A Minimal Model of Potential Energy Surface for the CO_2 – CO System

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Abstract. Analytical models of potential energy surfaces are desirable for applications to classical and quantum molecular dynamics simulations, as well as calculation of spectroscopic properties. Here, we present a minimal model based on the expansion in spherical harmonics of the interaction potential between CO_2 and CO molecules, both assumed as rigid rotors. This approach consists in determining a minimal number of energy points related to representative mutual orientations of the molecules (configurations) by *ab initio* calculations. The spherical harmonics expansion represents an exact transformation of these quantum chemical input data. The model permits interpolation and possible implementation of sets of input data at a higher level of theory.

Keywords: van der Waals clusters · Intermolecular interactions · Planetary atmospheres · Spherical harmonics expansion

1 Introduction

The CO_2 – CO system has a remarkable importance in many areas, that span from the environmental and industrial chemistry to the chemistry of terrestrial and other planetary atmospheres [1]. These molecules are interconverted in the Boudouard reaction, where CO disproportionates to give C and CO_2. This reaction has been traditionally studied because of its environmental and industrial implications [2], while more recently it attracted interest in physics of plasmas, where the reaction is induced by high vibrational excitation [3]. The van der Waals cluster CO_2 – CO was initially characterized by rotational and vibrational spectroscopy [4], where a T-shaped configuration (CO and CO_2 are perpendicularly oriented) was observed, while theoretical investigations on this weakly bound complex was performed by using molecular mechanics for cluster modeling [5]. The dimer was investigated in argon matrices, to study conformational dynamics [6, 7], and afterwards theoretically characterized by Symmetry Adapted Perturbation Theory [8]. Molecular beam electric resonance spectroscopy was then employed to measure the dipole moment [9]. More recently, *ab initio* methods were employed to calculate the vibrational spectrum of various van der Waals complexes, including CO_2 – CO.

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The most recent experimental study, performed by infrared spectroscopy, reported the existence of a new T-shaped isomer [10]. In 2019, a four-dimensional potential energy surface obtained by CCSD(T)-F12 method calculated on more than 30,000 energy points, employing 147 expansion terms, revealed dynamical features of this complex, such as the minima and the related saddle points and the temperature dependence of the second virial coefficient [11].

In this article, we consider the case of the CO_2 – CO system, where both molecules are treated as rigid rotors and represent the potential energy surface in the analytical form, suitable for classical and quantum treatment of collisional processes, as well as for the calculation of spectroscopical properties. The potential energy surface is expanded into a series of nine spherical harmonics. This method has been extensively used to represent the potential interaction of van der Waals complexes formed by four and five bodies [12, 13]. Previously, expansion of the intermolecular potential in spherical (and hyperspherical) harmonics has been employed to represent non reacting systems of molecular pairs: rigid diatomic molecules of increasing complexity such as O_2-O_2 [14], N_2-N_2 [15], H_2-H_2 [16], N_2-O_2 [17], N_2-NO [18] and more recently CO – CO and the general case CO – HF [19]; five-body systems containing water H_2O – H_2 [20], H_2O – N_2 and H_2O – O_2 [21], H_2O – HF [22]; hydrogen peroxide [23, 24] and hydrogen persulfide [25, 26], where the torsion motion is not hindered.

Here, we have calculated a minimal number of points, 243 points, of the potential energy surface corresponding to significant configurations, whose choice and number relies on symmetry properties of the system. These configurations are the input data of the potential expansion. Since CO_2 and CO belong to the group symmetries $D_{\infty h}$ and $D_{\infty v}$, respectively, this system is similar to N_2 – NO [18] and the potential energy surface is properly described by at least nine significant configurations, while for the simpler O_2 – O_2 system, five significant configurations were enough for a comprehensive description of the potential interaction. The potential energy surface depends on four coordinates: a radial and three angular coordinates. The radial coordinate is the distance between the center-of-mass of the interacting molecules, that for CO_2 corresponds to the C atom. The expansion is given in terms of spherical harmonics, which depend on the angular coordinates. Their choice depends on the dimension and on the symmetry properties of the system and the number corresponds to the number of significant configurations. The expansion moments are function of the radial coordinate and are determined by solving a system of linear equations, where the known vector is the energy of the significant configurations. This approach represents an exact transformation, permitting interpolation among the energy points as requested by dynamical applications [27]. For each of the nine configurations, 27 single energy points have been calculated at the MP2 level of theory, employing the aug-cc-pVQZ basis set.

The article is structured as follows: in Sect. 2, we give a description of the coordinates frame, of the significant configurations and of quantum mechanical calculations; in Sect. 3, we report the interaction potential expanded in spherical harmonics; in Sect. 4, the results are discussed; in Sect. 5, the conclusions end the paper.

2 Potential Energy Surface

2.1 Coordinates

The potential energy surface of CO_2 – CO depends on a radial and three angular coordinates. In Fig. 1, we report the system embedded in the *xyz* Cartesian reference frame, where the origin of the axes corresponds to the center-of-mass of the system. The radial coordinate r is the distance that separates the centers-of-mass of the molecules; θ_a, $0 \leq \theta_a, \leq \pi$ is the angle given by the intersection between the vector **r** that joins the centers-of-mass of the two molecules and the O – C – O bond in CO_2, while θ_b, $0 \leq \theta_b, \leq \pi$ is the angle given by the intersection between the vector **r** and the C – O bond in CO; finally, the dihedral angle ϕ, $0 \leq \phi < 2\pi$, is defined as the intersection between the semiplanes passing through the axes of the two molecules and the origin of the Cartesian axes.

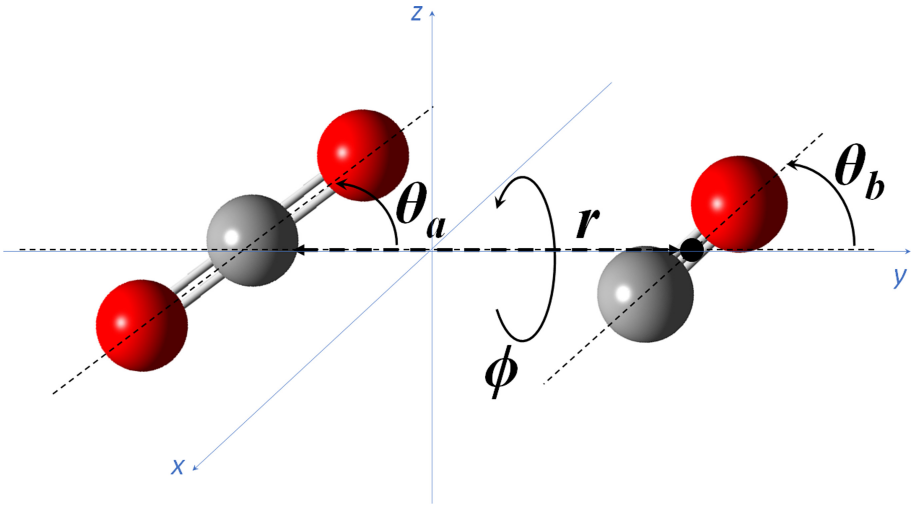

Fig. 1. The radial, r, and the angular, θ_a, θ_b, and ϕ, coordinates for the CO_2 - CO system (in red the oxygen atoms and in grey the carbon atoms). (Color figure online)

2.2 Configurations

The choice of the significant configurations relies on considerations upon geometry and symmetry properties of the system. A proper choice of these configurations would permit to represent uniformly the potential energy surface, although with a small number of terms, within the considered distance range. The significant configurations for CO_2 - CO (Fig. 2) are identified by capital letters: L, H, X, Z and T. The L configurations are characterized by a linear mutual orientation of the molecular axes, with $\theta_{a=0}$, while θ_b is 0 in the configuration corresponding to the carbon of CO in the closest position to CO_2, L_1, and π in the opposite case, L_2. In the H configuration the molecular axes are parallel, thus $\theta_a = \theta_b = \pi/2$, and $\phi = 0$. The X configuration is characterized by the dihedral angle $\phi = \pi/2$; both the angles θ_a and θ_b are also $\pi/2$. The Z_1 configuration presents a parallel orientation of the molecular axes, with $\theta_a = \theta_b = \pi/4$ and $\phi = 0$. The configuration Z_2 is characterized by $\theta_a = \pi/4$, $\theta_b = 3\pi/4$ and $\phi = 0$. Finally, in the T configurations the molecular axes are perpendicular, more precisely in T_1, $\theta_a = \pi/2$ and $\theta_b = 0$, in T_2 $\theta_a = \pi/2$, $\theta_b = 0$ and $\phi = 0$; in T_3 $\theta_a = \pi/2$, $\theta_b = 0$ and $\phi = \pi$.

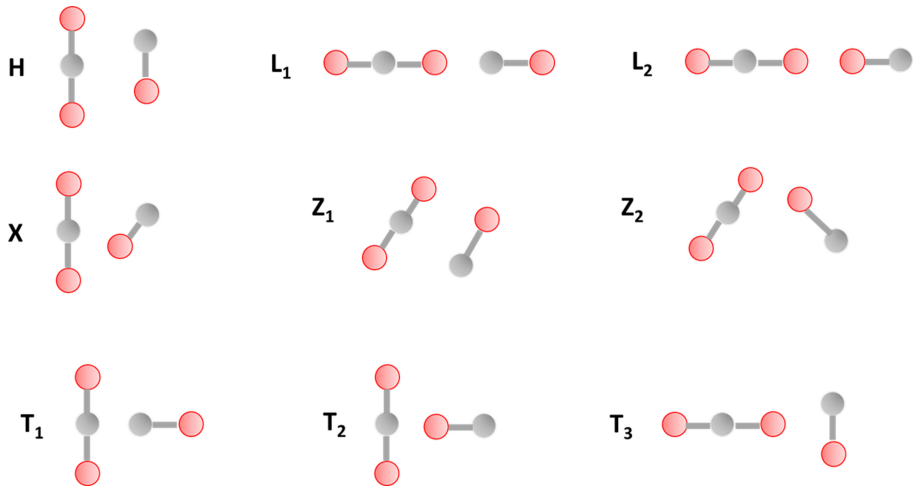

Fig. 2. The nine significant configurations chosen to construct the potential energy surface of CO_2 - CO (in red the oxygen atoms and in grey the carbon atoms). (Color figure online)

2.3 *Ab initio* Calculations

Ab initio calculations have been performed by the Gaussian09 software package [28]. The geometries have been optimized by MP2/aug-cc-pVTZ, obtaining the following geometries: in CO, the bond length is 1.14 Å, while in CO_2 the bond length is 1.17 Å and the bond angle is 180.0°. We have calculated about 250 energy points, corresponding to 27 radial grid points between 2.0 and 8.0 Å for each of the nine significant configurations at the MP2 level of theory with aug-cc-pVQZ basis set. For each configuration, we have estimated the Basis Set Superposition Error by counterpoise correction for the smallest value of the distance, 2.8 Å.

3 Spherical Harmonics Expansion of the Intermolecular Potential

The interaction potential is given by the expansion of a series of spherical harmonics $\mathcal{Y}^{L0}_{L_1L_2}(\theta_1, \theta_2, \phi)$ and their expansion terms $v_{L_1L_2L}(r)$:

$$V(r; \theta_1, \theta_2, \phi) = \sum_{L_1L_2L} v_{L_1L_2L}(r) \mathcal{Y}^{L0}_{L_1L_2}(\theta_1, \theta_2, \phi) \tag{1}$$

L_1 and L_2 are non-negative integer numbers and represent the order of the spherical harmonics, while L is a combination of L_1 and L_2 and is given by $|L_1 - L_2| \leq L \leq L_1 + L_2$. The spherical harmonic $\mathcal{Y}^{L0}_{L_1L_2}(\theta_1, \theta_2, \phi)$ is decomposed into two spherical harmonics $\mathcal{Y}^{m}_{L_1}(\theta_1, \phi_1)$ and $\mathcal{Y}^{-m}_{L_2}(\theta_2, \phi_2)$, where m is an integer number –min $(L_1, L_2) \leq m \leq$ min (L_1, L_2). The interaction potential is thus written as a product of the two spherical harmonics:

$$V(r; \alpha, \theta_1, \theta_2, \phi) = \sum_i w_i(\alpha) \sum_{L_1L_2L} \begin{pmatrix} L_1 & L_2 & L \\ m & -m & 0 \end{pmatrix} v_{L_1L_2L}(r) \mathcal{Y}^{m}_{L_1}(\theta_1, 0)\, \mathcal{Y}^{-m}_{L_2}(\theta_2, \phi) \tag{2}$$

Here, the 2 × 3 matrix within parenthesis is a 3-j symbol. The angular coordinates ϕ_1 and ϕ_2 are both dihedral angles, referred respectively to CO_2 and CO. The dihedral angle ϕ is the difference between ϕ_1 and ϕ_2. Thus, the spherical harmonics are written as $\mathcal{Y}^{m}_{L_1}(\theta_1, \phi)$ and $\mathcal{Y}^{-m}_{L_2}(\theta_2, 0)$.

The choice of the spherical harmonics of this expansion relies upon the symmetry characteristics of the system. The set of spherical harmonics is formed by only even values for L_1 and both even and odd values for L_2. Thus, the interaction potential for this system is given by

$$\begin{aligned} V_{CO_2-CO}(r; \theta_1, \theta_2, \phi) &= v_{000}(r) + \sqrt{3} v_{011}(r) \cos\theta_2 + \tfrac{\sqrt{5}}{4} v_{022}(r)(1 + \\ &3\cos(2\theta_2)) + \tfrac{\sqrt{5}}{4} v_{202}(r)(1 + 3\cos(2\theta_1)) - \tfrac{1}{2}\sqrt{\tfrac{3}{2}} v_{211}(r)[(1 + \\ &3\cos(2\theta_1)\cos\theta_2) + 3\cos\phi \sin(2\theta_1)\sin\theta_2] + \tfrac{3}{2} v_{213}(R)\left[\tfrac{1}{2}(1 + \right. \\ &\left. 3\cos(2\theta_1))\cos\theta_2 - \cos\phi \sin(2\theta_1)\sin\theta_2\right] + \tfrac{\sqrt{5}}{4} v_{220}(R)\left[\tfrac{1}{4}(1 + 3\cos(2\theta_1))(1 + \right. \\ &\left. 3\cos(2\theta_2)) + 3\cos\phi \sin(2\theta_1)\sin(2\theta_2) + \tfrac{3}{4} cos(2\phi)(cos(2\theta_1) - 1)(cos(2\theta_2) - \right. \\ &\left. 1)\right] - \tfrac{5}{4\sqrt{14}} v_{222}(r)\left[\tfrac{1}{2}(1 + 3\cos(2\theta_1))(1 + 3\cos(2\theta_2)) + \right. \\ &\left. 3\cos\phi \sin(2\theta_1)\sin(2\theta_2) - \tfrac{3}{2} cos(2\phi)(cos(2\theta_1) - 1)(cos(2\theta_2) - 1)\right] + \\ &3\sqrt{\tfrac{5}{14}} v_{224}(r)\left[\tfrac{1}{8}(1 + 3\cos(2\theta_1))(1 + 3\cos(2\theta_2)) - cos\,\phi\, sin(2\theta_1) sin(2\theta_2) + \right. \\ &\left. \tfrac{1}{16} cos\,(2\phi)(cos(2\theta_1) - 1)(cos(2\theta_2) - 1)\right] \end{aligned} \tag{3}$$

The expansion moments $v_{L_1L_2L}(r)$ are given as a linear combination of the energy points of the significant configurations as a function of the distance:

$$v_{000}(r) = \frac{1}{18}\left(4V_H(r) + V_{L_1}(r) + V_{L_2}(r) + 2V_{T_1}(r) + 2V_{T_2}(r) + 4V_{T_3}(r) + 4V_X(r)\right) \tag{4}$$

$$v_{011}(r) = \frac{V_{L_1}(r) - V_{L_2}(r) + 2V_{T_1}(r) - 2V_{T_2}(r)}{6\sqrt{3}} \tag{5}$$

$$v_{022}(r) = \frac{-2V_H(r) + V_{L_1}(r) + V_{L_2}(r) + 2V_{T_1}(r) + 2V_{T_2}(r) - 2V_{T_3}(r) - 2V_X(r)}{9\sqrt{5}} \tag{6}$$

$$v_{202}(r) = -\frac{2V_H(r) - V_{L_1}(r) - V_{L_2}(r) + V_{T_1}(r) + V_{T_2}(r) - 4V_{T_3}(r) + 2V_X(r)}{9\sqrt{5}} \tag{7}$$

$$v_{211}(r) = \frac{1}{30\sqrt{6}}\Big(6\sqrt{2}V_H(r) + \left(-4+3\sqrt{2}\right)V_{L_1}(r) + \left(4+3\sqrt{2}\right)V_{L_2}(r) + \left(4+3\sqrt{2}\right)V_{T_1}(r) + \left(-4+3\sqrt{2}\right)V_{T_2}(r) + 6\sqrt{2}V_{T_3}(r) - 12\sqrt{2}V_{Z_1}(r) - 12\sqrt{2}V_{Z_2}(r)\Big) \tag{8}$$

$$v_{213}(r) = \frac{1}{15\sqrt{2}}\Big(2V_H(r) + \left(1+\sqrt{2}\right)V_{L_1}(r) + \left(1-\sqrt{2}\right)V_{L_2}(r) + \left(1-\sqrt{2}\right)V_{T_1}(r) + \left(1+\sqrt{2}\right)V_{T_2}(r) + 2V_{T_3}(r) - 4V_{Z_1}(r) - 4V_{Z_2}(r)\Big) \tag{9}$$

$$v_{220}(r) = \frac{1}{45}\sqrt{\frac{2}{5}}\Big(7\sqrt{2}V_H(r) + \left(-3+\sqrt{2}\right)V_{L_1}(r) + \left(3+\sqrt{2}\right)V_{L_2}(r) - \left(3+\sqrt{2}\right)V_{T_1}(r) + \left(3-\sqrt{2}\right)V_{T_2}(r) - 2\sqrt{2}V_{T_3}(r) - 5\sqrt{2}V_X(r) + 6\sqrt{2}V_{Z_1}(r) - 6\sqrt{2}V_{Z_2}(r)\Big) \tag{10}$$

$$v_{222}(r) = \frac{1}{45\sqrt{14}}\Big(20V_H(r) + \left(-4+3\sqrt{2}\right)V_{L_1}(r) - \left(4+3\sqrt{2}\right)V_{L_2}(r) + \left(4+3\sqrt{2}\right)V_{T_1}(r) + \left(4-3\sqrt{2}\right)V_{T_2}(r) + 8V_{T_3}(r) - 28V_X(r) - 12V_{Z_1}(r) + 12V_{Z_2}(r)\Big) \tag{11}$$

$$v_{224}(r) = \frac{2}{15}\sqrt{\frac{2}{35}}\Big(2V_H(r) + \left(1+\sqrt{2}\right)V_{L_1}(r) + \left(1-\sqrt{2}\right)V_{L_2}(r) + \left(1+\sqrt{2}\right)V_{T_1}(r) - \left(1+\sqrt{2}\right)V_{T_2}(r) - 2V_{T_3}(r) - 4V_{Z_1}(r) + 4V_{Z_2}(r)\Big) \tag{12}$$

The binding energy of the CO_2 - CO van der Waals cluster is given by the difference between the energy of the complex and the energies of the isolate molecules:

$$Ebinding = E_{\mathrm{CO_2\text{-}CO}} - (E_{\mathrm{CO_2}} + E_{\mathrm{CO}}) \tag{13}$$

In Table 1, we report the BSSE estimation by counterpoise correction of the energies of the complex for each configuration at 2.8 Å. The BSSE is in average 3.33 kJ/mol; it is more pronounced in the L configurations, where the collinear orientation determines a very small distance between the O of CO_2 and one of the two atoms of CO.

4 Results and Discussions

In Fig. 3, we report the potential energy profiles of the configurations H and X. Both configurations present a minimum at *ca.* 3.4 Å; X is more attractive, the potential is about 2.5 kJ/mol, while the potential well of H is *ca.* 1.5 kJ/mol.

Table 1. The Basis Set Superposition Error, in kJ/mol, estimated for the nine significant configurations.

Configuration	BSSE (kJ/mol)
H	0.94
L1	10.42
L2	8.12
T1	2.12
T2	1.53
T3	0.74
X	0.90
Z1	2.21
Z2	3.02

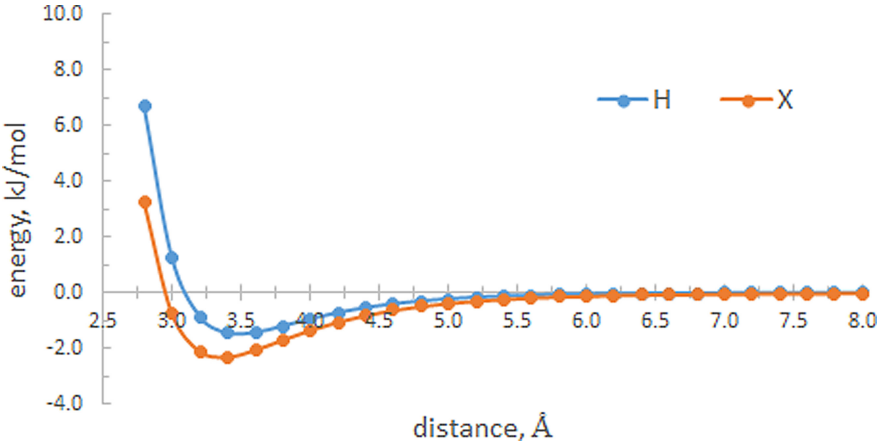

Fig. 3. Potential energy profiles of the configurations H and X.

In Fig. 4, we show the cuts of the potential energy surface related to L_1 and L_2. In these two collinearly oriented molecules, L_1 is more stable than L_2. This latter presents in fact a repulsive potential, while the first one shows a minimum at *ca.* 4.8 Å, with a potential well of about 1 kJ/mol.

In Fig. 5, the perpendicularly oriented configurations T_1, T_2 and T_3 are reported. The configuration T_1 is the most stable among the set of significant configurations we have considered, it coincides with the dimer observed experimentally by Legon *et al.* [4], the distance between the C atom of the CO and the C atom of CO_2 is *ca.* 3.1 Å, about 0.1 Å shorter than the complex found experimentally. The equilibrium distance of T_1 is located at *ca.* 3.9 Å and the depth of the well is about 6 kJ/mol, 1 kJ/mol more attractive than that obtained by Badri *et al.* [11], employing the best basis set at the CCSD(T) level of theory. The configuration T_2 presents a minimum at 3.7 Å, where the energy is about

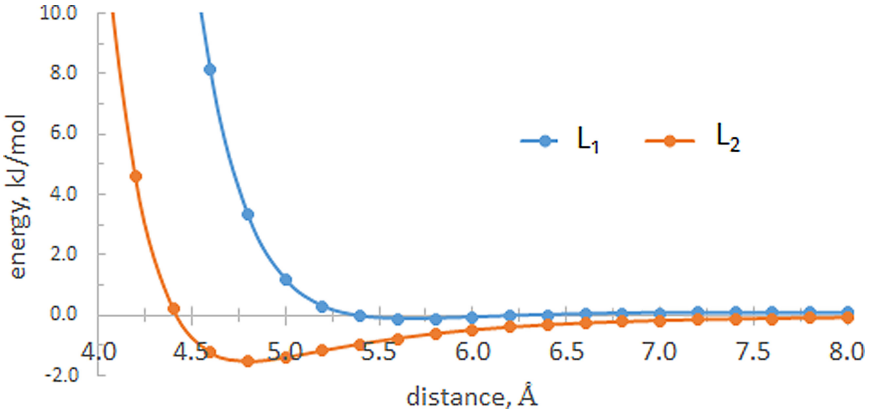

Fig. 4. Potential energy profiles of the configurations L_1 and L_2.

4 kJ/mol. The configuration T_3 is the least stable of these set of configurations, with a minimum of *ca.* 3 kJ/mol, at 4.4 Å.

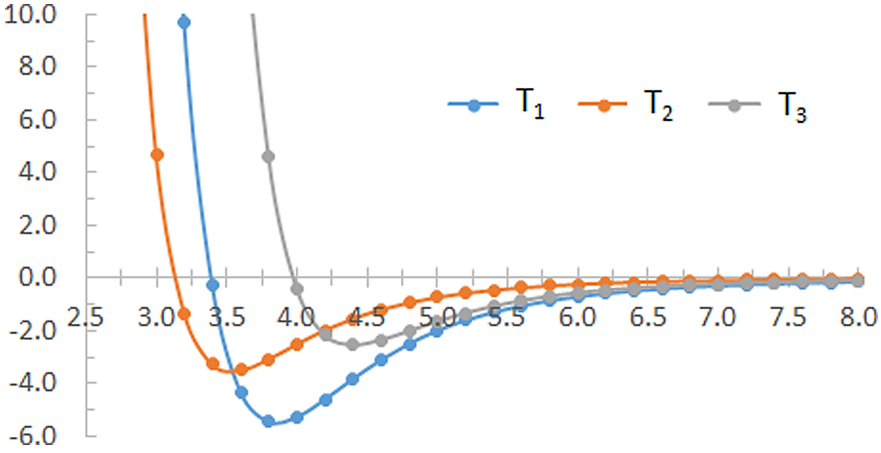

Fig. 5. Potential energy profiles of the configurations T_1, T_2 and T_3.

In Fig. 6, we finally report the potential energy profiles of the Z configurations. The configuration Z_1 presents a minimum of about 3.0 kJ/mol at 4.0 Å. The configuration Z_2 is less attractive then Z_1, having a minimum of *ca.* 1.0 kJ/mol.

In Fig. 7, we report the isotropic component of the potential, given by averaging the contributions to the interaction potential according to Eq. 4. The minimum is about 1 kJ/mol at 4.6 Å. Finally, in Fig. 8 we show the anisotropic components of the potential that correspond to the expansion terms as a function of the distance.

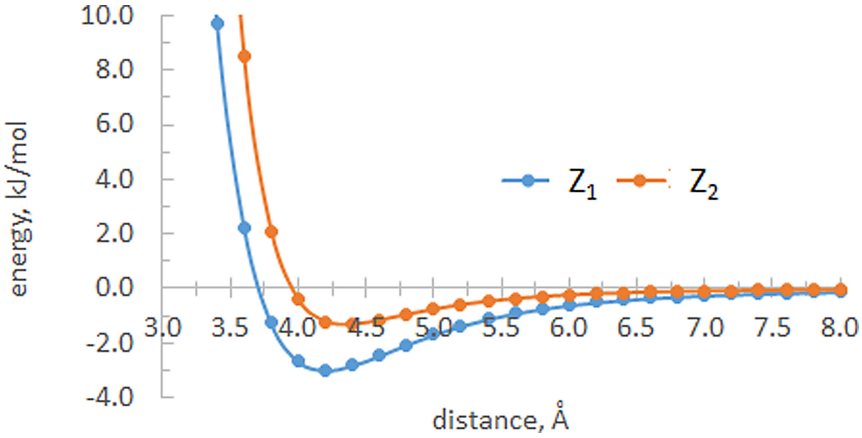

Fig. 6. Potential energy profiles of the configurations Z_1 and Z_2.

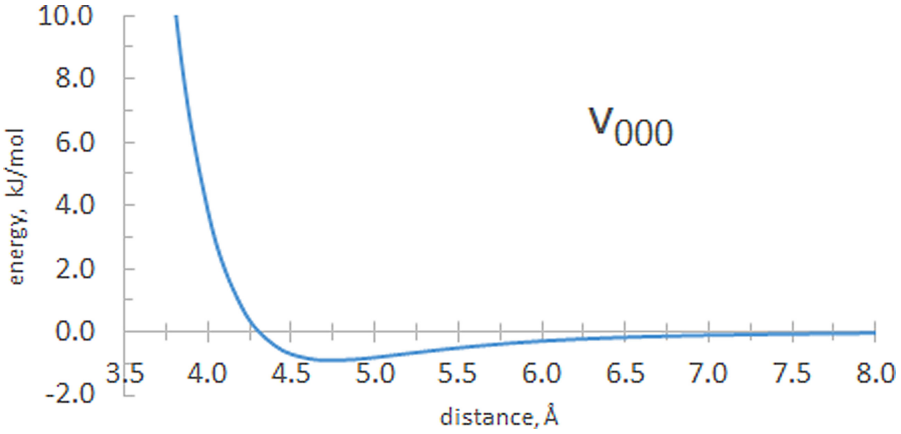

Fig. 7. The isotropic component of the potential energy surface, v_{000}, as a function of the distance.

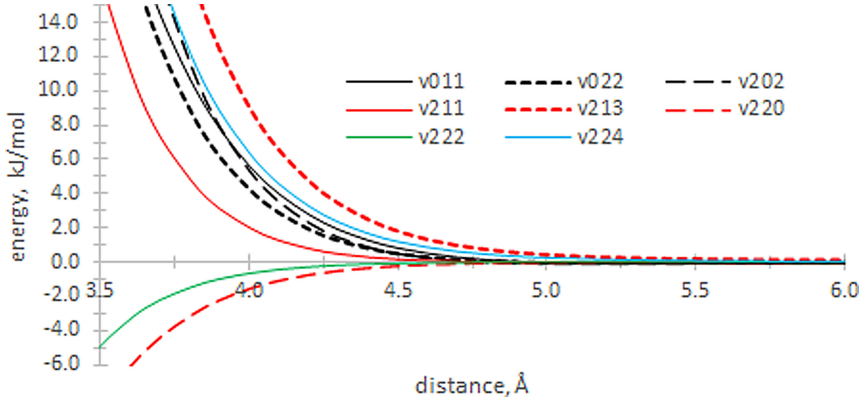

Fig. 8. The isotropic components of the potential energy surface, v_{011}, v_{022}, v_{200}, v_{211}, v_{213}, v_{220}, v_{222}, v_{224}, as a function of the distance.

5 Conclusions

We have proposed a minimal model of the potential energy surface for the CO_2 – CO system, based on the expansion of a limited number, nine, of spherical harmonics. The interaction potential expansion is an exact transformation of the input data, 243 energy points calculated at the MP2/aug-cc-pVQZ. These preliminary data are compared with experimental and state-of-art theoretical results; this latter presents a potential energy surface calculated on 30,000 energy points, involving 134 expansion terms. The configuration of the global minimum is a "T-shaped" one, similarly to that found experimentally. Future works will aim at improving the accuracy by increasing the level of theory of the *ab initio* calculations. Applications of the potential energy surface will concern elastic scattering simulations (see for example Ref. [27]).

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