]	<i>g</i> [4]	<i>x</i> ₁ [4]
$v_g = 3$	A-	<i>y</i> ₄ [6]		
$v_g = 3$	A-	<i>u</i> [6]	<i>s</i> [6]	<i>y</i> ₃ [6]

^aThe number of nodes along the entire disrotatory channel is given in square brackets. Bold-face stacks are new assignments. Stacks *y*₁ and *y*₂ are in the same group as stack *s*. ^bNot including the node for two small peaks.

D4. A+ Stacks. All low- J levels of the experimental A+ stacks have been observed.¹ In a recent paper, Rezaei et al. added the *n*(2) and *n*(3) levels.⁵⁶ The agreement between the

Table 8. Vibrational Levels (in cm^{-1}) of CO Dimer on PES CBS_PL up to 20 cm^{-1} and Their Associated Stacks^a

A+	stack	B+	stack	$\langle B_0 \rangle$	A-	stack	B-	stack	$\langle B_0 \rangle$
0.000	<i>a</i>	3.360	<i>e</i>	0.0673	11.500	<i>y</i> ₁	17.578	<i>x</i> ₅	0.0755
1.180	<i>c</i>	5.802	<i>j</i>	0.0710	17.172	<i>y</i> ₄			
6.854	<i>m</i>	12.805	<i>u</i>	0.0718					
11.733	<i>r</i>	19.834		0.0705					
18.089									

^aThe $\langle B_0 \rangle$ for B vibrational states are listed. The $\langle B_0 \rangle$ for A vibrational states are listed in Tables 5 and 6.

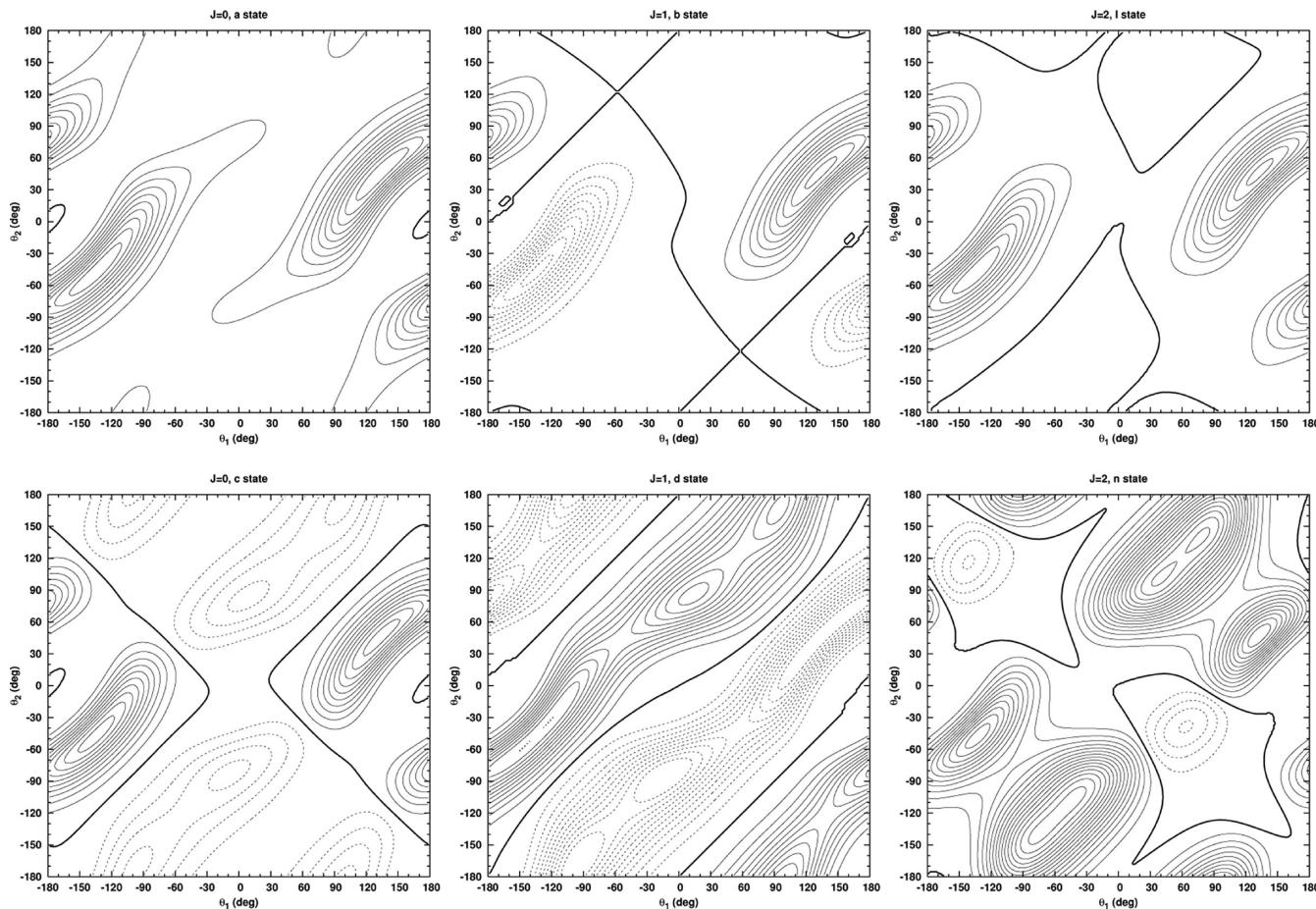


Figure 8. Wave functions of $v_g = 0$ states. The top three are $a(0)$, $b(1)$, and $l(2)$ states. The bottom three are $c(0)$, $d(1)$, and $n(2)$ states. States of the first, second, and third columns have $K = 0$, 1, and 2, respectively.

experimental levels and our levels is very good. There is one noticeable discrepancy: the order of the calculated and measured $g(6)$ and $o(6)$ levels is different. This simply means that levels of the experimental n stack cross levels of the experimental g stack, from below, at $J = 8$, while the calculated levels cross at $J = 7$. The c and b stacks also cross: at $J = 2$, the c level is below the b level, and the states are unmixed; at $J = 4, 6, 8$, they are mixed, but the c level is still below the b level; at $J = 10$, the c level is above b level.

We have also identified A+ stacks that do not have experimental counterparts. We label the new stacks x_i based on the order of fitted E_0 (Table 7). The x_5 stack is interesting because it is the only new $K = 0$ A+ stack. It is associated with the first B- vibrational state. Because its wave function has a B- vibrational factor, only J odd states are allowed, unlike all other A+, $K = 0$ stacks. The x_5 stack is also special because its vibrational factor is localized in the polar isomer region (Figure 7). However, the wave functions of higher J states in this stack are delocalized in the disrotatory channel. Stack x_3 is the lowest $K = 3$ stack.

D5. A- Stacks. Fourteen new A- stacks with energies above 13 cm^{-1} were observed in ref 1. In this region, there are some differences between the experimental and our calculated stack assignments. The first discrepancy is the order of the o and s stacks. The calculated o stack is close to but below the s stack. There are only two J ($J = 5$ and $J = 7$) levels for which both o and s are observed. In both cases, the observed o is above s . The second discrepancy is the order of $u(7)$ and $o(7)$. The observed

$u(7)$ (there is only one observed u level) is at 15.85 cm^{-1} , and the observed $o(7)$ is at 17.27 cm^{-1} . The calculated levels are flipped. Since the observed o and u stacks are missing many levels (only three o and one u levels are observed), they may be mis-assigned. It is also possible that the calculation is incorrect due to the inaccuracy of the PES used. The third discrepancy is between the experimental and theoretical fitted B (Table 7) for the o stack and for the p stack. There are five experimental p levels, so one would expect the experimental B to be accurate. However, because the p and o stacks are very close and both are $K = 2$ stacks, it is possible that some of the experimental p and o level assignments have been interchanged. The experimental $p(8)$ and $p(9)$ levels are closer to the calculated o levels with the same J , and the $o(8)$ and $o(9)$ levels are not observed experimentally. It is therefore possible that these levels, assigned to the p stack, should be in the o stack. The same thing might happen at $J = 7$ because the experimental $p(7)$ level at 15.596 is closer to the calculated $o(7)$ level at 15.998 than to the calculated $p(7)$ level. However, to reassign the experimental level as $o(7)$ level would require reassigning the observed $o(7)$ level at 17.267 . This $o(7)$ level is noticeably too high.

We have also found new A- stacks and labeled them y_i . The y_1 stack is a $K = 0$ stack with a relatively low $E_0 = 11.50 \text{ cm}^{-1}$. It is associated with the first A- vibrational state. Another new stack, similar to stack y_1 , called y_4 , is associated with the second A- vibrational state. Stacks y_1 and y_4 are the only A- $K = 0$ stacks with even J levels. Stack y_1 ($K = 0$) is mixed with stack s

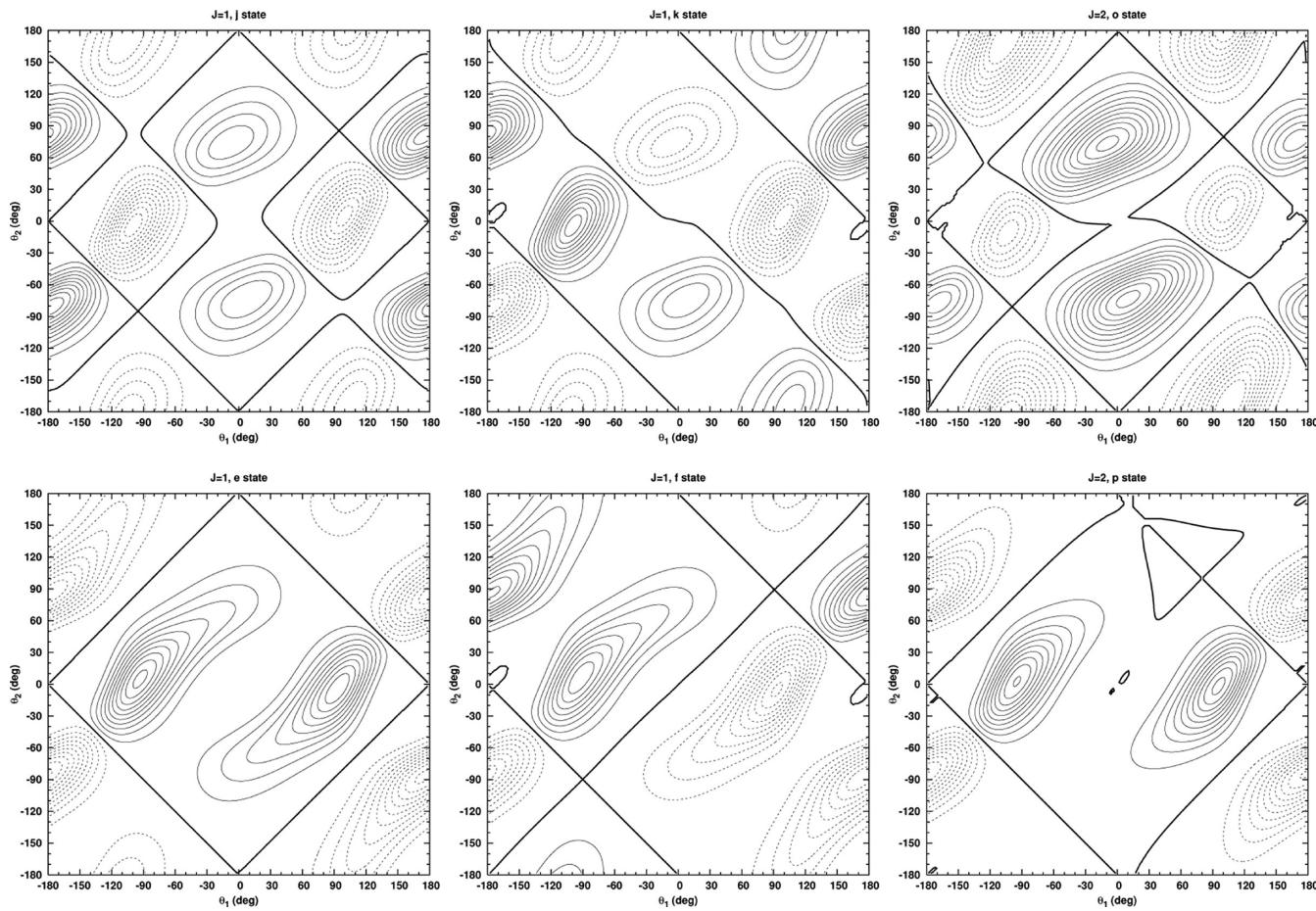


Figure 9. Wave functions of $v_g = 1$ states. The top three are $j(1)$, $k(1)$, and $o(2)$ states. The bottom three are $e(1)$, $f(1)$, and $p(2)$ states. States of the first, second, and third columns have $K = 0$, 1, and 2, respectively.

($K = 1$) as seen from P_K^J . The strength of the mixing increases with J . New stacks y_2 and y_3 are also found.

D6. Vibrational States and Their Associated Stacks. In Table 8, we report vibrational energy levels. Although there are no rovibrational states with $B+$ or $B-$ symmetry, there are stacks associated with $B+$ or $B-$ vibrational states with odd J that begin with $J = 1$. All $K = 0$ stacks can be associated with a vibrational level, and stack labels are included in Table 8. This implies that the rovibrational wave functions for the $K = 0$ stacks are well approximated by a product of a vibrational and a rotational factor. We denote the vibrational factor the vibrational parent (VP) of a stack. The VP is easily identified by comparing the fitted E_0 of a stack and the $J = 0$ levels (see Tables 7 and 8). It can be confirmed by doing a VP analysis, explained in ref 35. When we apply the VP analysis to $J = 1$ states, it is only for $K = 0$ states that we are able to determine a dominant VP. In this case, the VP is always the same as the one obtained by comparing $J = 0$ levels and E_0 . $B+$ and $B-$ vibrational levels on the hybrid PES are not available for comparison.

The dominant feature of the vibrational states in Table 8 is excitation along the disrotatory coordinate because of the low barrier. Wave functions with excitation in the torsion are observed at higher energies. PD plots show that all the odd-parity vibrational states in Table 8 have a node along the torsion coordinate (wave function plots for these states are not useful as they are all zero at the planar geometry).

D7. State Assignment Procedures. Vibrational and rovibrational states are assigned by making wave function plots.^{40,35} Rezaei et al. assigned two stacks to each (v_g , K) pair. The two stacks were associated with the C-bonded and O-bonded isomers based on energy, and B. Surin et al. have assigned v_g labels to stacks by examining rovibrational wave functions at fixed values of Euler angles. They extend the range of one of the theta coordinates from $[0, \pi]$ to $[-\pi, \pi]$ so that they can show polar and nonpolar geometries on the same plot. In contrast, we extend both theta coordinates, using the definitions in Figure 2 and ref 35. This figure illustrates how our wave functions computed using the nonextended coordinates are plotted as functions of the extended coordinates. For each combination of the signs of $\tilde{\theta}_1$, $\tilde{\theta}_2$, the recipe for obtaining the wave function in the extended coordinates from the wave function in the nonextended coordinates is different. Note that in quadrants II and III, the MF x - and y -axes are flipped and therefore $\gamma \rightarrow \gamma + \pi$. In all the wave function plots, \mathbf{r}_0 is fixed at 8.1836 bohr (the value at the global minimum), and β and γ are chosen so that wave functions have significant amplitude.

Examining the wave functions reveals that, due to the low-barrier along the minimum energy disrotatory path (MEP), most states are delocalized along this channel. It is often thought that many vibrational wave functions are localized in the global or the local well. If that were the case, it would be possible to assign $v_g = n$ to two vibrational states, each with n nodes along the disrotatory coordinate, but in different wells. However, on CBS_PL, it is only the vibrational state associated

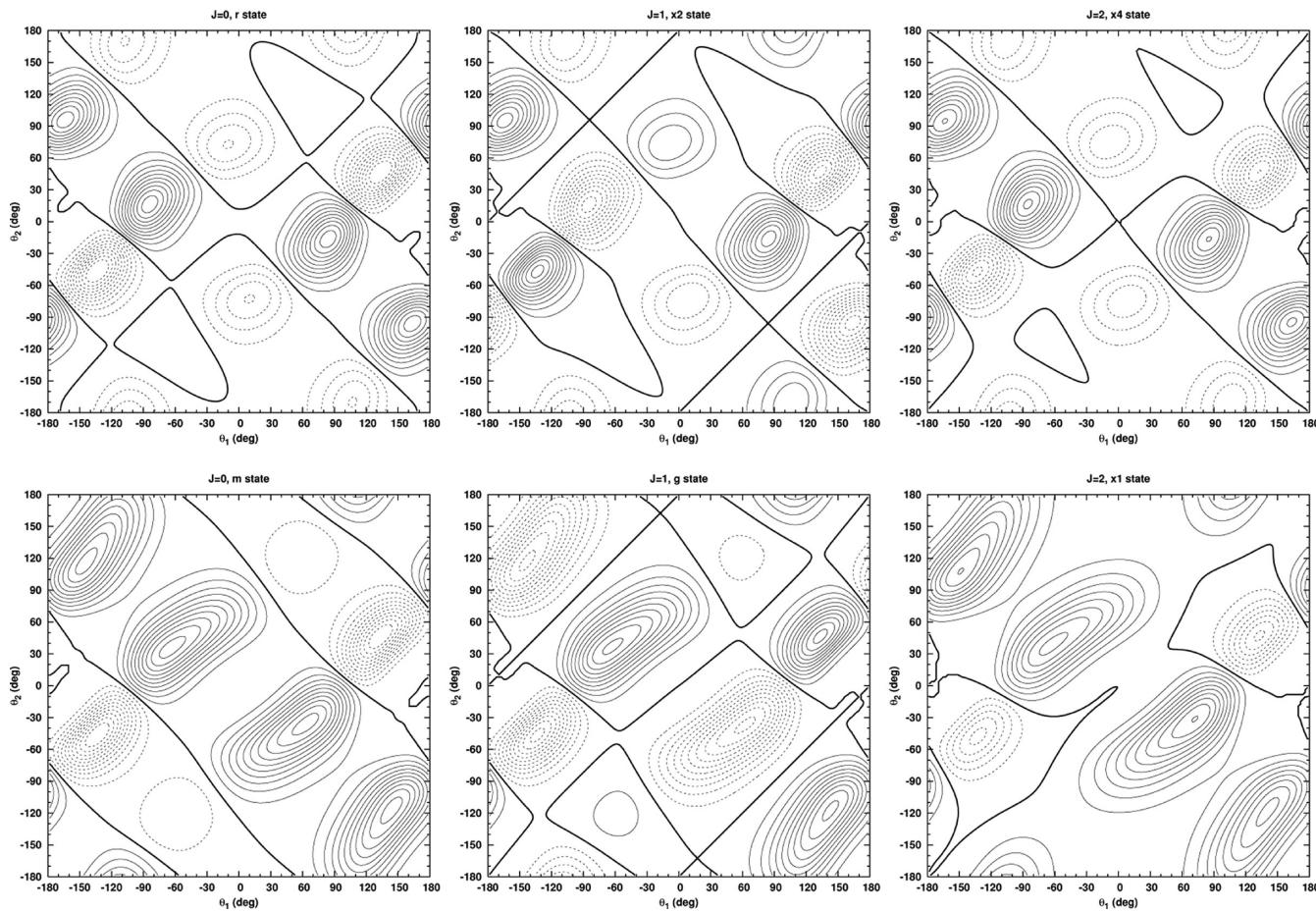


Figure 10. Wave functions of $\nu_g = 2$ states. The top three are $r(0)$, $x_2(1)$, and $x_4(2)$ states. The bottom three are $m(0)$, $g(1)$, and $x_1(2)$ states. States of the first, second, and third columns have $K = 0$, 1, and 2, respectively.

with the *a* stack that is well localized. All other vibrational wave functions are delocalized over the entire 2π range of the disrotatory cycle and therefore also have amplitude in the polar region. Even the *c* stack vibrational level, the ground state of O-bonded isomer, has a node in the polar region because the wave function leaks into the C-bonded isomer region. There would be no such node, and the *c* vibrational state would be a nodeless ground state, if the *c* state were truly localized.

Because of the fact that most of the wave functions are delocalized, it makes more sense to label wave functions by counting nodes along the entire 2π disrotatory cycle. The number of such nodes is given in square brackets in Table 9. There is no clear correlation between these labels and the ν_g assignment of Rezaei et al.⁵⁶ Rather than counting nodes, we can look at 2-d plots of wave functions in the extended coordinates. See Figures 8–11. The absolute value, $|\Psi|$, is similar for all wave functions in a row. Different columns correspond to different K . Each figure contains two sets of states assigned to the same value of ν_g by Rezaei et al. Interestingly, wave functions placed in a row in Figures 8–11, due to their similarity, are always wave functions assigned the same value of ν_g by Rezaei et al., see Table 9. For $\nu_g = 0$ (Figure 8), the wave functions in the first row all look like the *a* vibrational state, and the wave functions in the second row all look like the *c* vibrational state (the $n(2)$ is different because of two small additional peaks). In Figures 9 and 10, the similarity of wave functions in a row is more striking.

In addition, we note that $K = 0$ and $K = 2$ stacks have the same wave function structure (stack *n* is an exception). For $\nu_g > 0$ states, the first of the two rows has nodes along the diagonal line from $(-\pi, \pi)$ to $(\pi, -\pi)$, while wave functions in the second row have maxima along this line. Rezaei et al. assumed that wave functions in the two rows can be associated with C-bonded and O-bonded isomers. This is not consistent with the wave function delocalization. Only the *a* stack vibrational state has a localized wave function.

Except for the fact that we extend two angles and they extend one, many of the wave function plots of Surin et al. are similar to ours. The plots for stacks *c*, *d*, and *n* (the second $\nu_g = 0$ row in Figure 8) are exceptions. Whereas states *c*, *d*, and *n* of Surin et al. have no amplitude in the C-bonded region, our states have amplitudes in both wells. In Rezaei et al.'s paper, and hence in Figure 8, stacks *l* and *n* are assigned as $\nu_g = 0$, whereas Surin et al. assign them to $\nu_g = 2$. On the basis of the similarity of wave functions, we support Rezaei et al.'s assignment.

The new stacks can also be interpreted using the framework of Figures 8–11. New stacks x_1 , x_2 , and x_4 complete the $\nu_g = 2$ series up to $K = 2$. New stack x_3 is a $K = 3$ stack, and it is not included in the figures. New stacks y_i are all $\nu_g = 3$ states. States in stacks y_1 and y_2 have the same wave function structure as states in stack *s*, and one would expect them to also have $K = 1$. However, stack y_1 is a $K = 0$ stack. Stacks y_4 ($K = 0$) and y_3 ($K = 2$) are assigned as $\nu_g = 3$. The $K = 1$ and 2 stacks of the first $\nu_g = 3$ series are not found.

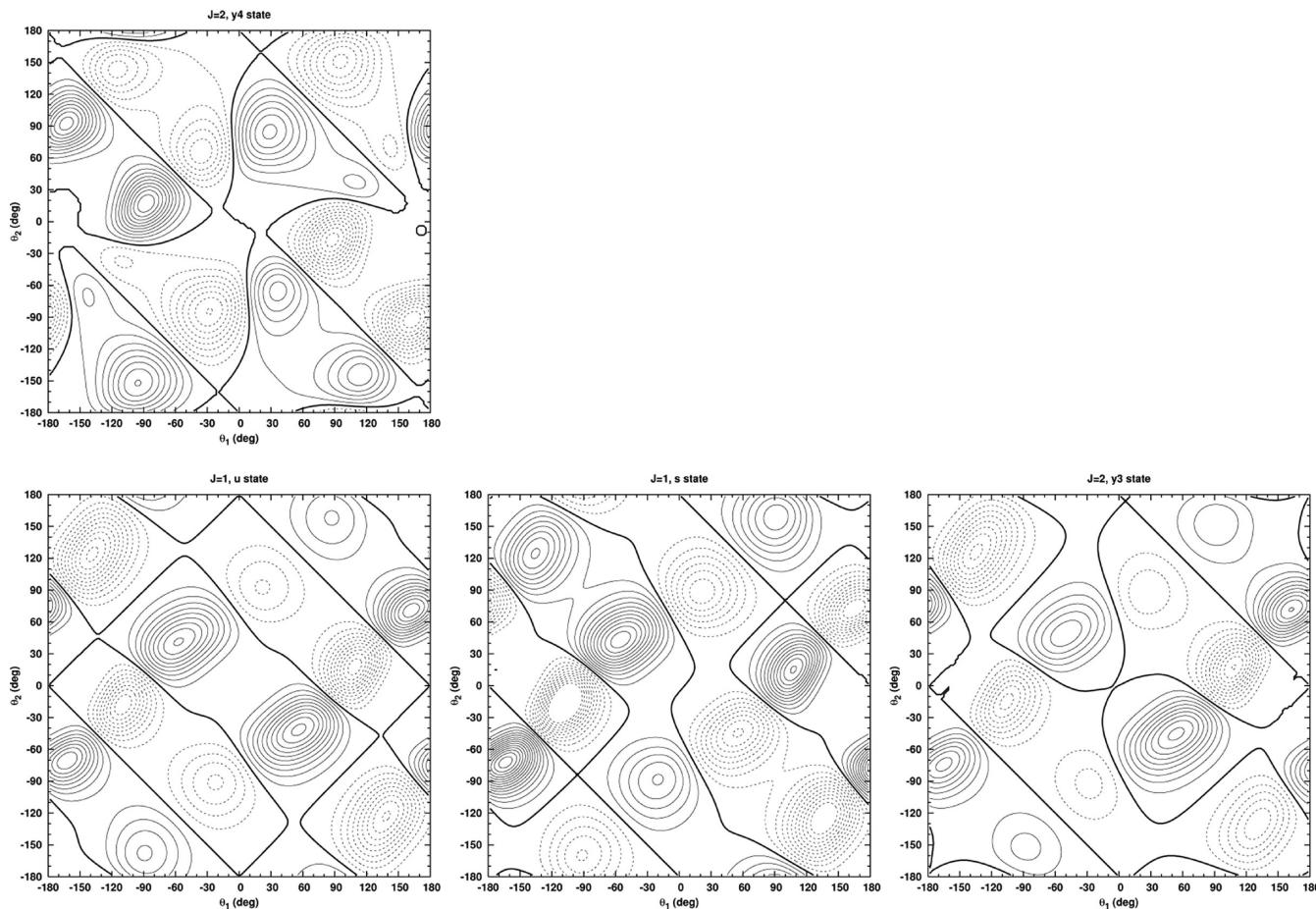


Figure 11. Wave functions of $v_g = 3$ states. The top one is the $y_4(2)$ state. The bottom three are $u(0)$, $s(1)$, and $y_3(2)$ states. States of the first, second, and third columns have $K = 0$, 1, and 2, respectively.

IV. CONCLUSION

We have demonstrated that rovibrational levels computed on a new CO dimer intermolecular PES built from explicitly correlated CCSD(T)-F12b points and an interpolating moving least-squares (IMLS) fitting procedure yields results in good agreement with experiment. Rovibrational levels are computed by using a parity-adapted angular basis, a symmetry adapted Lanczos algorithm to calculate eigenvalues and quadrature for potential matrix elements. The new ab initio PES is about as good as the hybrid surface of Surin et al. in terms of predicting levels, but many wave functions on the new PES are more delocalized. Because of the delocalization, only wave functions in the lowest stack have amplitude in one of the isomer wells.

Using ideas similar to those outlined in other papers on CO dimer, we have organized the rovibrational levels into stacks. In general, our results are in excellent agreement with experiment. We have found several stacks that have not yet been detected experimentally. As the new potential appears to be very accurate, it should be possible to observe the new stacks.

■ ASSOCIATED CONTENT

Supporting Information

The most accurate (CO)₂ potential surface constructed for the study (CBS_PL) is available for download as Supporting Information (SI). Also included in SI is a comparative discussion of single and multireference methods for the 1D CO monomer stretch potential energy curve (PEC). Vibra-

tional levels from an accurate fitted PEC (including spin-orbit and scalar relativistic corrections) are compared with experiment. The fitted PEC is provided in compact form. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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