

# Analytic Morse/long-range potential energy surfaces and predicted infrared spectra for CO<sub>2</sub>-H<sub>2</sub>

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Five-dimensional *ab initio* potential energy surfaces (PESs) for CO<sub>2</sub>-H<sub>2</sub> that explicitly incorporate dependence on the  $Q_3$  asymmetric-stretch normal-mode coordinate of the CO<sub>2</sub> monomer and are parametrically dependent on its  $Q_1$  symmetric-stretch coordinate have been calculated. Analytic four-dimensional PESs are obtained by least-squares fitting vibrationally averaged interaction energies for  $\nu_3(\text{CO}_2)=0$ , and 1 to the Morse/long-range potential function form. These fits to 23 113 points have root-mean-square (rms) deviations of 0.143 and 0.136 cm<sup>-1</sup>, and require only 167 parameters. The resulting vibrationally averaged PESs provide good representations of the experimental infrared data: for infrared transitions of *para*- and *ortho*-H<sub>2</sub>-CO<sub>2</sub>, the rms discrepancies are only 0.004 and 0.005 cm<sup>-1</sup>, respectively. The calculated infrared band origin shifts associated with the  $\nu_3$  fundamental of CO<sub>2</sub> are -0.179 and -0.092 cm<sup>-1</sup> for *para*-H<sub>2</sub>-CO<sub>2</sub> and *ortho*-H<sub>2</sub>-CO<sub>2</sub>, in good agreement with the (extrapolated) experimental values of -0.198 and -0.096 cm<sup>-1</sup>. © 2010 American Institute of Physics. [doi:10.1063/1.3428619]

## I. INTRODUCTION

Liquid <sup>4</sup>He and <sup>3</sup>He are the only substances that are known to exhibit superfluidity, and there is considerable interest in finding superfluidity in other materials.<sup>1</sup> Like <sup>4</sup>He atoms, *para*-H<sub>2</sub> molecules are spinless indistinguishable bosons, so they might also be expected to show superfluid behavior at low temperatures.<sup>2</sup> Recent spectroscopic studies of molecules embedded in helium droplets<sup>3-11</sup> suggest that a possible route for investigating superfluidity of parahydrogen (*p*-H<sub>2</sub>) is to consider *p*-H<sub>2</sub> clusters doped with a single chromophore molecule such as HCN, HF, CO, OCS, N<sub>2</sub>O, or CO<sub>2</sub>.<sup>12-16</sup> An accurate description of binary complexes is an essential starting point for the exploration of larger clusters, as quantum Monte Carlo simulations of doped He clusters are known to be very sensitive to the quality of the pair potentials utilized for the simulations.<sup>17,18</sup>

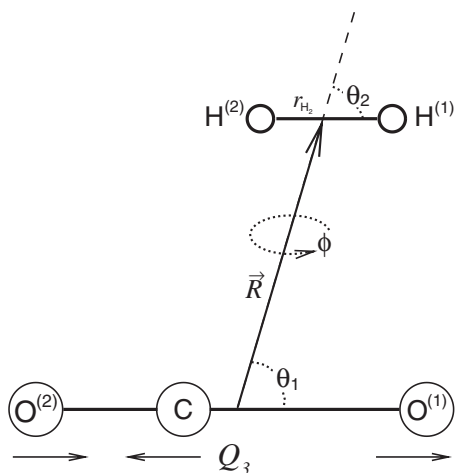
Since the first infrared spectrum of CO<sub>2</sub>-H<sub>2</sub> complexes in the region of the strong  $\nu_3$  fundamental band of CO<sub>2</sub> was recorded by McKellar,<sup>19</sup> two theoretical studies of this complex have been reported.<sup>20,21</sup> One was based on a four-dimensional (4D) potential energy surface (PES) with CO<sub>2</sub> fixed at its equilibrium geometry;<sup>20</sup> however, although a 4D treatment may be adequate for describing the microwave spectrum of a ground-state species, it cannot properly describe infrared spectra involving excitation of an intramolecular CO<sub>2</sub> vibrational mode. The other was a five-dimensional (5D) *ab initio* potential which explicitly took account of the  $\nu_3$  asymmetric-stretch vibrational motion of rigidly linear CO<sub>2</sub> while the symmetric-stretch  $Q_1$  coordinate was fixed at a value defined by the experimental ground-state inertial rotational constant  $B_0$ .<sup>21</sup> However, recent results of quantum Monte Carlo simulations of CO<sub>2</sub>(He)<sub>*n*</sub> clusters

show that the symmetric-stretch coordinate  $Q_1$  may *not* be ignored when predicting the  $\nu_3$  band-origin shifts for CO<sub>2</sub> in van der Waals clusters.<sup>18</sup> Moreover, the “working form” of the first of these PESs involves cubic spline interpolation over the three angles and use of the interpolating moving least-squares method for the intermolecular separation  $R$ ,<sup>20</sup> while that for the second was defined by fits to sums of products of linear and exponential angular terms at each pair of  $R$  and  $Q_3$  values, combined with spline interpolation over those two coordinates.<sup>21</sup> Neither of those approaches yields a readily “portable” functional form, or defines the PES in terms of parameters with real physical significance, and neither incorporates the correct theoretically known inverse-power long-range behavior.

Recently, Le Roy *et al.* introduced the “Morse/long-range” (MLR) radial potential function form which incorporates theoretically known long-range inverse-power behavior within a single smooth and flexible analytic function.<sup>22,23</sup> For atom-molecule or molecule-molecule systems, allowing parameters of that radial function to vary with angle and monomer-stretching coordinate yields a compact and flexible multidimensional functional form. Application of this approach to the CO<sub>2</sub>-He system yielded a function that explicitly incorporates the  $Q_3$  asymmetric-stretch vibrational motion of CO<sub>2</sub> and has the correct angle-dependent inverse-power long-range behavior.<sup>24,18</sup> Vibrationally averaging over  $Q_3$  for different vibrational levels of the CO<sub>2</sub> monomer yielded analogous two-dimensional (2D) forms and led to remarkably accurate predictions of the vibrational frequency shifts of CO<sub>2</sub> in (He)<sub>*n*</sub> for cluster sizes up to  $n=40$ .<sup>18</sup>

In the present work, 4D versions of such MLR functions (depending on three angles and  $R$ ) have been fitted to vibrationally averaged interaction energies obtained from new 5D *ab initio* PESs for CO<sub>2</sub>-H<sub>2</sub> which explicitly incorporate the  $Q_3$  asymmetric-stretch vibrational motion of CO<sub>2</sub>, but are

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FIG. 1. Jacobi coordinates for the  $\text{CO}_2\text{-H}_2$  complex.

associated with different values of the symmetric-stretch coordinate  $Q_1$ . The new *ab initio* calculations and the techniques used for computing the eigenvalues of the resulting PES are described in Sec. II. Section III then presents our analytic 4D potential function form and describes its fit to the *ab initio* results, while Sec. IV presents predictions of the infrared and microwave spectra for the  $\text{CO}_2\text{-H}_2$  dimer implied by this surface and compares them with experiment.

## II. COMPUTATIONAL METHODS

### A. *Ab initio* calculations

The geometry of a  $\text{CO}_2\text{-H}_2$  complex in which  $\text{CO}_2$  is rigidly linear can be described naturally using the Jacobi coordinates  $(R, \theta_1, \theta_2, \phi, Q_3)$  shown in Fig. 1; there,  $\vec{R}$  is a vector pointing from the center of mass of  $\text{CO}_2$  to the center of mass of  $\text{H}_2$ ,  $\theta_1$ , the angle between  $\vec{R}$ , and a vector pointing from atom  $\text{O}^{(2)}$  to atom  $\text{O}^{(1)}$ ,  $\theta_2$ , the angle between  $\vec{R}$ , and a vector pointing from  $\text{H}^{(2)}$  atom to  $\text{H}^{(1)}$ ,  $\phi$ , the dihedral angle between the two planes defined by  $\vec{R}$ , with the  $\text{CO}_2$  molecule and with  $\text{H}_2$ , and  $Q_3 = (r_{\text{CO}}^{[1]} - r_{\text{CO}}^{[2]})/\sqrt{2}$  is the normal mode coordinate for the  $\nu_3$  antisymmetric stretch vibration of  $\text{CO}_2$ . In all of these calculations, the bond length of the  $\text{H}_2$  molecule was fixed at the average value for the ground state,  $r_{\text{H}_2} \equiv \langle r \rangle_{0,0} = 0.766\,639\,3 \text{ \AA}$ .<sup>25</sup> Our recent work on  $\text{CO}_2\text{-He}$  showed that when the asymmetric-stretch mode of  $\text{CO}_2$  is excited, the effect of the associated change in the average value of the symmetric stretch coordinate  $Q_1 = (r_{\text{CO}}^{[1]} + r_{\text{CO}}^{[2]})/\sqrt{2}$  cannot be ignored.<sup>18,24</sup> Hence, in our *ab initio* calculations for the  $\text{CO}_2\text{-H}_2$  complex, the sum of the two C–O bond lengths was fixed at twice the average bond lengths implied by the experimental moments of inertia for the ground state  $(v_1, v_2, v_3) = (0, 0, 0)$ , and the first excited asymmetric-stretch level of  $\text{CO}_2$ ,  $(0, 0, 1)$ .

In a full six-dimensional treatment which also took account of the symmetric stretch coordinate  $Q_1$ , the total potential energy for  $\text{CO}_2\text{-H}_2$  would be written as

$$V(R, \theta_1, \theta_2, \phi, Q_3, Q_1) = V_{\text{CO}_2}(Q_3, Q_1) + \Delta V(R, \theta_1, \theta_2, \phi, Q_3, Q_1), \quad (1)$$

in which  $V_{\text{CO}_2}(Q_3, Q_1)$  is the effective 2D potential energy for the symmetric and asymmetric stretching of an isolated, rigidly linear  $\text{CO}_2$  molecule, and  $\Delta V(R, \theta_1, \theta_2, \phi, Q_3, Q_1)$  is the intermolecular interaction potential. However, our recent results for the  $\text{CO}_2\text{-He}$  system showed that a reduced-dimension treatment with the symmetric stretch coordinate  $Q_1$  fixed at its average values for the appropriate  $\nu_3$  vibrational level of  $\text{CO}_2$  was a good approximation which led to very accurate predicted vibrational frequency shifts for  $\text{CO}_2$  in  $(\text{He})_n$  clusters.<sup>18,24</sup> Following that approach, our effective 5D potentials for  $\text{CO}_2\text{-H}_2$  can be defined as

$$\begin{aligned} & \langle \psi_{v_1}^{v_3}(Q_1) | V(R, \theta_1, \theta_2, \phi, Q_3, Q_1) | \psi_{v_1}^{v_3}(Q_1) \rangle \\ & \approx V(R, \theta_1, \theta_2, \phi, Q_3; \bar{Q}_1^{v_3}) \\ & = V_{\text{CO}_2}(Q_3; \bar{Q}_1^{v_3}) + \Delta V(R, \theta_1, \theta_2, \phi, Q_3; \bar{Q}_1^{v_3}), \end{aligned} \quad (2)$$

in which the notation reminds us that the average value of  $Q_1$  depends on the asymmetric-stretch vibrational quantum number  $\nu_3$ .

The  $\text{CO}_2$  monomer geometry and hence the effective one-dimensional (1D) potentials  $V_{\text{CO}_2}(Q_3; \bar{Q}_1^{v_3})$  governing both the  $Q_3$  vibration of a free  $\text{CO}_2$  monomer and the intermolecular potential  $\Delta V(R, \theta_1, \theta_2, \phi, Q_3; \bar{Q}_1^{v_3})$  depend not only on  $Q_3$ , but also on the associated (fixed) value of the symmetric stretch coordinate  $\bar{Q}_1^{v_3}$ . The average values of the C–O bond length in the ground  $(v_1, v_2, v_3) = (0, 0, 0)$  and  $(0, 0, 1)$  excited states of  $\text{CO}_2$  implied by the experimental moments of inertia are known to be  $r_0 = 1.162\,086$  and  $1.166\,695 \text{ \AA}$ , respectively.<sup>26</sup> Our taking account of this difference differs from the approach used in recent 5D treatments of  $\text{CO}_2\text{-H}_2$  and of  $\text{N}_2\text{O-H}_2$ , in which the same fixed  $Q_1$  value was used to define the effective 1D monomer stretching potentials when treating states of the complex associated with the ground ( $\nu_3 = 0$ ) and first excited ( $\nu_3 = 1$ ) levels of the chromophore.<sup>21,27</sup>

The effective 1D potentials  $V_{\text{CO}_2}(Q_3; \bar{Q}_1^{v_3})$  governing the  $Q_3$  vibration of the isolated  $\text{CO}_2$  monomer were calculated using single- and double-excitation coupled-cluster theory with a noniterative perturbation treatment of triple excitations [CCSD(T)].<sup>28</sup> The basis set used was the augmented correlation-consistent quadruple-zeta (aug-cc-pVQZ) basis set of Woon and Dunning,<sup>29</sup> and counterpoise corrections were applied. For a chosen fixed value for the sum of the two C–O bond lengths, the potential energy was computed at 29 values of  $Q_3$  ranging from 0.0 to 0.5  $\text{\AA}$ , and those values were fitted to an even-power polynomial expansion:

$$V_{\text{CO}_2}(Q_3; \bar{Q}_1^{v_3}) = \sum_{n=0(2)} a_n (\bar{Q}_1^{v_3}) Q_3^n. \quad (3)$$

The coefficients of the polynomial expansions used to represent the 1D effective  $\text{CO}_2$  asymmetric-stretch potentials are presented in Table I of Ref. 24.

The intermolecular potential energies of  $\text{CO}_2\text{-H}_2$  were calculated at the [CCSD(T)]/aug-cc-pVTZ level, supple-

mented with an additional set of bond functions (3s3p2d1f1g) (where  $\alpha=0.9, 0.3, 0.1$  for 3s and 3p;  $\alpha=0.6, 0.2$ , for 2d;  $\alpha=0.3$  for f and g) placed at the midpoint of the intermolecular axis  $R$ .<sup>30,31</sup> The supermolecule approach was used to produce the intermolecular potential energy  $\Delta V(R, \theta_1, \theta_2, \phi, Q_3; \bar{Q}_1^{v_3})$ , which is defined as the difference between the energy of the CO<sub>2</sub>-H<sub>2</sub> complex and the sum of the energies of the CO<sub>2</sub> and H<sub>2</sub> monomers. The full counterpoise procedure was employed to correct for basis set superposition error.<sup>32</sup> All calculations were carried out using the MOLPRO package.<sup>33</sup>

Some 41 148 symmetry-unique *ab initio* points were calculated for both the ground ( $v_3=0$ ) and first excited ( $v_3=1$ ) states, with  $Q_1$  fixed at the values  $\bar{Q}_1^{v_3}$  defined by the experimental inertial rotational constants for the (0,0,0) and (0,0,1) levels of CO<sub>2</sub>. The calculations were performed on regular grids for all five degrees of freedom. Five grid points corresponding to  $Q_3=-0.115\ 863, -0.054\ 977, 0.0, 0.054\ 977, \text{ and } 0.115\ 863$  Å were chosen for the CO<sub>2</sub> stretching coordinate, while a relatively dense grid of 26 points ranging from 2.2 to 12.0 Å was used for the  $R$  intermolecular coordinate. The angular coordinates  $\theta_1$  and  $\theta_2$  range from 0° to 180° with step sizes of 15°, and the dihedral angle  $\phi$  ranges from 0° to 90° at intervals of 30°. This yielded two effective 5D *ab initio* PESs, for which the lists of symmetry-unique points may be obtained from the journal's online data archive.<sup>34</sup>

## B. Hamiltonian and reduced-dimension treatment

Within the Born-Oppenheimer approximation, without separating the intra- and intermolecular vibrations, the rovibrational Hamiltonian of the CO<sub>2</sub>-H<sub>2</sub> complex in the space-fixed frame has the form (in a.u.):<sup>35-37</sup>

$$\hat{H} = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{1}{2M} \frac{\partial^2}{\partial Q_3^2} + \frac{\hat{l}_1^2}{2I_{\text{CO}_2}} + B_{\text{H}_2} \hat{l}_2^2 + \frac{(\hat{J} - \hat{l}_1 - \hat{l}_2)^2}{2\mu R^2} + V(R, \theta_1, \theta_2, \phi, Q_3; \bar{Q}_1^{v_3}), \quad (4)$$

in which  $\mu^{-1} = (2m_{\text{H}})^{-1} + (2m_{\text{O}} + m_{\text{C}})^{-1}$  and  $M = m_{\text{C}}m_{\text{O}} / (2m_{\text{O}} + m_{\text{C}})$ , where  $m_{\text{H}}$ ,  $m_{\text{C}}$ , and  $m_{\text{O}}$  are the masses of the H, C, and O atoms,<sup>38</sup> respectively,  $B_{\text{H}_2}$  is the inertial rotational constant of H<sub>2</sub>,  $I_{\text{CO}_2} \equiv I(Q_3; \bar{Q}_1^{v_3})$  is the moment of inertia of an isolated CO<sub>2</sub> molecule, and  $V(R, \theta_1, \theta_2, \phi, Q_3; \bar{Q}_1^{v_3})$  is the total potential energy of the system.

The above Hamiltonian incorporates full coupling between the intermolecular and  $Q_3$  vibrations. However, convergence of the eigenvalue calculations is very slow at the high internal energies associated with excitation of the  $v_3$  vibration of CO<sub>2</sub>, since it requires a relatively large number of Lanczos iterations.<sup>21,24</sup> It is therefore highly desirable to separate the treatment of the inter- and intramolecular motions. Since the  $v_3$  vibrational mode of CO<sub>2</sub> has a much higher frequency than do the intermolecular modes, Born-Oppenheimer separation type arguments suggest that it should be a good approximation to introduce such a separation, as long as the off-diagonal vibrational coupling is suf-

ficiently small.<sup>21,24</sup> In this approximation, the total vibrational wave function would be written as the product

$$\Psi_{v_3}(R, \theta_1, \theta_2, \phi, Q_3; \bar{Q}_1^{v_3}) = \phi^{v_3}(R, \theta_1, \theta_2, \phi) \psi_v(Q_3; \bar{Q}_1^{v_3}), \quad (5)$$

in which  $v_3$  is the quantum number for a specific asymmetric-stretch vibrational state of the free CO<sub>2</sub> molecule, and the associated 1D vibrational wave function  $\psi_v(Q_3; \bar{Q}_1^{v_3})$  is obtained by solving the 1D Schrödinger equation:

$$\left[ \frac{-1}{2M} \frac{d^2}{dQ_3^2} + V_{\text{CO}_2}(Q_3; \bar{Q}_1) \right] \psi_v(Q_3; \bar{Q}_1) = E_v \psi_v(Q_3; \bar{Q}_1). \quad (6)$$

The present work focuses on complexes formed from CO<sub>2</sub> in the ground ( $v_3=0$ ) and first excited ( $v_3=1$ ) asymmetric stretch states of CO<sub>2</sub>. Using Eq. (5), the vibrationally averaged CO<sub>2</sub>-H<sub>2</sub> interaction potential for CO<sub>2</sub> in vibrational level  $v_3$  is

$$\begin{aligned} \bar{V}^{v_3}(R, \theta_1, \theta_2, \phi) &= \int_{-\infty}^{\infty} \psi_{v_3}^*(Q_3; \bar{Q}_1^{v_3}) \Delta V(R, \theta_1, \theta_2, \phi, Q_3; \bar{Q}_1^{v_3}) \\ &\quad \times \psi_{v_3}(Q_3; \bar{Q}_1^{v_3}) dQ_3, \end{aligned} \quad (7)$$

and the associated 4D intermolecular Hamiltonian in the space-fixed reference frame is

$$\hat{H} = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + B_{\text{CO}_2}^{v_3} \hat{l}_1^2 + B_{\text{H}_2}^v \hat{l}_2^2 + \frac{(\hat{J} - \hat{l}_1 - \hat{l}_2)^2}{2\mu R^2} + \bar{V}^{v_3}(R, \theta_1, \theta_2, \phi), \quad (8)$$

in which

$$B_{\text{CO}_2}^{v_3} = \left\langle \psi_{v_3} \left| \frac{1}{2I(Q_3; \bar{Q}_1^{v_3})} \right| \psi_{v_3} \right\rangle \quad (9)$$

is the CO<sub>2</sub> inertial rotational constant and  $I(Q_3; \bar{Q}_1^{v_3})$  is the instantaneous CO<sub>2</sub> moment of inertia. Note that the vibrationally averaged intermolecular potentials  $\bar{V}^{v_3}(R, \theta_1, \theta_2, \phi)$  for different values of  $v_3$  differ because the 5D PESs being averaged over are associated with different values of  $\bar{Q}_1^{v_3}$ , and because the wave functions  $\psi_{v_3}(Q_3)$  are associated with different values of  $v_3$ , and because they were obtained from effective 1D potentials associated with different values of  $\bar{Q}_1^{v_3}$ .

In order to solve our 4D Schrödinger equation numerically in terms of the body-fixed angles ( $\theta_1, \theta_2, \phi$ ), the Hamiltonian in the body-fixed reference frame is written as<sup>39-42</sup>

$$\hat{H} = \hat{T}_{\text{str}} + \hat{T}_{\text{diag}} + \hat{T}_{\text{off}} + \hat{T}_{\text{Cor}} + \bar{V}^{v_3}(R, \theta_1, \theta_2, \phi), \quad (10)$$

in which

$$\hat{T}_{\text{str}} = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2}, \quad (11)$$

$$\hat{T}_{\text{diag}} = - \left( \frac{1}{2\mu R^2} + B_{\text{CO}_2}^v \right) \left[ \frac{\partial^2}{\partial \theta_1^2} + \cot \theta_1 \frac{\partial}{\partial \theta_1} - \frac{1}{\sin^2 \theta_1} (\hat{J}_z - \hat{l}_{2z})^2 \right] + \left[ \frac{1}{2\mu R^2} + B_{\text{H}_2} \right] \hat{l}_2^2 + \frac{1}{2\mu R^2} [\hat{J}^2 - 2(\hat{J}_z - \hat{l}_{2z})^2 - 2\hat{J}_z \hat{l}_{2z}], \quad (12)$$

$$\hat{T}_{\text{off}} = \frac{1}{2\mu R^2} [\hat{l}_{2+} \hat{a}_1^- + \hat{l}_{2-} \hat{a}_1^+], \quad (13)$$

$$\hat{T}_{\text{Cor}} = - \frac{1}{2\mu R^2} [\hat{J}_z \hat{a}_1^+ + \hat{J}_+ \hat{a}_1^- + \hat{J}_- \hat{l}_{2+} + \hat{J}_+ \hat{l}_{2-}], \quad (14)$$

where

$$\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y, \quad \hat{l}_{2\pm} = \hat{l}_{2x} \pm i\hat{l}_{2y}, \quad (15)$$

$$\hat{a}_1^{\pm} = \pm \frac{\partial}{\partial \theta_1} - \cot \theta_1 (\hat{J}_z - \hat{l}_{2z}). \quad (16)$$

Here, the operators  $\hat{J}_x$ ,  $\hat{J}_y$ , and  $\hat{J}_z$  are the components of the total angular momentum operator  $\hat{J}$  in the body-fixed frame, the  $z$  axis of the body-fixed frame lies along the Jacobi radial vector  $\vec{R}$ , and its  $x$  axis is in the plane that contains  $\vec{R}$  and the  $\text{CO}_2$  molecule. The above Hamiltonian contains full vibration-rotation coupling.

### C. Basis function and matrix elements

A discrete variable representation (DVR) grid<sup>43</sup> was used for the radial part of the 4D Schrödinger equation. The angular part was then treated using parity-adapted rovibrational basis functions, which are linear combinations of the functions

$$\langle \theta_1, \theta_2, \phi; \alpha, \beta, \gamma | l_1 l_2 m; JKM \rangle = \sqrt{\frac{2J+1}{8\pi^2}} \Theta_{l_1}^{K-m}(\theta_1) Y_{l_2}^m(\theta_2, \phi) D_{MK}^*(\alpha, \beta, \gamma), \quad (17)$$

in which  $l_1$  and  $l_2$  are the total angular momentum quantum numbers for free rotation of the  $\text{CO}_2$  and  $\text{H}_2$  moieties, respectively,

$$Y_{l_2}^m(\theta_2, \phi) = \frac{1}{\sqrt{2\pi}} \Theta_{l_2}^m(\theta_2) e^{im\phi}$$

are the familiar spherical harmonics,  $\Theta_l^m$  is the normalized associated Legendre functions with the  $(-1)^m$  Condon-Shortley phase factor,<sup>44</sup> and  $D_{MK}^J$  are the Wigner functions.<sup>44</sup> The body-fixed frame is related to the space-fixed frame via a rotation by the three Euler angles  $(\alpha, \beta, \gamma)$ . The projection of the total angular momentum  $\vec{J}$  onto the space-fixed or body-fixed frame is given by  $M$  or  $K$  quantum numbers. The effect of the parity operator  $\hat{E}^*$  on rovibrational functions is given by

$$\hat{E}^* | l_1 l_2 m K; JM \rangle = (-1)^J | l_1 l_2 - m K; JM \rangle, \quad (18)$$

so the parity-adapted basis functions can be written as

$$| l_1 l_2 m K; JMP \rangle = \frac{1}{\sqrt{(2 + 2\delta_{m,0}\delta_{K,0})}} \{ | l_1 l_2 m K; JM \rangle + (-1)^{J+P} | l_1 l_2 - m K; JM \rangle \}, \quad (19)$$

where for  $K > 0$ ,  $P = 0$  and 1 correspond to even and odd parities, respectively. If  $K = 0$ , the constraint that  $m \geq 0$  is applied, and the combination  $m = K = 0$  and  $(-1)^{J+P} = -1$  is not allowed.

In the parity-adapted angular finite basis representation (FBR), the kinetic energy terms have simple matrix elements. The diagonal matrix elements are

$$\langle l_1 l_2 m K; JMP | \hat{T}_{\text{diag}} | l_1 l_2 m K; JMP \rangle = B_{\text{CO}_2} l_1(l_1 + 1) + B_{\text{H}_2}^v l_2(l_2 + 1) + \frac{1}{2\mu R^2} [J(J + 1) + l_1(l_1 + 1) + l_2(l_2 + 1) - 2K^2 + 2m(K - m)], \quad (20)$$

and the three types of off-diagonal matrix elements are

$$\langle l_1 l_2 m + 1 K; JMP | \hat{T}_{\text{off}} | l_1 l_2 m K; JMP \rangle = \frac{\sqrt{1 + \delta_{m,0}\delta_{K,0}}}{2\mu R^2} \lambda_{l_1, K-m}^- \lambda_{l_2, m}^+, \quad (21)$$

$$\langle l_1 l_2 m K + 1; JMP | \hat{T}_{\text{Cor}} | l_1 l_2 m K; JMP \rangle = - \frac{\sqrt{1 + \delta_{m,0}\delta_{K,0}}}{2\mu R^2} \lambda_{l_1, K-m}^+ \lambda_{J, K}^+, \quad (22)$$

$$\langle l_1 l_2 m + 1 K + 1; JMP | \hat{T}_{\text{Cor}} | l_1 l_2 m K; JMP \rangle = - \frac{\sqrt{1 + \delta_{m,0}\delta_{K,0}}}{2\mu R^2} \lambda_{l_2, m}^+ \lambda_{J, K}^+, \quad (23)$$

with two special cases

$$\langle l_1 l_2 - m 1; JMP | \hat{T}_{\text{Cor}} | l_1 l_2 m 0; JMP \rangle = \frac{-(-1)^{J+P}}{2\mu R^2} \lambda_{l_1, K-m}^- \lambda_{J, 0}^- (m > 0), \quad (24)$$

$$\langle l_1 l_2 - m + 11; JMP | \hat{T}_{\text{Cor}} | l_1 l_2 m 0; JMP \rangle = \frac{-(-1)^{J+P}}{2\mu R^2} \lambda_{l_2, m}^- \lambda_{J, 0}^- (m > 0). \quad (25)$$

For the potential part, the matrix elements are not diagonal in the angular FBR basis. However, they could be calculated in the grid representation by applying a three-dimensional transformation<sup>37</sup> for the angles  $\theta_1$ ,  $\theta_2$ , and  $\varphi$ , respectively, in which the potential energy matrix is diagonal. These integrals need first the application of a transformation from the parity-adapted FBR to the DVR basis, then multiplication by a diagonal potential matrix, and finally to be transformed back.<sup>37,41</sup> Gauss-Legendre quadrature was used for both the  $\theta_1$  and  $\theta_2$  angles, and Gauss-Chebyshev quadratures of the first kind and second kind were used to integrate  $\varphi$  for even and odd parity cases, respectively. The

Lanczos algorithm was then used to calculate the rovibrational energy levels by recursively diagonalizing the resulting discretized Hamiltonian matrix.<sup>45</sup>

### III. ANALYTIC POTENTIAL ENERGY SURFACE FOR CO<sub>2</sub>-H<sub>2</sub>

#### A. Potential energy function

The vibrational-averaged *ab initio* intermolecular potential energies  $\bar{V}^{\{v_3\}}(R, \theta_1, \theta_2, \phi)$ , for CO<sub>2</sub>-H<sub>2</sub> obtained from Eq. (7), were fitted to a generalization of the MLR potential function form,<sup>23,46</sup> which is written as

$$\bar{V}_{\text{MLR}}(R, \theta_1, \theta_2, \phi) = \mathcal{D}_e(\theta_1, \theta_2, \phi) \times \left\{ -1 + \left[ 1 - \frac{u_{\text{LR}}(R, \theta_1, \theta_2, \phi)}{u_{\text{LR}}(R_e, \theta_1, \theta_2, \phi)} e^{-\beta(R, \theta_1, \theta_2, \phi) \cdot y_p^{\text{eq}}(R, \theta_1, \theta_2, \phi)} \right]^2 \right\}, \quad (26)$$

in which  $\mathcal{D}_e(\theta_1, \theta_2, \phi)$  is the depth and  $R_e \equiv R_e(\theta_1, \theta_2, \phi)$  is the position of the minimum on a radial cut through the potential for angles  $\{\theta_1, \theta_2, \phi\}$ , while  $u_{\text{LR}}(R, \theta_1, \theta_2, \phi)$  is a function which defines the (attractive) limiting long-range behavior of the effective 1D potential along that cut as

$$\bar{V}(R, \theta_1, \theta_2, \phi) \simeq \mathcal{D}_e(\theta_1, \theta_2, \phi) - u_{\text{LR}}(R, \theta_1, \theta_2, \phi) + \dots \quad (27)$$

Because both H<sub>2</sub> and CO<sub>2</sub> are nonpolar, an appropriate functional form for  $u_{\text{LR}}(R, \theta_1, \theta_2, \phi)$  is

$$u_{\text{LR}}(R, \theta_1, \theta_2, \phi) = \frac{\bar{C}_5(\theta_1, \theta_2, \phi)}{R^5} + \frac{\bar{C}_6(\theta_1, \theta_2, \phi)}{R^6} + \frac{\bar{C}_8(\theta_1, \theta_2, \phi)}{R^8}, \quad (28)$$

in which the long-range coefficients  $\bar{C}_n$  have also been averaged over the CO<sub>2</sub> asymmetric-stretch coordinate  $Q_3$ , and the denominator factor  $u_{\text{LR}}(R_e, \theta_1, \theta_2, \phi)$  is that same function evaluated at  $R=R_e(\theta_1, \theta_2, \phi)$ . The radial distance variable in the exponent in Eq. (26) is the dimensionless quantity

$$y_p^{\text{eq}}(R, \theta_1, \theta_2, \phi) = \frac{R^p - R_e(\theta_1, \theta_2, \phi)^p}{R^p + R_e(\theta_1, \theta_2, \phi)^p}, \quad (29)$$

where  $p$  is a small positive integer which must be greater than the difference between the largest and smallest (inverse) powers appearing in Eq. (28),  $p > (8-5)$ ,<sup>23</sup> and the exponent coefficient function  $\beta(R, \theta_1, \theta_2, \phi)$  is a (fairly) slowly varying function of  $R$ , which is written as the constrained polynomial

$$\beta(R, \theta_1, \theta_2, \phi) = y_p^{\text{ref}}(R, \theta_1, \theta_2, \phi) \beta_\infty(\theta_1, \theta_2, \phi) + [1 - y_p^{\text{ref}}(R, \theta_1, \theta_2, \phi)] \times \sum_{i=0}^N \beta_i(\theta_1, \theta_2, \phi) y_q^{\text{ref}}(R, \theta_1, \theta_2, \phi)^i, \quad (30)$$

whose behavior is defined in terms of the two new radial variables:

$$y_p^{\text{ref}}(R, \theta_1, \theta_2, \phi) = \frac{R^p - R_{\text{ref}}^p}{R^p + R_{\text{ref}}^p} \quad \text{and} \quad (31)$$

$$y_q^{\text{ref}}(R, \theta_1, \theta_2, \phi) = \frac{R^q - R_{\text{ref}}^q}{R^q + R_{\text{ref}}^q},$$

in which  $R_{\text{ref}} \equiv f_{\text{ref}} \times R_e(\theta_1, \theta_2, \phi)$ . Although most previous work with this model was performed using a single radial variable to define the exponent coefficient function  $\beta(R, \theta_1, \theta_2, \phi)$  (i.e., with  $q=p$ ) and with  $R_{\text{ref}}=R_e$ , (i.e., with  $f_{\text{ref}}=1$ ), it has recently been shown that use of  $f_{\text{ref}} > 1$ , and of a separate smaller power  $q < p$ , to define the radial variable in the power-series portion of Eq. (30) can lead to more compact and robust potential functions.<sup>46</sup> In the potential function model used in the present work,  $p=4$ ,  $q=3$ , and  $f_{\text{ref}}=1.5$ .

The definition of  $y_p^{\text{eq}}(R, \theta_1, \theta_2, \phi)$  and the algebraic structure of Eqs. (26) and (30) mean that

$$\begin{aligned} \lim_{R \rightarrow \infty} \beta(R, \theta_1, \theta_2, \phi) &= \lim_{R \rightarrow \infty} \{ \beta(R, \theta_1, \theta_2, \phi) \cdot y_p^{\text{eq}}(R, \theta_1, \theta_2, \phi) \} \\ &\equiv \beta_\infty(\theta_1, \theta_2, \phi) \\ &= \ln\{2\mathcal{D}_e(\theta_1, \theta_2, \phi)/u_{\text{LR}}(R_e, \theta_1, \theta_2, \phi)\}. \end{aligned} \quad (32)$$

The parameters  $\mathcal{D}_e(\theta_1, \theta_2, \phi)$ ,  $R_e(\theta_1, \theta_2, \phi)$ , and the various exponent expansion coefficients  $\beta_i(\theta_1, \theta_2, \phi)$ , all are expanded in the form

$$F(\theta_1, \theta_2, \phi) = \sum_{l_1, l_2, l} F_{l_1 l_2 l} A_{l_1 l_2 l}(\theta_1, \theta_2, \phi), \quad (33)$$

in which  $F = \mathcal{D}_e$ ,  $R_e$  or  $\beta_i$ ,  $\phi = \phi_1 - \phi_2$ , and  $l$  is the label associated with the vector sum of  $l_1$  and  $l_2$  and has the range of values  $|l_1 - l_2| \leq l \leq |l_1 + l_2|$ . These three indices must also satisfy the restrictions that all of  $l_1$ ,  $l_2$ , and  $l_1 + l_2 + l$  must be even, because both CO<sub>2</sub> and H<sub>2</sub> have centers of symmetry. The angular basis functions appearing here are defined as

$$\begin{aligned} A_{l_1 l_2 l}(\theta_1, \theta_2, \phi) &= \sum_{m=-l_{\min}}^{l_{\min}} \begin{pmatrix} l_1 & l_2 & l \\ m & -m & 0 \end{pmatrix} C_{l_1, m}(\theta_1, \phi_1) C_{l_2, -m}(\theta_2, \phi_2), \end{aligned} \quad (34)$$

in which  $C_{l, m}(\theta, \phi) = [4\pi/(2l+1)]^{1/2} Y_{l, m}(\theta, \phi)$  are the spherical harmonic functions defined with Racah normalization,<sup>47</sup> the quantity in large brackets is the Wigner 3j factor,<sup>48</sup> and  $l_{\min} = \min(l_1, l_2)$ .

The presence of permanent quadrupole moments on CO<sub>2</sub> and H<sub>2</sub> means that the leading term in the expression for  $u_{\text{LR}}(R, \theta_1, \theta_2, \phi)$  is the electrostatic quadrupole-quadrupole interaction,<sup>49</sup> whose (vibrationally averaged) coefficient may be written as

TABLE I. Expansion coefficients  $\bar{\mathcal{D}}_e^{l_1 l_2 l} [\text{cm}^{-1}]$  defining our 4D vibrationally averaged PES for  $^{12}\text{C } ^{16}\text{O}_2(v_3=0) - \text{H}_2$ .

$\bar{\mathcal{D}}_e^{0,0,0}$	77.548	$\bar{\mathcal{D}}_e^{0,2,2}$	-40.2	$\bar{\mathcal{D}}_e^{0,4,4}$	1.63	$\bar{\mathcal{D}}_e^{0,6,6}$	-0.48
$\bar{\mathcal{D}}_e^{2,0,2}$	-91.82	$\bar{\mathcal{D}}_e^{2,2,0}$	23.03	$\bar{\mathcal{D}}_e^{2,4,2}$	-45.0	$\bar{\mathcal{D}}_e^{2,6,4}$	0.61
$\bar{\mathcal{D}}_e^{4,0,4}$	94.86	$\bar{\mathcal{D}}_e^{2,2,2}$	38.79	$\bar{\mathcal{D}}_e^{2,4,4}$	7.4	$\bar{\mathcal{D}}_e^{2,6,6}$	-0.4
$\bar{\mathcal{D}}_e^{6,0,6}$	-64.98	$\bar{\mathcal{D}}_e^{2,2,4}$	460.77	$\bar{\mathcal{D}}_e^{2,4,6}$	5.3	$\bar{\mathcal{D}}_e^{2,6,8}$	0.5
$\bar{\mathcal{D}}_e^{8,0,8}$	39.23	$\bar{\mathcal{D}}_e^{4,2,2}$	-26.01	$\bar{\mathcal{D}}_e^{4,4,0}$	60.6	$\bar{\mathcal{D}}_e^{4,6,2}$	-0.31
$\bar{\mathcal{D}}_e^{10,0,10}$	-22.19	$\bar{\mathcal{D}}_e^{4,2,4}$	10.56	$\bar{\mathcal{D}}_e^{4,4,2}$	-2.53	$\bar{\mathcal{D}}_e^{4,6,4}$	0.2
$\bar{\mathcal{D}}_e^{12,0,12}$	7.79	$\bar{\mathcal{D}}_e^{4,2,6}$	-239.78	$\bar{\mathcal{D}}_e^{4,4,4}$	1.5	$\bar{\mathcal{D}}_e^{4,6,6}$	0.5
		$\bar{\mathcal{D}}_e^{6,2,4}$	21.21	$\bar{\mathcal{D}}_e^{4,4,6}$	-3.8	$\bar{\mathcal{D}}_e^{4,6,10}$	-0.8
		$\bar{\mathcal{D}}_e^{6,2,6}$	-10.9	$\bar{\mathcal{D}}_e^{4,4,8}$	-47.5	$\bar{\mathcal{D}}_e^{6,6,0}$	0.11
		$\bar{\mathcal{D}}_e^{6,2,8}$	11.6	$\bar{\mathcal{D}}_e^{6,4,2}$	2.1	$\bar{\mathcal{D}}_e^{6,6,2}$	-0.1
		$\bar{\mathcal{D}}_e^{8,2,6}$	-14.9	$\bar{\mathcal{D}}_e^{6,4,4}$	-1.1	$\bar{\mathcal{D}}_e^{6,6,6}$	-0.2
		$\bar{\mathcal{D}}_e^{8,2,8}$	6.7	$\bar{\mathcal{D}}_e^{6,4,6}$	2.2	$\bar{\mathcal{D}}_e^{6,6,10}$	-0.16
		$\bar{\mathcal{D}}_e^{8,2,10}$	-63.5	$\bar{\mathcal{D}}_e^{6,4,10}$	-1.7	$\bar{\mathcal{D}}_e^{6,6,12}$	-0.37
		$\bar{\mathcal{D}}_e^{10,2,8}$	14.6	$\bar{\mathcal{D}}_e^{8,4,4}$	18.9		
		$\bar{\mathcal{D}}_e^{10,2,10}$	-4.5	$\bar{\mathcal{D}}_e^{8,4,6}$	-3.0		
		$\bar{\mathcal{D}}_e^{10,2,12}$	26.4	$\bar{\mathcal{D}}_e^{8,4,8}$	1.6		
		$\bar{\mathcal{D}}_e^{12,2,10}$	-13.7	$\bar{\mathcal{D}}_e^{8,4,10}$	-2.2		
		$\bar{\mathcal{D}}_e^{12,2,12}$	2.2	$\bar{\mathcal{D}}_e^{8,4,12}$	2.4		
				$\bar{\mathcal{D}}_e^{10,4,6}$	2.9		
				$\bar{\mathcal{D}}_e^{10,4,8}$	-0.9		
				$\bar{\mathcal{D}}_e^{10,4,10}$	0.5		
				$\bar{\mathcal{D}}_e^{10,4,12}$	2.4		
				$\bar{\mathcal{D}}_e^{12,4,8}$	2.9		
				$\bar{\mathcal{D}}_e^{12,4,10}$	-0.9		
				$\bar{\mathcal{D}}_e^{12,4,12}$	0.5		

$$\bar{C}_5(\theta_1, \theta_2, \phi) = -(3\sqrt{70})\bar{Q}_{\text{H}_2}\bar{Q}_{\text{CO}_2}A_{224}(\theta_1, \theta_2, \phi), \quad (35)$$

in which  $\bar{Q}_{\text{H}_2}$  and  $\bar{Q}_{\text{CO}_2}$  are the vibrationally averaged quadrupole moments of ground-state  $\text{H}_2$  and  $\text{CO}_2$ .<sup>50,51</sup> Our  $v_3$ -dependent values of  $\bar{Q}_{\text{CO}_2}$  were obtained by averaging over the  $Q_3$ -dependence of the quadrupole moment function reported by Haskopoulos and Maroulis.<sup>51</sup>

The vibrationally averaged dispersion coefficients  $\bar{C}_{6(8)}(\theta_1, \theta_2, \phi)$  may be expanded as

$$\bar{C}_{6(8)}(\theta_1, \theta_2, \phi) = \sum_{l_1 l_2 l} \bar{C}_{6(8)}^{l_1 l_2 l} A_{l_1 l_2 l}(\theta_1, \theta_2, \phi).$$

An experimental value of the leading totally isotropic coefficient  $\bar{C}_{6,\text{exp}}^{000}$  has been obtained from dipole oscillator strength distributions by Jhanwar and Meath,<sup>52</sup> but no angle- or stretching-dependent long-range coefficients have been reported for this system. Estimates of the dispersion coefficients for  $(l_1, l_2, l) \neq (0, 0, 0)$ , were therefore obtained from the geometric-mean averages  $\bar{C}_{6(8),\text{gm}}^{l_1 l_2 l}$  of the analogous coefficients for the  $\text{CO}_2 - \text{CO}_2$  and  $\text{H}_2 - \text{H}_2$  interactions.<sup>53,54</sup> Our final values of the coefficients for these angle-dependent terms were then obtained by scaling these calculated “geometric-mean” coefficients by the ratios of the “experimental” to the geometric-mean isotropic  $C_6$  coefficients:

$$\bar{C}_{6(8)}^{l_1 l_2 l} = \bar{C}_{6(8),\text{gm}}^{l_1 l_2 l} \times (\bar{C}_{6,\text{exp}}^{000} / \bar{C}_{6,\text{gm}}^{000}). \quad (36)$$

Since our *ab initio* 5D PES incorporates the  $Q_3$  asymmetric-stretch normal-mode coordinate of the  $\text{CO}_2$  monomer, the Van der Waals interaction will also include induction terms. Following Buckingham,<sup>55</sup> the coefficient of the  $R^{-6}$  induction term was taken to be

$$\begin{aligned} \bar{C}_{6,\text{ind}}(\theta_1, \theta_2, \phi) &= \sum_{l_1 l_2 l} \bar{C}_{6,\text{ind}}^{l_1 l_2 l} A_{l_1 l_2 l}(\theta_1, \theta_2, \phi) \\ &= [\overline{\mu_{\text{CO}_2}(Q_3)}]^2 \times \left[ \alpha_{\text{H}_2}^{\text{av}}(A_{000} + \sqrt{5}A_{202}) \right. \\ &\quad + (\alpha_{\text{H}_2}^{\parallel} - \alpha_{\text{H}_2}^{\perp}) \left( \frac{\sqrt{5}}{3}A_{022} + \frac{3}{\sqrt{5}}A_{220} \right. \\ &\quad \left. \left. - \frac{\sqrt{10}}{\sqrt{7}}A_{222} + \frac{2\sqrt{2}}{\sqrt{35}}A_{224} \right) \right], \quad (37) \end{aligned}$$

in which the leading factor on the right hand side is the vibrational average of the square of the instantaneous  $\text{CO}_2$  dipole moment, while  $\alpha_{\text{H}_2}^{\parallel}$ ,  $\alpha_{\text{H}_2}^{\perp}$ , and  $\alpha_{\text{H}_2}^{\text{av}}$  are, respectively, the parallel, perpendicular, and isotropic-average polarizabilities of  $\text{H}_2$ . The latter were defined by the vibrationally averaged values for ground-state  $\text{H}_2$  reported by Bishop and Cheung,<sup>56</sup> while the former was calculated using the  $Q_3$ -dependent  $\text{CO}_2$  dipole moment reported by Haskopoulos and Maroulis.<sup>51</sup>

Finally, while the  $v_3$ -dependence of the angle-dependent dispersion terms was neglected, that for the leading isotropic coefficient was assumed to scale as the isotropic average polarizability of  $\text{CO}_2$   $\alpha_{\text{CO}_2}^{\text{av}}(Q_3) = [\alpha_{\text{CO}_2}^{\parallel}(Q_3) + 2\alpha_{\text{CO}_2}^{\perp}(Q_3)]/3$ . Using the  $Q_3$ -dependent polarizabilities for  $\text{CO}_2$  reported by Haskopoulos and Maroulis,<sup>51</sup> this yields

$$\bar{C}_{6,\text{disp}}^{000}(v_3 = 1) = \bar{C}_{6,\text{disp}}^{000}(v_3 = 0) \times \frac{\langle \psi_{v_3=1} | \alpha_{\text{CO}_2}^{\text{av}}(Q_3) | \psi_{v_3=1} \rangle}{\langle \psi_{v_3=0} | \bar{\alpha}_{\text{CO}_2}^{\text{av}}(Q_3) | \psi_{v_3=0} \rangle}. \quad (38)$$

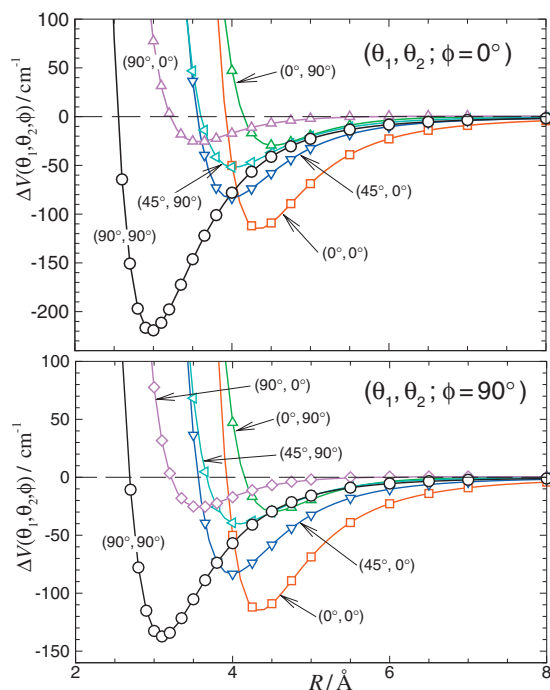


FIG. 2. Vibrational averaged *ab initio* interaction energies (points) along cuts through the analytic 4D PES for CO<sub>2</sub>-H<sub>2</sub> at various relative orientations.

### B. Least-squares fits

To commence any nonlinear least-squares fit, it is necessary to have realistic initial trial values of the fitting parameters. In the present case of fits to the 4D-MLR form of Eq. (26), they were obtained in the following manner. First, a fit to the ordinary 1D MLR form (depending only on  $R$ ) was performed for all distinct combinations of  $\theta_1$ ,  $\theta_2$ , and  $\phi$ , using program betaFIT.<sup>57</sup> This involved some experimentation to ascertain the most appropriate choice for the integer parameters  $p$  and  $q$  and the factor  $f_{\text{ref}}$  appearing in the definitions of the radial variables  $y_p^{\text{cd}}(R; \theta_1, \theta_2, \phi)$ ,  $y_p^{\text{ref}}(R; \theta_1, \theta_2, \phi)$ , and  $y_q^{\text{ref}}(R; \theta_1, \theta_2, \phi)$  of Eqs. (29) and (31), and for the order  $N$  of the exponent polynomial of Eq. (30). As was pointed out above, the present potential function model used  $p=4$ ,  $q=3$ , and  $f_{\text{ref}}=1.5$ , and the exponent polynomial order was  $N=5$ . The resulting values of  $\mathcal{D}_e(\theta_1, \theta_2, \phi)$ ,  $R_e(\theta_1, \theta_2, \phi)$ , and  $\beta_i(\theta_1, \theta_2, \phi)$  (for  $i=0-N$ ) were then fitted to Eq. (33), and the resulting expansion coefficients  $F_{l_1 l_2 l}$  used as starting parameters in the global 4D fits of the vibrationally averaged potential energies to Eq. (26).

In the final fits, the input *ab initio* energies were weighted by assigning uncertainties of  $u_i=0.1 \text{ cm}^{-1}$  to points in the attractive well region where  $V(R, \theta_1, \theta_2, \phi) \leq 0.0 \text{ cm}^{-1}$ , and  $u_i=[V(R, \theta_1, \theta_2, \phi)+10.0]/100.0 \text{ cm}^{-1}$ , to those in the repulsive wall region where  $V(R, \theta_1, \theta_2, \phi) > 0.0 \text{ cm}^{-1}$ . Using these weights, our final 167-parameter fits to the 23 113 vibrationally averaged interaction energies below  $1000 \text{ cm}^{-1}$  yielded dimensionless rms residual discrepancies of only 1.43 and 1.36 for  $v_3=0$  and  $v_3=1$ , respectively. For data points in the well region,  $V(R, \theta_1, \theta_2, \phi) < 0$ , this corresponds to rms discrepancies of 0.143 and  $0.141 \text{ cm}^{-1}$ , respectively. Over one-third of (63/167) of

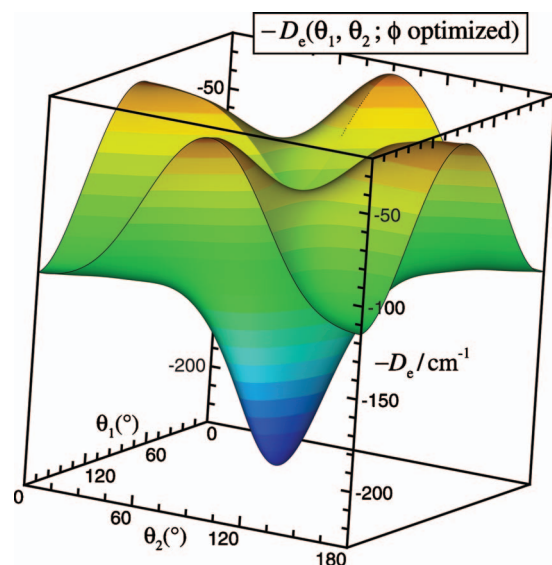


FIG. 3. Minimum energy on our vibrationally averaged 4D PES for CO<sub>2</sub>( $v_3=0$ )-H<sub>2</sub> as a function of angles  $\theta_1$  and  $\theta_2$ , for optimized values of  $\phi$  and  $R$ .

those fitting parameters are required to define  $\mathcal{D}_e(\theta_1, \theta_2, \phi)$  (see Table I), 42 to define  $R_e(\theta_1, \theta_2, \phi)$ , and 31, 15, 4, 4, 3, and 5 to define  $\beta_i(\theta_1, \theta_2, \phi)$  for  $i=0-5$ , respectively. Our use of the sequential rounding and refitting procedure of Ref. 58 means that the parameter sets are relatively compact (e.g., see Table I). The resulting sets of potential parameters and a FORTRAN subroutine for generating these potentials may be obtained from the authors or from the journal's supplementary data archive.<sup>34</sup>

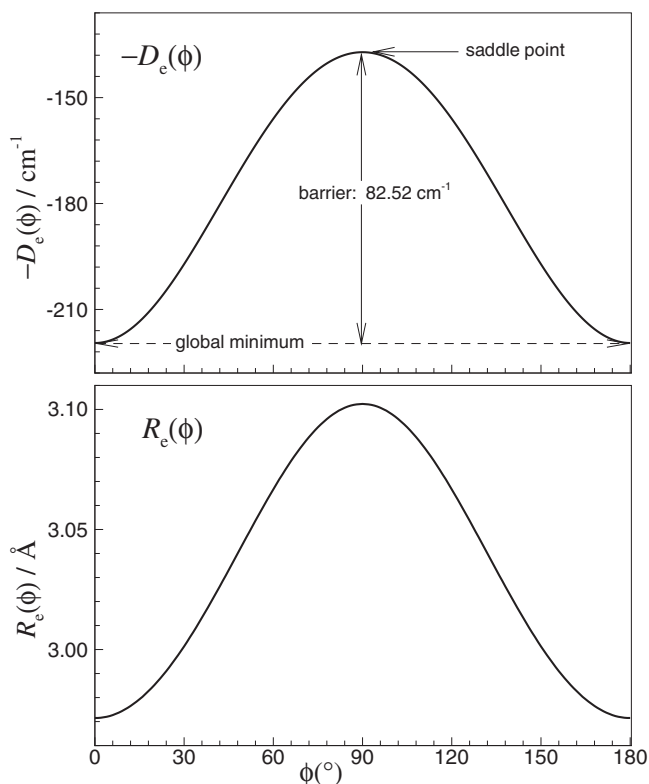


FIG. 4. Energies (upper) and radial positions (lower) along the  $\phi$ -rotation isomerization path between global minima on our vibrationally averaged 4D PES for CO<sub>2</sub>( $v_3=0$ )-H<sub>2</sub>.

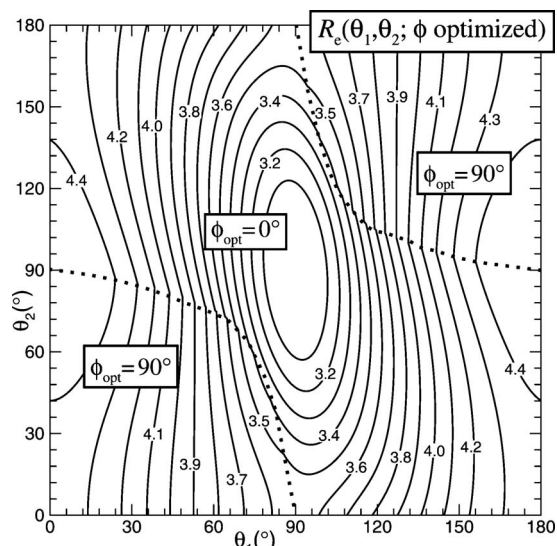


FIG. 5. Radial positions of the minimum on our vibrationally averaged 4D PES for  $\text{CO}_2(v_3=0)\text{-H}_2$  as a function of angles  $\theta_1$  and  $\theta_2$ , for optimized values of  $\phi$  and  $R$ .

## IV. RESULTS AND DISCUSSION

### A. Features of the four-dimensional potential energy surface

Figure 2 illustrates the behavior of our potential along some cuts through our 4D PES for  $v_3=0$ . Figure 3 then shows how the well depth of our fitted, vibrationally averaged, 4D PES for  $\text{CO}_2(v_3=0)\text{-H}_2$  depends on  $\theta_1$  and  $\theta_2$  when  $\phi$  is optimized to minimize the energy for each  $(\theta_1, \theta_2)$ . The complex structure seen there indicates why so many parameters (63) are required to represent  $\mathcal{D}_e(\theta_1, \theta_2, \phi)$  accurately. The global minima well depth of  $219.65\text{ cm}^{-1}$  occurs at the parallel geometry  $\theta_1=\theta_2=90^\circ$  with  $R=2.970\text{ \AA}$  and  $\phi=0^\circ$  (and by symmetry,  $\phi=180^\circ$ ). Figure 4 illustrates the nature of the lowest-energy isomerization pathway, which is a rotation along the  $\phi$  coordinate with  $\theta_1=\theta_2=90^\circ$  with a barrier of height  $82.36\text{ cm}^{-1}$  located at  $R=3.102\text{ \AA}$ . Figure 3 also shows that in the  $(\theta_1, \theta_2)$  domain, equivalent global minima are separated by four equivalent saddle points with energies of  $-114.91\text{ cm}^{-1}$  at collinear geometries where  $R=4.342\text{ \AA}$  and  $\theta_1$  and  $\theta_2$  are equal to either  $0^\circ$  or  $180^\circ$ . It also shows that there are two types of minimum energy paths joining these saddle points to global

minima. The first is a barrierless path along which the  $\text{H}_2$  and  $\text{CO}_2$  monomers remain coplanar ( $\phi=0$ ) and  $\theta_1$  increases while  $\theta_2$  decreases (or vice versa), so that relative to  $\vec{R}$ , each rotates through  $90^\circ$  in a direction counter to the rotation of the other as they move to a collinear arrangement. The second is a path with a barrier of height  $162.58\text{ cm}^{-1}$  along which both  $\theta_1$  and  $\theta_2$  increase (or decrease) in concert; the transition state on this path is located at  $R=3.786\text{ \AA}$  and  $\phi=90^\circ$ , for either  $\theta_1=59.3^\circ$  and  $\theta_2=45.3^\circ$ , or  $\theta_1=120.7^\circ$  and  $\theta_2=134.7^\circ$ .

Figure 5 shows how the radial positions of the minimum energy depend on  $\theta_1$  and  $\theta_2$  when  $\phi$  is optimized at every point. The dotted curves seen there indicate configurations at which the optimum value of  $\phi$  switches abruptly between  $0^\circ$  and  $90^\circ$ . As may be expected, contours which cross these dotted curves show small discontinuities at these switchover points. Nonetheless, the fact that the structure seen here is somewhat simpler than that seen in Fig. 3 indicates why the description of  $R_e(\theta_1, \theta_2, \phi)$  requires only about 2/3 as many parameters (42 versus 63) as are required to define  $\mathcal{D}_e(\theta_1, \theta_2, \phi)$ . One of the nice features of the generalized MLR form is the fact that these two physically meaningful quantities,  $\mathcal{D}_e(\theta_1, \theta_2, \phi)$  and  $R_e(\theta_1, \theta_2, \phi)$ , which are directly determined by the fit, incorporate most of the basic structural information about our 4D surfaces.

The geometries and energies of the global minimum and the saddle points separating them are summarized in Table II; those for  $v_3=0$  are in good agreement with these features of a previous *ab initio* surface for this system calculated by Ran *et al.*,<sup>21</sup> but differ somewhat from those of the potential calculated by Wang *et al.*<sup>20</sup> For the vibrationally averaged excited-state ( $v_3=1$ ) surface, the contour plots look almost the same as those for the ground state ( $v_3=0$ ), and, as shown in Table II, the positions and energies of the stationary points are shifted only slightly.

### B. Bound states and band origin shifts

The rovibrational energy levels of  $\text{CO}_2\text{-H}_2$  were calculated using the radial DVR and parity-adapted angular FBR methods described in Sec. II B and II C. Because of the symmetry properties associated with  $P$ ,  $l_1$ , and  $l_2$ , there exist eight symmetry blocks, and the rovibrational energy levels for each block could be calculated separately. An 80-point

TABLE II. Properties of stationary points of the  $\text{CO}_2\text{-H}_2$  PES and comparisons with results for previously reported surfaces. All entries are given as  $\{R[\text{\AA}], \theta_1^\circ, \theta_2^\circ, \phi^\circ, \bar{V}[\text{cm}^{-1}]\}$ .

	Global minimum	$\phi$ -rotation saddle point <sup>a</sup>	Reference
4D-MLR( $v_3=0$ )	{2.970, 90.0, 90.0, 0.0, -219.65}	{3.102, 90.0, 90.0, 90.0, -137.13}	Present
4D-MLR( $v_3=1$ )	{2.972, 90.0, 90.0, 0.0, -219.26}	{3.104, 90.0, 90.0, 90.0, -136.96}	Present
$Q_3=0$	{2.970, 90.0, 90.0, 0.0, -219.68}	{3.100, 90.0, 90.0, 90.0, -137.27}	21
$Q_3=0$	{2.978, 90.0, 90.0, 0.0, -211.93}	{2.978, 90.0, 90.0, 90.0, -122.55}	20
	Collinear saddle point	$\theta_1/\theta_2$ -rotation saddle point <sup>b</sup>	
4D-MLR( $v_3=0$ )	{4.342, 0.0, 0.0, 0.0, -114.91}	{3.786, 59.3, 45.3, 90.0, -57.07}	Present
4D-MLR( $v_3=1$ )	{4.346, 0.0, 0.0, 0.0, -114.62}	{3.785, 59.4, 45.5, 90.0, -57.46}	Present

<sup>a</sup>Lowest energy barrier between equivalent minima, see text.

<sup>b</sup>Saddle point between global minimum and collinear minimum, see text.



TABLE III. Energies (in cm<sup>-1</sup>) for vibrational levels of our vibrationally averaged 4D-MLR PESs for CO<sub>2</sub>-H<sub>2</sub> expressed relative to the relevant asymptote, with assigned vibrational quantum labels given in parentheses ( $n_s, n_b, l_2, p_{m_2}$ ), compared to published results for some previously reported surfaces. Entries in the first row for each case are for the CO<sub>2</sub>( $v_3=0$ ) complex and those in the second row for CO<sub>2</sub>( $v_3=1$ ), while  $\Delta v_0$  is the band origin shift.

Parity	$l_1$	<i>Para</i> -H <sub>2</sub> -CO <sub>2</sub>				<i>Ortho</i> -H <sub>2</sub> -CO <sub>2</sub>			
		( $n_s, n_b, l_2, p_{m_2}$ )	Present	Reference 21	Reference 20	( $n_s, n_b, l_2, p_{m_2}$ )	Present	Reference 21	Reference 20
$P=0$	Even	(0,0,0,0)	-54.437	-54.390	-50.383	(0,1,1,1)	-50.990	-49.884	-46.472
			-54.616	-54.504			-51.210	-50.021	
		(0,2,0,0)	-25.392	-25.525	-23.544	(0,3,1,1)	-38.228	-37.323	-35.693
			-25.660	-25.651			-38.433	-37.443	
		(0,4,0,0)	-17.113	-17.237	-15.116	(0,3,1,0)	-28.492	-27.929	-25.547
	Odd		-17.405	-17.376			-28.752	-28.047	
		(1,0,0,0)	-5.058	-5.052	-3.335	(0,1,1,0)	-22.231	-21.002	-18.368
			-5.242	-5.132			-22.523	-21.138	
		(0,6,0,0)	-0.756	-0.722					
			-0.912	-0.790					
$P=1$	Even	(1,1,0,0)	-0.161						
			-0.163						
		(0,1,0,0)	-31.013	-31.118	-28.316	(0,0,1,1)	-77.633	-76.303	-71.704
			-31.272	-31.248			-77.725	-76.402	
		(0,3,0,0)	-22.006	-22.214	-20.235	(0,2,1,0)	-40.916	-39.842	-37.837
	Odd		-22.303	-22.365			-41.129	-39.951	
		(0,5,0,0)	-9.046	-9.157	-7.107	(0,2,1,1)	-34.830	-33.875	-31.789
			-9.371	-9.285			-35.055	-34.006	
						(1,0,1,0)	-22.276	-21.237	-19.099
							-22.525	-21.331	
$\Delta v_0$	Theory		-0.179	-0.113			-29.049	-27.523	-24.993
			-0.198				-29.295	-27.627	
	Experiment								
					(0,0,1,-1)	-56.312	-55.030	-51.068	
						-56.458	-55.117		
					(1,0,1,-1)	-19.538		-16.172	
						-19.788			
						-0.092	-0.099		
						-0.096			

sine-DVR grid with points ranging from 3.0 to 20.0 bohr was used for the radial ( $R$ ) stretching coordinate, and 27 and 19 associated Legendre basis functions were used for the angular coordinates  $\theta_1$  and  $\theta_2$ , respectively. The integration over  $\theta_1$  and  $\theta_2$  used 32 and 24 Gauss-Legendre quadrature points, respectively, and that over  $\phi$  used 52 equally spaced points in the range  $[0, 2\pi]$ .

Table III lists the energies of the ( $J=0$ ) intermolecular vibrational energy levels of CO<sub>2</sub>( $v_3=0$ )-H<sub>2</sub> and CO<sub>2</sub>( $v_3=1$ )-H<sub>2</sub> on our 4D-MLR surfaces and compares them to published results for previously reported surfaces.<sup>20,21</sup> It is known that the rotation of H<sub>2</sub> in the complex is dominated by  $l_2=0$ , terms for *para*-H<sub>2</sub> and by  $l_2=1$ , for *ortho*-H<sub>2</sub>, due to the large spacings between the rotational energy levels of molecular hydrogen. However, the small rotational level spacings of CO<sub>2</sub> mean that the quantum label  $l_1$  is best replaced by a  $\theta_1$ -bending quantum label  $n_b$ . The rovibrational energy levels may then be labeled by the six quantum numbers:  $v_3, J, n_s, n_b, l_2$ , and  $p_{m_2}$ , where  $v_3$  is the asymmetric stretch quantum number of CO<sub>2</sub>,  $J$  is the total angular momentum,  $n_s$  is the Van der Waals vibrational stretch quantum numbers, and  $p_{m_2}$  is a composite index giving the parity of the state.<sup>20</sup> Following the approach of Ref. 59, our calcula-

tions for *para*-H<sub>2</sub>-CO<sub>2</sub> complexes used an effective H<sub>2</sub>-molecule inertial rotational constant  $B_{H_2}$  calculated from the experimental  $l_2=0 \rightarrow 2$ , level spacing, while our *ortho*-H<sub>2</sub>-CO<sub>2</sub> calculations used a value of  $B_{H_2}$  defined by the  $l_2=1 \rightarrow 3$  monomer level spacing.

For *para*-H<sub>2</sub>-CO<sub>2</sub>, our surface supports nine bound vibrational levels for complexes formed from either ground-state ( $v_3=0$ ) or excited ( $v_3=1$ ) CO<sub>2</sub>, and the level energies for those two cases are very similar to one another. The present surface for this species supports one more level than was reported for the surface of Ref. 21 and two more than does the PES of Ref. 20. The zero-point energy on our ground-state ( $v_3=0$ ) surface is 165.213 cm<sup>-1</sup>, about 3/4 of the global well depth, a result which is very similar to that of Ref. 21 (165.29 cm<sup>-1</sup>), but somewhat larger than that of Ref. 20 (161.549 cm<sup>-1</sup>).

For the *ortho*-H<sub>2</sub>-CO<sub>2</sub> complex, whose level energies are expressed relative to the  $j_{H_2}=1$ , dissociation channel, we find a total of 27 bound intermolecular vibrational states with energies lower than its asymptote (at<sup>59</sup>  $2B_{H_2}=118.48675$  cm<sup>-1</sup>), three times more than were found for the *para*-H<sub>2</sub>-CO<sub>2</sub> complex. Because of the strong mixing of

TABLE IV. Infrared transition energies (in  $\text{cm}^{-1}$ ) of *para*- $\text{H}_2$ - $\text{CO}_2$  ( $v_3=0 \rightarrow 1$ ) calculated from our vibrationally averaged 4D MLR PESs and comparisons with experiment and with previous theoretical predictions.

Levels $J'_{K'_a K'_c} - J''_{K''_a K''_c}$	Obs.	Present		Reference 21	
		Calc.	Diff.	Calc.	Diff.
Frequencies relative to the 2349.1433 $\text{cm}^{-1}$ band origin of $\text{CO}_2$					
$1_{01}-0_{00}$	0.456	0.472	0.016	0.549	0.093
$1_{10}-1_{11}$	-0.049	-0.030	0.019	0.045	0.094
$2_{12}-1_{11}$	0.953	0.968	0.015	1.049	0.096
$1_{01}-2_{02}$	-1.479	-1.457	0.022	-1.381	0.098
$2_{21}-2_{02}$		1.554		1.631	
$2_{21}-2_{20}$		-0.225		-0.146	
$3_{03}-2_{02}$	1.611	1.623	0.012	1.716	0.105
$3_{21}-2_{02}$		3.663		3.758	
$3_{21}-2_{20}$		1.884		1.981	
$1_{10}-2_{11}$	-1.663	-1.644	0.019	-1.569	0.094
$2_{12}-2_{11}$		-0.646		-0.566	
$3_{12}-2_{11}$	1.939	1.955	0.016	2.057	0.118
$2_{12}-3_{13}$		-1.902		-1.822	
$4_{14}-3_{13}$	2.030	2.041	0.011	2.144	0.114
Average			0.017		0.102
RMSD			0.017		0.102
Frequencies relative to the 2348.9452 $\text{cm}^{-1}$ band origin of <i>para</i> - $\text{H}_2$ - $\text{CO}_2$					
$1_{01}-0_{00}$	0.654	0.652	-0.002	0.662	0.008
$1_{10}-1_{11}$	0.149	0.149	0.000	0.158	0.009
$2_{12}-1_{11}$	1.151	1.147	-0.004	1.162	0.011
$1_{01}-2_{02}$	-1.281	-1.278	0.003	-1.268	0.013
$2_{21}-2_{02}$		1.733		1.744	
$2_{21}-2_{20}$		-0.045		-0.033	
$3_{03}-2_{02}$	1.809	1.802	-0.007	1.829	0.020
$3_{21}-2_{02}$		3.843		3.871	
$3_{21}-2_{20}$		2.064		2.094	
$1_{10}-2_{11}$	-1.465	-1.465	0.000	-1.456	0.009
$2_{12}-2_{11}$		-0.467		-0.453	
$3_{12}-2_{11}$	2.137	2.134	-0.003	2.170	0.033
$2_{12}-3_{13}$		-1.723		-1.709	
$4_{14}-3_{13}$	2.228	2.221	-0.007	2.257	0.029
Average			-0.002		0.017
RMSD			0.004		0.020

angular and radial functions, making  $\{n_s, n_b\}$  assignments based on the nodal structures of the wave functions becomes increasingly difficult with increasing energy, and Table III lists only the lowest 11 assigned vibrational levels; a listing of all 27 level energies is included in the supplemental data.<sup>34</sup> As seen in Table III, the ground state of *ortho*- $\text{H}_2$ - $\text{CO}_2$  is bound by  $-77.633$  and  $-77.725$   $\text{cm}^{-1}$  for  $v_3=0$  and  $v_3=1$ , respectively, which makes this species some 23  $\text{cm}^{-1}$  more stable than is *para*- $\text{H}_2$ - $\text{CO}_2$ , a result consistent with previous results.<sup>20,21</sup>

As shown in the last two rows of Table III, the calculated band origin shifts predicted by our 4D-MLR surfaces are  $\Delta v_0 = -0.179$  and  $-0.092$   $\text{cm}^{-1}$  for *para*- $\text{H}_2$ - $\text{CO}_2$  and *ortho*- $\text{H}_2$ - $\text{CO}_2$ , respectively, results in very good agreement with the experimental values of  $-0.198$  and  $-0.096$   $\text{cm}^{-1}$ .<sup>19</sup> The analogous predictions of Ref. 21 are  $-0.113$  and  $-0.099$   $\text{cm}^{-1}$ , respectively. Since the *ab initio* calculations of Ref. 21 were performed using a very similar level of theory,

we speculate that the relatively large discrepancy for *para*- $\text{H}_2$ - $\text{CO}_2$  is probably due to their neglect of the effect of the change in the average value of  $Q_1$  on excitation of the  $v_3$  mode. The relatively better agreement for *ortho*- $\text{H}_2$ - $\text{CO}_2$  is consistent with a finding from our work on the  $\text{He}-\text{CO}_2$  system that neglect of the effect of changes in  $\bar{Q}_1$  becomes increasingly serious at geometries farther from equilibrium, a consideration which becomes particularly important in treatments of larger clusters.<sup>18,24</sup>

### C. Predicted Infrared Spectra

Infrared  $v_3=0 \rightarrow 1$ , transition energies calculated from our vibrationally averaged 4D PESs for *para*- $\text{H}_2$ - $\text{CO}_2$  and *ortho*- $\text{H}_2$ - $\text{CO}_2$  are listed and compared with experiment and with previous theoretical predictions in Tables IV and V, respectively. The transitions shown there are all for complexes which remain in their ground intermolecular vibra-

TABLE V. Infrared transition energies (in cm<sup>-1</sup>) of *ortho*-H<sub>2</sub>-CO<sub>2</sub>(*v*<sub>3</sub>=0→1) calculated from our vibrationally averaged 4D MLR PESs and comparisons with experiment and with previous theoretical predictions.

Levels $J'_{K'_a K'_c} - J''_{K''_a K''_c}$	Obs.	Present		Reference 21	
		Calc.	Diff.	Calc.	Diff.
Frequencies relative to the 2349.1433 cm <sup>-1</sup> band origin of CO <sub>2</sub>					
0 <sub>00</sub> -1 <sub>01</sub>	-0.720	-0.715	0.005	-0.722	-0.002
2 <sub>02</sub> -1 <sub>01</sub>	1.123	1.123	0.000	1.128	0.005
1 <sub>11</sub> -1 <sub>10</sub>	-0.213	-0.210	0.003	-0.214	-0.001
2 <sub>11</sub> -1 <sub>10</sub>	1.256	1.256	0.000	1.263	0.007
1 <sub>11</sub> -2 <sub>12</sub>	-1.231	-1.223	0.008	-1.228	0.003
2 <sub>11</sub> -2 <sub>12</sub>	0.238	0.243	0.005	0.249	0.011
3 <sub>13</sub> -2 <sub>12</sub>	1.574	1.572	-0.002	1.583	0.009
2 <sub>20</sub> -2 <sub>21</sub>	-0.083	-0.079	0.004	-0.078	0.005
3 <sub>22</sub> -2 <sub>21</sub>	1.751	1.749	-0.002	1.761	0.010
2 <sub>02</sub> -3 <sub>03</sub>	-1.907	-1.897	0.010	-1.893	0.014
<b>3<sub>22</sub>-3<sub>03</sub></b>	1.865	1.911	<b>0.047</b>	1.921	<b>0.056</b>
4 <sub>04</sub> -3 <sub>03</sub>	2.196	2.191	-0.004	2.218	0.022
2 <sub>11</sub> -3 <sub>12</sub>	-2.144	-2.135	0.009	-2.129	0.015
4 <sub>13</sub> -3 <sub>12</sub>	2.545	2.542	-0.003	2.579	0.034
4 <sub>22</sub> -3 <sub>21</sub>	2.501	2.512	0.011	2.546	0.045
3 <sub>13</sub> -4 <sub>14</sub>	-2.348	-2.336	0.012	-2.327	0.021
RMSD (including 3 <sub>22</sub> -3 <sub>03</sub> )			0.014		0.023
RMSD (excluding 3 <sub>22</sub> -3 <sub>03</sub> )			0.007		0.018
Frequencies relative to the 2349.0473 cm <sup>-1</sup> band origin of <i>ortho</i> -H <sub>2</sub> -CO <sub>2</sub>					
0 <sub>00</sub> -1 <sub>01</sub>	-0.625	-0.623	0.002	-0.623	0.002
2 <sub>02</sub> -1 <sub>01</sub>	1.218	1.215	-0.003	1.227	0.009
1 <sub>11</sub> -1 <sub>10</sub>	-0.118	-0.118	0.000	-0.115	0.003
2 <sub>11</sub> -1 <sub>10</sub>	1.351	1.348	-0.003	1.362	0.011
1 <sub>11</sub> -2 <sub>12</sub>	-1.136	-1.131	0.005	-1.129	0.007
2 <sub>11</sub> -2 <sub>12</sub>	0.333	0.335	0.002	0.348	0.015
3 <sub>13</sub> -2 <sub>12</sub>	1.669	1.664	-0.005	1.682	0.013
2 <sub>20</sub> -2 <sub>21</sub>	0.012	0.013	0.001	0.021	0.009
3 <sub>22</sub> -2 <sub>21</sub>	1.846	1.841	-0.005	1.860	0.014
2 <sub>02</sub> -3 <sub>03</sub>	-1.812	-1.805	0.007	-1.794	0.018
<b>3<sub>22</sub>-3<sub>03</sub></b>	1.960	2.003	<b>0.043</b>	2.020	<b>0.060</b>
4 <sub>04</sub> -3 <sub>03</sub>	2.291	2.283	-0.008	2.317	0.026
2 <sub>11</sub> -3 <sub>12</sub>	-2.049	-2.043	0.006	-2.030	0.019
4 <sub>13</sub> -3 <sub>12</sub>	2.640	2.634	-0.006	2.678	0.038
4 <sub>22</sub> -3 <sub>21</sub>	2.596	2.604	0.008	2.645	0.049
3 <sub>13</sub> -4 <sub>14</sub>	-2.253	-2.244	0.009	-2.228	0.025
RMSD (including 3 <sub>22</sub> -3 <sub>03</sub> )			0.012		0.026
RMSD (excluding 3 <sub>22</sub> -3 <sub>03</sub> )			0.005		0.021

tional level ( $n_3=0$ ). The rotational levels of these complexes were assigned using the conventional asymmetric-rotor labels  $J$ ,  $K_a$ , and  $K_c$ , where  $J$  is the total angular momentum and  $K_a$  and  $K_c$  denote the projections of  $J$  onto the  $a$  and  $c$  principal axes of inertia. Due to the interchange symmetry of the indistinguishable zero-spin <sup>16</sup>O nuclei, the allowed rotational states for C<sup>16</sup>O<sub>2</sub> in its ground state ( $v_3=0$ ) only have even values of the angular momentum quantum number  $l_1$ , while for the first excited asymmetric-stretch state ( $v_3=1$ ) state only odd values of  $l_1$  are allowed.<sup>20</sup> Hence, for *para*-H<sub>2</sub>-CO<sub>2</sub>, the allowed rotational levels have  $(K_a, K_c) = (\text{even}, \text{even})$ , or  $(\text{odd}, \text{odd})$  for the CO<sub>2</sub> ground state ( $v_3=0$ ), and  $(K_a, K_c) = (\text{even}, \text{odd})$ , or  $(\text{odd}, \text{even})$  for the excited state ( $v_3=1$ ). Similarly, for *ortho*-H<sub>2</sub>-CO<sub>2</sub>, the allowed rota-

tional levels have  $(K_a, K_c) = (\text{even}, \text{odd})$  or  $(\text{odd}, \text{even})$  for  $v_3=0$ , and  $(K_a, K_c) = (\text{even}, \text{even})$ , or  $(\text{odd}, \text{odd})$  when  $v_3=1$ .

The upper part of Table IV expresses the infrared transition energies of *para*-H<sub>2</sub>-CO<sub>2</sub> relative to the  $\nu_3$  fundamental band origin of CO<sub>2</sub>. Column 3 shows the transition energies yielded by our vibrationally averaged 4D PESs, which are seen to agree very well with the experimental values shown in column 2.<sup>19</sup> The differences seen in column 4 are very small and the fact that the average and rms discrepancies are very similar shows that most of these differences are due to the 0.019 cm<sup>-1</sup> error in our calculated band origin shift. If the experimental and calculated transition energies are expressed to their respective band origins, we obtain the results seen in the lower half of Table IV. As is seen in the

lower half of column 4, the differences with experiment<sup>19</sup> are then significantly reduced, yielding average and rms discrepancies of only  $-0.002$  and  $0.004$   $\text{cm}^{-1}$ , respectively. The results presented in columns 5 and 6 show that our surfaces yield approximately five times better agreement with experiment than do the predictions of Ref. 21.

For *ortho*-H<sub>2</sub>-CO<sub>2</sub>, the calculated infrared transition frequencies expressed relative to the band origin of free CO<sub>2</sub> are given in the upper part of Table V. Again, column 2 lists the experimental results from Ref. 19 and column 3 the values calculated from our vibrationally averaged 4D PESs. The differences seen in column 4 are very small except for the transition 3<sub>22</sub>-3<sub>03</sub> (shown in bold font), for which the discrepancy of  $0.047$   $\text{cm}^{-1}$  is anomalously large relative to the rms discrepancy of  $0.007$   $\text{cm}^{-1}$  for the others. If the infrared transitions are expressed relative to the band origin for the *ortho*-H<sub>2</sub>-CO<sub>2</sub> complex, as shown in the lower part of Table V, the discrepancy of  $0.043$   $\text{cm}^{-1}$  for the 3<sub>22</sub>-3<sub>03</sub> transition remains anomalously large relative to the rms discrepancy of  $0.005$   $\text{cm}^{-1}$  for the others. Although their overall agreement with experiment is roughly a factor of 3 worse than ours, this anomaly is also evident in the predictions of Ref. 21. This led us to speculate that there might have been an error in the assignment of this experimental datum.

To address this question, our calculations for both the *para*- and *ortho*-H<sub>2</sub>-CO<sub>2</sub> complexes were extended to higher  $J$ , and predictions were generated for all possible transitions in the neighborhood of the observed line at  $2351.008$   $\text{cm}^{-1}$ , with the simulated transition energies being based on combining the level energies on our upper and lower PESs with the experimental band origin energies. The portion of those results shown in Table VI shows that there are no other transitions of *ortho*-H<sub>2</sub>-CO<sub>2</sub> which could account for the line that had been assigned<sup>19</sup> as the 3<sub>22</sub>-3<sub>03</sub> transition of *ortho*-H<sub>2</sub>-CO<sub>2</sub>, but that it is coincident with our prediction for the 3<sub>21</sub>-2<sub>20</sub> transition of *para*-H<sub>2</sub>-CO<sub>2</sub>. Thus, we conclude that the this apparent anomaly in our *para*-H<sub>2</sub>-CO<sub>2</sub> predictions is most likely due to the presence of a small amount of *para*-H<sub>2</sub>-CO<sub>2</sub> impurity in the *ortho*-H<sub>2</sub>-CO<sub>2</sub> experiment which led to a misassignment of this transition.

## V. DISCUSSION AND CONCLUSIONS

This paper presents accurate analytic vibrationally averaged 4D PESs for H<sub>2</sub>-CO<sub>2</sub>( $v_3$ ) complexes for  $v_3=0$  and 1 which were obtained from effective six-dimensional *ab initio* potential energies that explicitly incorporate the dependence of the interaction energy on both the  $Q_1$  and  $Q_3$  normal-mode coordinate of CO<sub>2</sub>. The *ab initio* interaction energies were obtained at the CCSD(T) level using a large aug-cc-pVTZ basis set and with bond functions placed at the midpoint of the intermolecular axis. The vibrationally averaged potential energies were fitted to a 4D generalization of the MLR potential form which incorporates the correct theoretically known long-range inverse-power behavior;<sup>22,23</sup> having this correct long-range behavior is important if this potential is to provide a good description of a CO<sub>2</sub> molecule in medium to large sized (H<sub>2</sub>)<sub>*n*</sub> clusters. The global 4D fit to the 23 113

TABLE VI. Predicted infrared transition energies for *ortho*-H<sub>2</sub>-CO<sub>2</sub> and *para*-H<sub>2</sub>-CO<sub>2</sub> near the observed line at  $2351.008$   $\text{cm}^{-1}$ , as generated from our vibrationally averaged 4D MLR PES, comparison with experiment.

$J'_{k'_a k'_c} - J''_{k''_a k''_c}$	Obs.	Calc.
<i>Ortho</i> -H <sub>2</sub> -CO <sub>2</sub>		
4 <sub>13</sub> -4 <sub>14</sub>		2350.153
2 <sub>02</sub> -1 <sub>01</sub>	2350.266	2350.263
2 <sub>11</sub> -1 <sub>10</sub>	2350.399	2350.397
3 <sub>13</sub> -2 <sub>12</sub>	2350.717	2350.711
3 <sub>22</sub> -2 <sub>21</sub>	2350.894	2350.889
<b>3<sub>22</sub>-3<sub>03</sub></b>	<b>2351.008</b>	2351.051
6 <sub>15</sub> -6 <sub>16</sub>		2351.242
4 <sub>04</sub> -3 <sub>03</sub>	2351.339	2351.331
5 <sub>24</sub> -5 <sub>05</sub>		2351.409
4 <sub>31</sub> -3 <sub>30</sub>		2351.529
4 <sub>22</sub> -3 <sub>21</sub>	2351.644	2351.652
4 <sub>13</sub> -3 <sub>12</sub>	2351.688	2351.682
5 <sub>15</sub> -4 <sub>14</sub>		2351.756
5 <sub>24</sub> -4 <sub>23</sub>		2352.055
5 <sub>42</sub> -4 <sub>41</sub>		2352.098
5 <sub>33</sub> -4 <sub>32</sub>		2352.131
5 <sub>33</sub> -5 <sub>14</sub>		2352.181
2 <sub>20</sub> -1 <sub>01</sub>		2352.243
6 <sub>06</sub> -5 <sub>05</sub>		2352.291
3 <sub>31</sub> -3 <sub>12</sub>		2352.564
6 <sub>51</sub> -5 <sub>50</sub>		2352.646
6 <sub>42</sub> -5 <sub>41</sub>		2352.718
6 <sub>15</sub> -5 <sub>14</sub>		2352.827
6 <sub>33</sub> -5 <sub>32</sub>		2352.854
6 <sub>24</sub> -5 <sub>23</sub>		2353.026
4 <sub>22</sub> -3 <sub>03</sub>		2353.774
5 <sub>42</sub> -5 <sub>23</sub>		2354.229
<i>Para</i> -H <sub>2</sub> -CO <sub>2</sub>		
2 <sub>12</sub> -3 <sub>31</sub>		2343.342
1 <sub>01</sub> -2 <sub>20</sub>		2345.887
3 <sub>12</sub> -3 <sub>31</sub>		2345.943
2 <sub>21</sub> -3 <sub>22</sub>		2346.992
3 <sub>03</sub> -3 <sub>22</sub>		2347.061
2 <sub>12</sub> -3 <sub>13</sub>		2347.221
1 <sub>10</sub> -2 <sub>11</sub>	2347.480	2347.480
1 <sub>01</sub> -2 <sub>02</sub>	2347.664	2347.666
2 <sub>12</sub> -2 <sub>11</sub>		2348.478
2 <sub>21</sub> -2 <sub>20</sub>		2348.899
3 <sub>30</sub> -3 <sub>31</sub>		2348.939
1 <sub>10</sub> -1 <sub>11</sub>	2349.094	2349.093
3 <sub>21</sub> -3 <sub>22</sub>		2349.101
1 <sub>01</sub> -0 <sub>00</sub>	2349.599	2349.596
3 <sub>12</sub> -3 <sub>13</sub>		2349.822
2 <sub>12</sub> -1 <sub>11</sub>	2350.096	2350.091
2 <sub>21</sub> -2 <sub>02</sub>		2350.678
3 <sub>03</sub> -2 <sub>02</sub>	2350.754	2350.747
<b>3<sub>21</sub>-2<sub>20</sub></b>		<b>2351.008</b>
3 <sub>12</sub> -2 <sub>11</sub>	2351.082	2351.079
4 <sub>14</sub> -3 <sub>13</sub>	2351.173	2351.165
4 <sub>23</sub> -3 <sub>22</sub>		2351.477
4 <sub>32</sub> -3 <sub>31</sub>		2351.528
3 <sub>21</sub> -2 <sub>02</sub>		2352.787
3 <sub>30</sub> -2 <sub>11</sub>		2354.075
4 <sub>32</sub> -3 <sub>13</sub>		2355.407
4 <sub>41</sub> -3 <sub>22</sub>		2356.588

interaction energies had a root-mean-square (rms) residual in the well region of only 0.143 and 0.136 cm<sup>-1</sup> for  $v_3=0$  and 1, respectively, and required only 167 fitting parameters.

The type of analytic potential energy function expression used here differs from the “damped electrostatic and dispersion attraction plus exponential repulsion” form used in much other work on van der Waals molecules.<sup>21,27,47,53,60</sup>

While both types of functions may accurately represent such surfaces, we believe that the extended MLR form used here has significant advantages. In particular, it is explicitly defined in terms of two key physically interesting properties of the system, the well depth  $\mathcal{D}_e(\theta_1, \theta_2, \phi)$  and the position of the radial minimum  $R_e(\theta_1, \theta_2, \phi)$ , and most of its fitting parameters (here, 105 out of 167) are involved in defining how those two properties depend on relative molecular orientations. Figures 3 and 5 illustrate the fact that considerable physical insight may be gained by characterizing potentials in this way. In contrast, all of the fitting parameters in the conventional forms are involved in characterizing exponential and pre-exponential product functions which cannot be readily related to any physical properties of the system. It is also noteworthy that the MLR-type functions may also be used for chemically bound systems, while “inverse-power attraction plus exponential repulsion” forms can only really be used for van der Waals systems. Moreover, while the version of the MLR form used here does not explicitly incorporate “damping” into the inverse-power terms, its effect is implicitly incorporated into the behavior of the exponent coefficient  $\beta(R, \theta_1, \theta_2, \phi)$ .

Rovibrational energy levels for *para*-H<sub>2</sub>-CO<sub>2</sub> and *ortho*-H<sub>2</sub>-CO<sub>2</sub> were obtained by the radial DVR/angular FBR method. Our potentials support 9 and 27 bound intermolecular vibrational states for *para*-H<sub>2</sub> and *ortho*-H<sub>2</sub>-CO<sub>2</sub> complexes, respectively. The calculated band origin shifts associated with the  $\nu_3$  fundamental transition of CO<sub>2</sub> are -0.179 and -0.092 cm<sup>-1</sup> for *para*-H<sub>2</sub>-CO<sub>2</sub> and *ortho*-H<sub>2</sub>-CO<sub>2</sub>, respectively, which results in good agreement with the experimental values of -0.198 and -0.096 cm<sup>-1</sup>. This suggests that these surfaces will yield reliable predictions for the  $\nu_3$  vibrational shifts of CO<sub>2</sub> in (H<sub>2</sub>)<sub>n</sub> clusters. The calculated spectroscopic properties of our vibrationally averaged 4D PESs are in excellent agreement with experiment: for infrared transitions of *para*-H<sub>2</sub>-CO<sub>2</sub> and *ortho*-H<sub>2</sub>-CO<sub>2</sub>, the rms discrepancies are 0.004 and 0.005 cm<sup>-1</sup>, respectively. The accuracy of the present PESs allowed us to discern a probably misassignment of one of the reported experimental lines of *ortho*-H<sub>2</sub>-CO<sub>2</sub>.

One consideration entirely missing from the present discussion (and from all analogous previous work) is the possible effect of the CO<sub>2</sub> bending coordinate,  $Q_2$ . Within the context of an adiabatic separation of fast versus slow molecular motions, we believe that this is not a serious omission. In particular, the fact that the average structure is linear for both the (0,0,0) and (0,0,1) vibrational states of CO<sub>2</sub> suggests that this degree of freedom should not contribute significantly to the observed  $\nu_3$  band origin shifts for CO<sub>2</sub> in CO<sub>2</sub>-(H<sub>2</sub>)<sub>n</sub> clusters.<sup>61</sup> On the other hand, the nonzero average value of the square of the instantaneous perpendicular dipole moment will contribute a small additional induction

term to the overall interaction energy. If this is slightly larger for CO<sub>2</sub>( $v_3=1$ ) than for CO<sub>2</sub>( $v_3=0$ ), it would affect the predicted  $\nu_3$  vibrational frequency shifts and might even explain the residual 10% discrepancy between the experimental and calculated shifts for this system. Work to examine this question is now under way.

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