Accurate *ab initio* intermolecular potential energy surface for the quintet state of the $\text{O}_2(^3\Sigma_g^-)-\text{O}_2(^3\Sigma_g^-)$ dimer

Massimiliano Bartolomei,^{1,a)} Estela Carmona-Novillo,¹ Marta I. Hernández,¹ José Campos-Martínez,¹ and Ramón Hernández-Lamóneda²

¹*Instituto de Matemáticas y Física Fundamental, Consejo Superior de Investigaciones Científicas, Serrano 123, 28006 Madrid, Spain*

²*Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, 62210 Cuernavaca, Mor. Mexico*

(Received 11 March 2008; accepted 25 April 2008; published online 3 June 2008)

A new potential energy surface (PES) for the quintet state of rigid $\text{O}_2(^3\Sigma_g^-)+\text{O}_2(^3\Sigma_g^-)$ has been obtained using restricted coupled-cluster theory with singles, doubles, and perturbative triple excitations [RCCSD(T)]. A large number of relative orientations of the monomers (65) and intermolecular distances (17) have been considered. A spherical harmonic expansion of the interaction potential has been built from the *ab initio* data. It involves 29 terms, as a consequence of the large anisotropy of the interaction. The spherically averaged term agrees quite well with the one obtained from analysis of total integral cross sections. The absolute minimum of the PES corresponds to the crossed (D_{2d}) structure (X shape) with an intermolecular distance of 6.224 bohrs and a well depth of 16.27 meV. Interestingly, the PES presents another (local) minimum close in energy (15.66 meV) at 6.50 bohrs and within a planar skewed geometry (S shape). We find that the origin of this second structure is due to the orientational dependence of the spin-exchange interactions which break the spin degeneracy and leads to three distinct intermolecular PESs with singlet, triplet, and quintet multiplicities. The lowest vibrational bound states of the O_2-O_2 dimer have been obtained and it is found that they reflect the above mentioned topological features of the PES: The first allowed bound state for the ^{16}O isotope has an X structure but the next state is just 0.12 meV higher in energy and exhibits an S shape. © 2008 American Institute of Physics. [DOI: 10.1063/1.2929852]

I. INTRODUCTION

Interactions between oxygen molecules are of great interest in a variety of fields, such as atmospheric physics and chemistry,^{1–3} in the condensed phase,⁴ or in laser technologies with developments in the so-called chemical oxygen iodine laser.^{5,6} Many interesting phenomena stem from the nonzero electronic spin in the ground electronic state of the monomers ($^3\Sigma_g^-$) that leads to the splitting in three surfaces and, in fact, this property is meant to be exploited in an interesting emerging topic as the quest of buffer gas cooling and trapping of oxygen,^{7–9} for which the quintet multiplicity state^{10,11} plays a key role. These and many other subjects implied in this challenging system have been reviewed, for instance, in Refs. 12 and 13.

In 1993, Bussery and Wormer¹⁴ published the first reliable potential energy surfaces (PESs) for the rigid $\text{O}_2(^3\Sigma_g^-)+\text{O}_2(^3\Sigma_g^-)$ dimer with singlet, triplet, and quintet multiplicities (hereafter referred as the BW PES). The PESs were built combining *ab initio* calculations by Wormer and van der Avouird using first order exchange perturbation theory at the Hartree–Fock level¹⁵ and a second-order polarization energy evaluated semiempirically,¹⁶ circumventing in this way the difficulty inherent to an *ab initio* determination of the dispersion terms. Subsequent bound state calculations¹⁷ were of

great help in the analysis of the highly congested spectra recorded by Campargue *et al.* and Biennier *et al.*^{18,19} Additional interesting information has come from scattering experiments by the Perugia group.^{12,20} From these measurements, full dimensional PESs were obtained (hereafter referred as the Perugia PES). This PES compares qualitatively well with the BW PES, as both PESs give the H geometry as the most stable one for the singlet and triplet states, while the crossed X geometry (D_{2d} symmetry) is the most stable one for the quintet state. However, they differ significantly in quantitative aspects, such as the degree of anisotropy, equilibrium distances, and well depths at several geometries. Bound state calculations were carried out using the Perugia PES,^{21–23} and resulting energies and vibrational frequencies differ from those¹⁷ based in the BW PES. Importantly, the BW isotropic term is much shallower than the Perugia one, producing a considerable dephasing in the *glory* pattern of the total integral cross sections. Clearly, progress in the development of accurate *ab initio* PESs for this system is highly desirable, and very recently we have started work in this direction.^{13,24–26}

In the last decade, an impressive development of very accurate and highly correlated *ab initio* methods properly representing weak intermolecular forces has been achieved.^{27,28} It should be pointed out that the most reliable methods apply to closed-shell systems or some open-shell cases for which restricted Hartree–Fock provides a reason-

^{a)}Electronic mail: maxbart@imaff.cfmac.csic.es.

TABLE I. Energies (in meV) for the four limiting configurations at intermolecular distances (in a.u.) close to the minima, as obtained from RCCSD(*T*) with B3 and B4 basis sets.

	H		X		T		L	
	<i>R</i>	<i>D_e</i>	<i>R</i>	<i>D_e</i>	<i>R</i>	<i>D_e</i>	<i>R</i>	<i>D_e</i>
B3	6.5	13.685	6.25	16.242	7.25	12.890	8.25	11.600
B4	6.5	13.690	6.25	16.253	7.25	13.056	8.25	12.220

able zero-order wavefunction. This is the case of the oxygen dimer in the first quintet state. We have recently performed²⁴ RCCSD(*T*) (restricted coupled cluster with single, double, and perturbative triple excitations) calculations for a limited set of geometries: linear ($D_{\infty h}$), T-shaped (C_{2v}), rectangular (D_{2h}), and crossed (D_{2d}) arrangements (in the following, referred to as L, T, H, and X, respectively). In subsequent works^{25,26} we extended the calculations to the lowest singlet and triplet states using a variety of multiconfigurational approaches, which are less accurate than RCCSD(*T*) but unavoidable in the case of these spin multiplicities. A detailed comparison with previous PESs Refs. 12, 14, and 15 can be found in Refs. 13 and 24–26. Very recently, Zuchowski has performed symmetry adapted perturbation theory (SAPT) calculations for the quintet state,²⁹ finding a remarkable agreement with our RCCSD(*T*) calculations.²⁴ However, in order to properly compare with measurements,^{19,20,30–32} it is necessary to build full-dimensional PESs including their detailed dependence with the angular degrees of freedom.

In this work, we report a new PES for the first quintet state of the $O_2(^3\Sigma_g^-)-O_2(^3\Sigma_g^-)$ dimer, based on RCCSD(*T*) *ab initio* calculations. Details for the calculations, involving computation at more than a thousand spatial configurations, are given in Sec. II. A comparison with previous potentials and an analysis of the topography of the new PES are provided in Sec. III. In Sec. IV, we report bound state calculations for the lowest vibrational states. Finally, Sec. V is devoted to a summary and conclusions.

II. THE O_2-O_2 QUINTET PES: CALCULATIONS

Since $^3\Sigma_g^-$ monomers have $S_a=S_b=1$ electronic spin, the intermolecular potential depends on the spin couplings between monomers which generate three distinct PESs with singlet ($S=0$), triplet ($S=1$), and quintet ($S=2$) multiplicities. We have performed calculations for $S=2$ using the RCCSD(*T*) approach, as done in a preliminary Communication.²⁴

Starting from diatom-diatom Jacobi vectors $\mathbf{R}$, $\mathbf{r}_a$, and $\mathbf{r}_b$, the six internal coordinates determining the O_2+O_2 PES are the intermolecular and intramolecular distances R , r_a , and r_b and θ_a and θ_b , and ϕ are the angles formed by $\mathbf{R}$ and $\mathbf{r}_a$ and $\mathbf{R}$ and $\mathbf{r}_b$ and the torsional angle, respectively. The interatomic distance in O_2 has been fixed to its equilibrium distance, $r_e=2.28$ bohrs (rigid monomers).

We have considered the geometries coming out from nine Gauss–Legendre quadrature points in the $-1 \leq \cos \theta_a$ and $\cos \theta_b \leq 1$ ranges and from five Gauss–Chebyshev quadrature points for $0 \leq \theta \leq \pi$. An initial range in the torsional angle from $[0:2\pi]$ has been reduced to $[0:\pi]$ by the

use of the permutation-inversion symmetry of the system,³³ which allows us to also reduce the initial $9 \times 9 \times 5$ grid to a $5 \times 5 \times 5$ grid ($-1 \leq \cos \theta_a$ and $\cos \theta_b \leq 0$). If we further consider the following equivalences due to symmetry, $(\theta_a, \theta_b, \phi) \equiv (\theta_b, \theta_a, \phi)$ and $(\theta_a, \pi/2, \phi) \equiv (\theta_a, \pi/2, \pi - \phi)$, we finally are left with 65 “irreducible” geometries. For each angular arrangement, 17 points in the intermolecular coordinate R , ranging from 16.0 to 5.0 bohrs, were considered.

A. RCCSD(*T*) *ab initio* calculations

First, we have tested basis set saturation and performances for the H, X, T, and L limiting configurations. The initial basis was that already used in Ref. 24 which was demonstrated to give well-converged interaction energies. This set, denoted by B3 in the following, consists of a 6s5p3d2f atomic natural orbital (ANO) set³⁴ plus a bond function set $[3s3p2d1f]$ developed by Tao³⁵ and placed in the middle of the complex as customary. In order to reduce computing time we also used a new reduced set, denoted by B4, composed by a 5s4p3d2f ANO functions and keeping the same bond functions as in the B3 set. Interaction energies obtained from the two basis sets are compared in Table I. As can be noticed both sets provide quite similar results: The largest differences, corresponding to T and L configurations, are within 5%. We considered these deviations acceptable and we decided to choose the B4 basis set for all RCCSD(*T*) calculations, as it allows us to save about 15% of computing time. The counterpoise method^{36,37} was applied to correct for the basis set superposition error. All calculations were performed with the MOLPRO2002.3 package.³⁸

For all orientations, except those with $(\theta_a, \theta_b, \phi) = \{(\pi/2, \pi/2, \pi/2), (\pi/2, \pi/2, 0), (0, 0, 0)\}$, a convergence problem occurred for small intermolecular distances when using the Hartree–Fock reference wave function. This is due to an instability of the Hartree–Fock $O_2(^3\Sigma_g^-)$ wave function with respect to breaking of the $D_{\infty h}$ symmetry in the π system, as already noted for the He– O_2 system.^{39,40} The problem is avoided by obtaining the molecular orbitals to be used in the RCCSD(*T*) calculation as the natural orbitals of a complete active space multiconfigurational self consistent field wave function. The active space consists of 12 electrons distributed in eight orbitals correlating with the lowest O_2 π molecular orbitals.

B. Spherical harmonics expansion

The interaction potential V is expressed in a spherical harmonics expansion as¹⁵

TABLE II. Comparison of *ab initio* energies with energies resulting from the spherical harmonic expansion of Eq. (1) using the set of 29 radial terms detailed in the text, for several orientations and intermolecular distances.

Geometry				V _{ab initio} (meV)	V _{expansion} (meV)	%
θ _a (deg)	θ _b	φ	R (a ₀)			
90	H	0	5.0	118.61	116.96	1.39
			5.5	18.56	18.48	0.43
			6.25	-12.91	-12.84	0.54
			6.5	-13.69	-13.60	0.66
			7.0	-11.73	-11.71	0.17
			12.0	-0.490	-0.494	0.82
			14.0	-0.180	-0.182	1.11
90	X	90	5.0	59.26	58.92	0.57
			5.5	-0.996	-1.101	10.54
			6.0	-15.40	-15.41	0.06
			6.25	-16.26	-16.26	0.02
			6.5	-15.44	-15.52	0.52
			12.0	-0.485	-0.484	0.21
			14.0	-0.179	-0.179	0.06
90	T	0	5.0	813.95	815.57	0.20
			5.5	251.73	251.98	0.10
			7.0	-12.05	-12.05	0.01
			7.25	-13.06	-13.06	0.01
			7.50	-12.52	-12.52	0.04
			12.0	-0.748	-0.753	0.67
			14.0	-0.267	-0.271	1.50
0	L	0	5.0	6437.76	6321.98	1.80
			5.5	2305.67	2294.63	0.48
			8.0	-11.96	-11.98	0.17
			8.25	-12.22	-12.24	0.16
			8.50	-11.36	-11.38	0.18
			12.0	-1.183	-1.187	0.34
			14.0	-0.401	-0.401	0.00
71	S	0	5.0	135.03	134.63	0.30
			5.5	22.10	21.97	0.59
			6.25	-14.66	-14.61	0.34
			6.5	-15.68	-15.66	0.13
			7.0	-13.55	-13.56	0.07
			12.0	-0.560	-0.559	0.18
			14.0	-0.206	-0.206	0.07
45	A	0	5.0	1784.90	1789.38	0.25
			5.5	614.43	614.92	0.08
			7.50	-8.96	-8.96	0.09
			8.0	-9.45	-9.44	0.11
			8.25	-8.59	-8.58	0.12
			12.0	-0.817	-0.816	0.12
			14.0	-0.286	-0.285	0.28

$$V(R, \theta_a, \theta_b, \phi) = (4\pi)^{3/2} \sum_{l_a, l_b, l} f^{l_a l_b l}(R) A_{l_a l_b l}(\theta_a, \theta_b, \phi), \quad (1)$$

with

$$A_{l_a l_b l}(\theta_a, \theta_b, \phi) = \left(\frac{2l+1}{4\pi} \right)^{1/2} \sum_m \begin{pmatrix} l_a & l_b & l \\ m & -m & 0 \end{pmatrix} Y_{l_a m}(\theta_a, 0) \times Y_{l_b, -m}(\theta_b, \phi), \quad (2)$$

where $Y_{l_a m}$ and $Y_{l_b, -m}$ are spherical harmonics which are coupled with the aid of a 3-*j* symbol, l_a , l_b , and l are even integers (due to symmetry), and m runs from $-\min(l_a, l_b)$ to

$\min(l_a, l_b)$. The radial coefficients are obtained by integrating V over the following angular variables:

$$f^{l_a l_b l}(R) = \pi^{1/2} \int_{-1}^1 d(\cos \theta_a) \int_{-1}^1 d(\cos \theta_b) \int_0^{2\pi} d\phi V(R, \theta_a, \theta_b, \phi) A_{l_a l_b l}^*(\theta_a, \theta_b, \phi). \quad (3)$$

Integrals were computed for each intermolecular distance R by means of Gauss-Legendre and Gauss-Chebyshev quadratures,⁴¹ using the initial grid of $9 \times 9 \times 5$ angular orientations, after identifying the orientations which give the same value for the interaction energy due to the permutation-

FIG. 1. Main radial coefficients f^{abl} of the expansion of Eq. (1) as functions of R , for the quintet state of $\text{O}_2(^3\Sigma_g^-)-\text{O}_2(^3\Sigma_g^-)$. Solid lines: present RCCSD(T) calculations. Dashed-dotted lines: the Perugia PES (Ref. 12) (note that this expansion only considers four terms). Dashed lines: the semi-*ab initio* BW PES (Ref. 14). Dotted curve: estimate of f^{000} based on RCCSD(T) calculations using only four limiting orientations (Ref. 24). See text for discussion.

inversion symmetry. Previous checks using larger numbers of Gauss points, at the Hartree–Fock level, give us confidence that the chosen angular grid is sufficient to describe the anisotropy of the interaction.

After a careful analysis of all the radial coefficients that can be obtained from the present set of quadrature points [up to $(l_a l_b l) = (8\ 8\ 16)$], we have selected a set of 29 radial coefficients from which the interaction potential is well represented. It consists in the complete subset emerging from $l_a = 0, 2, 4$, $l_b \leq l_a$, and $l_a - l_b \leq l \leq l_a + l_b$ (14 terms) plus $(l_a l_b l) = (6\ 0\ 6)$, $(6\ 2\ 4)$, $(6\ 2\ 6)$, $(6\ 2\ 8)$, $(6\ 4\ 6)$, $(6\ 4\ 8)$, $(6\ 4\ 10)$, $(6\ 6\ 12)$, $(8\ 0\ 8)$, $(8\ 2\ 8)$, $(8\ 2\ 10)$, $(8\ 4\ 4)$, $(8\ 4\ 12)$, $(8\ 6\ 14)$, and $(8\ 8\ 16)$. We have computed the root mean square (rms) relative and absolute errors of the expansion with respect to the *ab initio* energies, averaged over all distances and quadrature points, obtaining 1% and 0.95 meV, respectively. If the calculation of errors is restricted to interaction energies smaller than 100 meV, we obtain 1% and 0.02 meV for relative and absolute rms errors, respectively.

Further indication of the quality of the spherical harmonics expansion is given in Table II, where a comparison between *ab initio* interaction energies and those corresponding to the 29-term expansion is given for a group of selected geometries. This is an independent check of the accuracy of the expansion, since, except for the X geometry, none of these geometries belong to the set of Gaussian quadrature

points chosen to build the PES and they have been computed independently. It can be seen that agreement is very good in the short range as well as in the van der Waals (vdW) and long range regions, and for all orientations. The exception is the X geometry at 5.5 bohrs, where the relative error is about 10% although the absolute error is about 0.1 meV.

Values at intermolecular distances different from those used in the *ab initio* calculations have been obtained, when needed, by cubic spline interpolation.

III. RESULTS AND DISCUSSION

A. Comparison with previous PESs

In Fig. 1, the main six radial coefficients of the interaction f^{abl} are shown together with those of the BW (Ref. 14) and the Perugia¹² PESs. In the left-hand upper panel, where we present the spherically averaged potential $f^{000}(R)$, we have also added our preliminary estimate,²⁴ based on data of RCCSD(T) interaction energies just for the four limiting orientations. As can be seen, the preliminary estimate and present calculation differ in the repulsive and well regions of the potential curve, while in the long range the present term is slightly more attractive. Thus, as expected, it is necessary to consider more than four orientations for an accurate calculation of the spherical term.

Regarding comparison with the Perugia PES, it must be first noted that it consists of just four terms of the spherical harmonic expansion—as it was built with the aim of characterizing the four basic configurations of the dimer—which were derived from a multiproperty analysis and therefore must be considered as effective ones. Nevertheless, it can be seen that our new spherical term compares quite well with the Perugia term at all intermolecular distances. Agreement is almost perfect in the repulsive region, while some differences remain in the well depth (about 0.8 meV) as well as in the long range tail. We consider this agreement a very good result taking into account the very different origin of both PESs. For the main anisotropic coefficient (right upper panel of Fig. 1), it can be seen that our term exhibits a larger long range attraction, a deeper well and it is more repulsive in the short range. Since our isotropic term is slightly shallower, it follows that the present PES is probably as attractive as the Perugia PES but more anisotropic in both long and short ranges. The stronger anisotropy of the present PES can be checked by comparing the shapes of the four limiting configurations with that of the isotropic term: As it follows from Fig. 1 of Ref. 24, differences between the isotropic and the H, X, and L curves are stronger in the *ab initio* than in the Perugia PES.

Finally, the present PES compares qualitatively well with the semi-*ab initio* BW PES, but it is generally more attractive, as can be noticed by looking at the main (isotropic) term. It can be also noticed from a detailed inspection of Fig. 1 that for those radial terms exhibiting wells or “inverted” wells (as f^{222} , for instance), our PES gives less repulsive walls and deeper wells, while for those radial terms exhibiting an exponential-like behavior [as the $(l_a, l_b, l) = (4\ 4\ 8)$ one], our terms are larger in absolute values than the BW ones. We have checked that this behavior maintains

FIG. 2. Cuts of the quintet PES (in meV), as a function of θ_a and θ_b , for different intermolecular distances (in a.u.) and values of the torsional angle. See text for details.

for the rest of the radial terms not shown in Fig. 1. In order to find an explanation to these differences, we have compared the different interaction components of the BW PES with those of the SAPT potential curves of Zuchowski²⁹ (computed near equilibrium distances of the limiting geometries and shown in Table 2 of Ref. 29). The comparison is relevant to the present discussion since, as mentioned previously, SAPT and RCCSD(T) calculations agree at a quantitative level (see Fig. 2 of Ref. 29). We have found that the BW PES underestimates both SAPT exchange-repulsion and dispersion. The underestimation of dispersion is in general more significant, the total balance of the interaction resulting in less attractive potential curves. This is particularly evident at the equilibrium distance of the most “repulsive” configurations (T and L) giving as a result much shallower wells. On the other hand, the underestimation of the exchange-repulsion can be noticed by comparing with our PES those radial terms not affected by attractive components, such as the (4 4 8) one shown in Fig. 1.

B. Topography of the RCCSD(T) PES

Contours of the PES as a function of θ_a and θ_b , for two torsional angles $\phi=0$ (upper panel) and $\phi=\pi/2$ (lower panel), and for several fixed values of the intermolecular

distance, are presented in Fig. 2. In the first column, contour plots are displayed for an intermolecular distance of $R=6.25$ bohrs. It must be pointed out that such a distance nearly equals the equilibrium distance for the crossed configuration X (more exactly, it is 6.224 a.u. with an energy of 16.27 meV). Indeed, we have checked that the minimum seen at $\theta_a=\theta_b=\phi=\pi/2$ (lower panel) corresponds to the absolute minimum of the PES, in agreement with previous estimates.^{12,14} On the other hand, in the upper panel, $\phi=0$, there are two minima (at least with respect to θ_a and θ_b coordinates) corresponding to the planar orientations $\theta_a=\theta_b=71^\circ$ and $\theta_a=\theta_b=109^\circ$, which have been denoted by S in Table II. We have checked that close to these structures, true local minima of the PES (taking into account all coordinates), are given, specifically at $(R, \theta_a, \theta_b, \phi) = (6.5 \text{ a.u.}, 71^\circ, 71^\circ, 0)$ and $(6.5 \text{ a.u.}, 109^\circ, 109^\circ, 0)$. As can be seen in Table II its dissociation energy is slightly smaller than that corresponding to the absolute minimum at the X configuration. It has also been checked that the rectangular H configuration corresponds to a saddle point connecting X and S minima.

In the second column of Fig. 2, contour plots are shown for $R=7.25$ bohrs. This intermolecular distance corresponds to the minimum *within* the perpendicular T orientation, as can be seen in Table II. However, as can be noticed in the

FIG. 3. The quintet PES (solid line) along the path L-H-X and for the intermolecular distance fixed at $R = 6.25$ a.u., whose values, in meV, are indicated in the left-hand-side ordinate. Also, in dashed line, the spin-exchange parameter J , whose values are indicated (in meV) in the right-hand-side ordinate.

upper panel, this structure does not match a local minimum of the PES, but a saddle point. For instance, beginning at $(\theta_a, \theta_b, \phi) = (0, \pi/2, 0)$ (T-shape) and locally increasing θ_a , the interaction energy decreases, reaching a minimum at nearly $(\theta_a, \theta_b) = (28^\circ, \pi/2)$ for R and ϕ fixed at $R = 7.25$ bohrs and zero, respectively. However, we have checked that the minima seen in the upper panel are not local minima of the PES. Rather, these structures belong to a minimum energy path leading to the S minima. On the other hand, for the $\phi = 0$ panel, it can be noticed a trend to favor S-type geometries ($\theta_a = \theta_b$) against A-type structures ($\theta_b = \pi - \theta_a$). In the $\phi = \pi/2$ panel such a trend disappears as A-type and S-type structures become equivalent for this value of the torsional angle. Same features can be observed in the panels corresponding to $R = 6.25$ a.u. (first column).

Finally, in the third column of Fig. 2, similar plots as before are given for $R = 8.25$ bohrs. This intermolecular distance nearly equals the equilibrium distance within the L geometry (see Table II). In these panels, linear structures appear as minima and hence are confirmed to be local minima of the PES. On the other hand and as expected, at this intermolecular distance the PES is quite flat, the maximum gap between the different energy contours being of about 6.5 meV. For $\phi = 0$ the contour lines show now a slight preference for A-type against S-type structures in contrast with that observed for lower intermolecular distances. This is due to the role of the long range attractive forces which are dominant at such a large intermolecular distance and to the reduction of repulsive forces which are more important for A-type structures.

The complexity of the present PES is mainly due to exchange interactions which break the spin degeneracy of the $O_2(^3\Sigma_g^-) + O_2(^3\Sigma_g^-)$ interaction, leading to the three intermolecular PES with singlet, triplet, and quintet multiplicities. As originally proposed by van Hemert *et al.*,⁴² exchange interactions in $O_2 + O_2$ can be fairly well represented by the Heisenberg exchange operator $\hat{H}_{\text{ex}} = -2JS_a \cdot S_b$, where S_a and

S_b are the electron spin operators of the two diatoms and J is the spin-exchange interaction parameter. Within this framework, the quintet PES can be written as

$$V^{S=2} = V_{\text{sa}} - 2J, \quad (4)$$

where V_{sa} is a spin-average interaction potential, i.e., excluding spin-exchange interactions. In order to investigate this point, we have computed the J parameter from the splitting between singlet and quintet energies computed at the multi-reference configuration interaction level, as explained in detail in Ref. 25. Very recently, we have shown²⁶ that there are non-negligible deviations from the Heisenberg Hamiltonian at small intermolecular distances. However, in order to provide insight into the origin of the most prominent features of the present PES, it is sufficient the calculation reported here.

In Fig. 3 we report values of the J parameter along a path going from the L to the H geometry (by keeping $\theta_a = \theta_b$, $\phi = 0$, S-type structure), and then from the H to the X orientation (by increasing the torsional angle from 0 to $\pi/2$), and for the intermolecular distance fixed at 6.25 a.u. (the absolute minimum). Values of the present quintet PES are also given. The dependence of J with these orientations is in qualitative agreement with that reported by Wormer and van der Avoird¹⁵ and, as they already noted, it is similar to the dependence of the $(l_a, l_b, l) = (4, 4, 8)$ term of the potential expansion which, in turn, must be related to the nodal character of the open-shell antibonding π_g orbitals of the monomers. Beginning with the X configuration, the J parameter is nearly zero at this orientation (due to a very small orbital overlap). Considering that the electrostatic quadrupole-quadrupole interaction is quite small⁴³ and that for this geometry it has positive values (repulsive interaction), it can be concluded that the absolute minimum at the X orientation is just determined by van der Waals interactions. When moving from the crossed to the rectangular (H) orientation, it can be noticed that there is a direct correlation between the behavior of J and that of the interaction energy: J is negative and

increasing in absolute value, and the quintet energy increases up to a maximum. In view of Eq. (4), and considering that electrostatic and vdW components should have a negligible orientational dependence,⁴⁴ the saddle point at H should be due to a repulsive contribution of the spin-exchange interaction. When moving from H to the linear geometry, the J parameter becomes less negative and is eventually positive for $60 < \theta_a = \theta_b < 75^\circ$. A balance between the averaged interaction, which becomes rapidly repulsive when approaching the linear configuration, and the spin-exchange interaction, results in a local minimum near $\theta_a = \theta_b = 75^\circ$, the **S** minimum. Hence this minimum of the PES is due to a small attractive contribution of the spin-exchange interaction.

We have found that other topological features of the quintet PES are also due to the role of the spin-exchange interaction. For instance, in the panel of Fig. 2 corresponding to $R=7.25$ a.u. and $\phi=0$, the stabilization of the interaction energy for distorted T-shape orientation against a pure T geometry is due to the spin-exchange interaction which provides positive J values for distorted T geometries and negative values for the pure T one. For large intermolecular distances the spin-exchange contribution no longer plays an important role. Henceforth, for these distances, the most stable geometries correspond to the collinear (**L**) orientation as usual for closed-shell van der Waals complexes.

Bussery and Wormer¹⁴ reported an analysis of the topology of the O₂–O₂ intermolecular PES. As they focused on the singlet PES, we cannot compare with them in detail in the case of the present quintet PES. We have performed some analysis of the quintet BW PES and found that it also exhibits a local minimum with an **S** structure (near $\theta_a = \theta_b = 80^\circ$ and $R=6.44$ a.u.), although it is more shallower than in our PES, i.e., the barrier to the saddle point at the H orientation is around 0.2 meV while within our PES it is about 2 meV.

IV. BOUND STATE CALCULATIONS

In this section, we report energies and geometries of the lowest vibrational states of the O₂–O₂ dimer using the present quintet PES. Since in this PES the intramolecular distances have been fixed to the O₂(²Σ_g[−]) equilibrium distance, each monomer will be treated as a rigid rotor, i.e., the wide amplitude intermonomer (van der Waals) vibrations, studied here, are decoupled from the high frequency intramonomer vibrations. In this way, the Hamiltonian describing the nuclear motion on a space-fixed frame can be written as⁴⁵

$$H = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hat{\ell}^2}{2\mu R^2} + B(\hat{\mathbf{j}}_a^2 + \hat{\mathbf{j}}_b^2) + V, \quad (5)$$

where atomic units are used ($\hbar=1$) and the coordinates are the diatom-diatom Jacobi vectors $\mathbf{R}$, $\mathbf{r}_a$, and $\mathbf{r}_b$ (as in Sec. II), μ is the reduced mass of the dimer, V is the quintet PES, B is the rotational constant of the monomers, and $\hat{\ell}$, $\hat{\mathbf{j}}_a$, and $\hat{\mathbf{j}}_b$ are angular momentum operators associated to rotations of $\mathbf{R}$, $\mathbf{r}_a$, and $\mathbf{r}_b$, respectively. Thus, total rotational angular momentum is $\mathbf{J} = \hat{\ell} + \hat{\mathbf{j}}_a + \hat{\mathbf{j}}_b$. This Hamiltonian implicitly includes the spin-dependent Heisenberg Hamiltonian,^{15,33,42} which commutes with total electronic spin **S** and, in fact, corresponds to

$S=2$. This scheme neglects relativistic terms due to the interaction between the spin and orbital angular momenta of nuclei and electrons (spin-spin, spin-orbit, and spin-rotation interactions),⁴⁶ which would cause couplings between **S** and **J**. Henceforth, both S and J are good quantum numbers within this framework.

The time-independent Schrödinger equation has been solved using the BOUND package.⁴⁷ A complete description of the method is given by Hutson.⁴⁸ Eigenfunctions of the total Hamiltonian are sought by expanding $\Psi(\mathbf{R}, \hat{\mathbf{r}}_a, \hat{\mathbf{r}}_b)$ in a convenient basis set,^{45,49}

$$\Psi^{\text{JM}}(\mathbf{R}, \hat{\mathbf{r}}_a, \hat{\mathbf{r}}_b) = \sum_{j_a j_b j_{ab} \ell} \frac{g_{j_a j_b j_{ab} \ell}^{\text{JM}}(R)}{R} I_{j_a j_b j_{ab} \ell}^{\text{JM}}(\hat{\mathbf{R}}, \hat{\mathbf{r}}_a, \hat{\mathbf{r}}_b), \quad (6)$$

where the angular wavefunctions are detailed elsewhere.^{45,49}

The appropriate molecular symmetry group for describing the rather floppy oxygen dimer is G_{16} , which involves the symmetry operations of spatial inversion E^* , permutation of nuclei within the monomers P_{12} and P_{34} , and simultaneous permutation of nuclei between monomers a and b , P_{ab} . The basis of Eq. (6) is already adapted to E^* [with a parity given by $(-1)^{J+j_a+j_b+\ell}$] and P_{12} and P_{34} (by only including j_a and j_b values of the same parity in the expansion). Regarding to the P_{ab} symmetry, a symmetry adapted basis is built as given in Eq. (14) of Ref. 45. The program BOUND works using this symmetry adapted basis, hence the resulting eigenfunctions are labeled by the irreducible representations (irreps) of G_{16} .

In this work, the coupled differential equations (resulting from substituting the wavefunction's expansion into the time-independent Schrödinger equation) were propagated (from 5.0 to 12.55 a.u. with a step size of 0.076 a.u.) using Manolopoulos's modified log-derivative algorithm,⁵⁰ and eigenvalues were located iteratively using Johnson's method,⁵¹ as implemented in BOUND. We have considered the most abundant ¹⁶O isotope, hence the reduced mass of the dimer and the rotational constant were taken to be 15.9994 amu and 1.438 cm^{−1} (0.178 meV), respectively. An angular basis set with odd $j_a, j_b \leq 13$ was used. The resulting calculations are converged within 10^{−6} cm^{−1}.

In Table III we report the energies of the three lowest bound states of the dimer (for $J=0$), labeled as lev0, lev1, and lev2. The behavior of the rovibrational wavefunctions under the group operations is also indicated and they are labeled by the corresponding irrep. In addition, the behavior of the *total* wavefunction—the rovibrational times the electronic wavefunction—under the group operations is shown in parenthesis. We have taken into consideration that the electronic wavefunction of the monomers is odd under P_{12} and P_{34} permutations.^{17,22} On the other hand, the quintet electronic wavefunction can be written by coupling the monomers electronic spins using Clebsch Gordan coefficients^{52,53} and it can be shown that this wavefunction is even under P_{ab} permutation. Finally, it has been shown that the electronic wavefunction is even under inversion.⁵⁴ The resulting symmetry of the total wavefunctions is shown in parenthesis in the last column of Table III. As we are considering the ¹⁶O isotope, which is a boson with zero nuclear spin, only states symmetric with respect to P_{12} , P_{34} , and P_{ab} will be

TABLE III. Lowest energy levels (in meV and in cm^{-1}) of the $\text{O}_2\text{--O}_2$ complex in the quintet electronic spin state. The ^{16}O isotope is considered for all nuclei. The parity of j_1 , j_2 , and l in the basis set corresponding to each symmetry block is indicated, together with the parity of the rovibrational eigenfunctions with respect to the operations of the G_{16} group and their symmetry (irrep). Symmetry label of the *total* wavefunctions (including the electronic part) is indicated in parenthesis.

	(meV)	(cm^{-1})	j_1	j_2	l	P_{12}	P_{34}	P_{ab}	E^*	irrep
lev0	-10.77	-86.845	<i>e</i>	<i>e</i>	<i>e</i>	$+(-)$	$+(-)$	$+$	$+$	$A_1^+(B_1^+)$
lev1	-10.41	-83.966	<i>o</i>	<i>o</i>	<i>o</i>	$-(+)$	$-(+)$	$+$	$-$	$A_1^-(B_1^-)$
lev2	-10.29	-82.960	<i>o</i>	<i>o</i>	<i>e</i>	$-(+)$	$-(+)$	$+$	$+$	$B_1^+(A_1^+)$

populated,^{17,22} that is, lev1 and lev2 with symmetries B_1^- and A_1^+ , respectively.

Unfortunately, energy levels reported here cannot be compared with spectroscopic data since they refer to the singlet state of the dimer.^{18,19,30} Carmona-Novillo *et al.*²³ did study the bound states for the quintet multiplicity using the Perugia PES,¹² obtaining an energy of -93.17 cm^{-1} for the first allowed state, somewhat lower than the energies obtained in this work. Taking into account that the well depth (in the X geometry) is very similar for both present and Perugia PES,²⁴ this difference must be due to the stronger anisotropy of the present PES.

In order to get insight into the connection between the bound states and the topography of the present PES, we have computed the wavefunctions associated to the states of Table III. This has been achieved using the method developed by Thornley and Hutson.⁵⁵ Despite the fact that the state lev0 is forbidden, we will also show its features for the sake of completeness. In Fig. 4, the probability density as a function of the intermolecular coordinate is depicted. All states exhibit similar distributions centered about 6.6–6.8 bohrs, and with a width of about 1 bohrs.

In Fig. 5, wavefunctions associated to lev0, lev1, and lev2 are depicted. They have been computed using Eq. (6), with $\hat{\mathbf{R}}=(\theta_{\mathbf{R}}, \phi_{\mathbf{R}})$, $\hat{\mathbf{r}}_{\mathbf{a}}=(\theta_{\mathbf{a}}, \phi_{\mathbf{a}})$, and $\hat{\mathbf{r}}_{\mathbf{b}}=(\theta_{\mathbf{b}}, \phi_{\mathbf{b}})$, and setting $(\theta_{\mathbf{R}}, \phi_{\mathbf{R}})=(0, 0)$, $\phi_{\mathbf{a}}=-\phi_{\mathbf{b}}=\phi/2$ (such as $\phi_{\mathbf{a}}+\phi_{\mathbf{b}}=0$ and $\phi_{\mathbf{a}}-\phi_{\mathbf{b}}=\phi$). In addition, R has been fixed to the value corresponding to the maximum of the corresponding radial distribution. In this way, a relationship between the wavefunctions and the PES (which has been obtained in the internal coordinates $\theta_{\mathbf{a}}$, $\theta_{\mathbf{b}}$, and ϕ) can be established. In the upper panels, the dependence of the wavefunctions against $\theta_{\mathbf{a}}=\theta_{\mathbf{b}}$ and ϕ is

FIG. 4. Probability density [in $(\text{a.u.})^{-1}$] of the three lowest states of the $\text{O}_2\text{--O}_2$ complex as a function of the intermolecular coordinate (in a.u.).

shown, while dependence on $\theta_{\mathbf{a}}$ and $\theta_{\mathbf{b}}$ for fixed ϕ values is given in the lower panels. It can be seen that the ground state (lev0), in Fig. 5(a), is very floppy with respect to the torsional angle although a larger amplitude is observed for the X orientation (in accordance with the absolute minimum of the PES). In Fig. 5(d), where ϕ has been fixed to $\pi/2$, the maximum at $\theta_{\mathbf{a}}=\theta_{\mathbf{b}}=\pi/2$ (X geometry) can be clearly noticed (note also the accordance with the PES in lower left panel of Fig. 2). As expected, the wavefunction is more compact with respect to $\theta_{\mathbf{a}}$ and $\theta_{\mathbf{b}}$ coordinates, as there is a larger anisotropy in the PES with respect to these coordinates. The first excited (and first allowed) state, lev1, exhibits in Fig. 5(b) a more pronounced probability amplitude (and a rather more compact wavefunction) in the X configuration due to the existence of a node in the planar orientation ($\phi=0, \pi$). Figure 5(e) corresponds to $\phi=\pi/2$ and the corresponding wavefunction is very similar to that of Fig. 5(d) except for larger numerical values of the amplitude. Finally, the second excited state lev2 is shown in Fig. 5(c) and exhibits nodes for the crossed orientation ($\phi=\pi/2, 3\pi/2$) and is peaked for the planar conformation ($\phi=0, \pi$). Largest amplitudes are found for $\phi=0$ and in Fig. 5(f); the dependence on $\theta_{\mathbf{a}}$ and $\theta_{\mathbf{b}}$ coordinates for this value of the torsional angle is shown. It can be clearly seen that there are two maxima in the amplitude corresponding with the S orientation, related to the local minima found in the PES for this conformation (see upper left panel of Fig. 2).

V. SUMMARY AND CONCLUSIONS

In this work we have reported a fully *ab initio* PES for the quintet state of the $\text{O}_2(^3\Sigma_g^-)\text{--O}_2(^3\Sigma_g^-)$ dimer, taking into account all degrees of freedom, except for the intramolecular distance of the monomers which has been kept to its equilibrium value. Calculations were carried out by means of the RCCSD(T) method and for a large number of relative orientations and intermolecular distances (1105 *ab initio* points in total, after fully considerations of the high symmetry for this system). The PES is then built using a spherical harmonic expansion and it is found to be very anisotropic. The semi-*ab initio* PES of Bussery and Wormer¹⁴ presents a similar degree of anisotropy but is rather less attractive than our PES. We think that our PES constitutes an improvement over previous PES since it is fully *ab initio* and involves an accurate account of electron correlation, while the BW PES combines first order exchange perturbation theory at the Hartree-Fock level with a second-order polarization energy evaluated semiempirically. On the other hand, the Perugia PES Ref. 12

FIG. 5. Wavefunctions (in arbitrary units) associated to lev0 [(a) and (d)], lev1 [(b) and (e)], and lev2 [(c) and (f)]. Coordinates [from Eq. (6)]: θ_R and ϕ_R have been set to zero, $\phi_a = -\phi_b = \phi/2$ and R has been set to 6.727, 6.667, and 6.758 a.u., for lev0, lev1, and lev2, respectively, corresponding to the maximum of the distributions shown in Fig. 4. Dependence with $\theta_a = \theta_b$ and ϕ is presented in the upper panels whereas dependence with θ_a and θ_b for selected values of ϕ is given in the lower panels. For lev0 and lev2 states the real part of the wavefunction is plotted, as the imaginary part is strictly zero. The reverse occurs for the lev1 state. See text for more details and discussion.

agrees quite well with the present one regarding the spherically averaged potential, but is less anisotropic.

Topological features of the quintet O₂–O₂ PES are quite interesting. The absolute minimum is found to correspond to a crossed (X) orientation, and to be mainly due to van der Waals forces. However, there is another (local) minimum very close in energy corresponding to a planar skewed structure (referred to as S in this work), which is mainly due to the spin-exchange interaction. The rectangular limiting geometry (H) acts as a saddle point in a minimum energy path connecting both minima. The linear structure constitutes another local minimum of the PES (although at a rather higher energy with respect to X and S) whereas T structures become saddle points.

Bound states of the dimer (at zero total angular momentum) have been computed for the most abundant ¹⁶O isotope and taking into account all the symmetries of the system. It is found that they are quite floppy, particularly regarding the mode associated to the torsional angle. As a consequence, energy differences between the lowest energy levels can be assigned to low frequency excitations in that mode. Interestingly, the first (forbidden) state exhibits amplitude both over the X and the S configurations, the first excited (and first allowed) state is located over the X geometry, and the second excited (and second allowed) state, just 1 cm^{−1} above the first excited one, exhibits a S geometry. A more detailed account of the rovibrational structure of the O₂–O₂ dimer is now in progress, as well as a study of the collisional dynamics.

A challenging task is the calculation of reliable PESs of O₂(³Σ_g[−])–O₂(³Σ_g[−]) for the singlet and triplet multiplicities, since in these cases the use of multiconfigurational reference wave functions is unavoidable and, unfortunately, most methods of practical use do not account for dynamical electron correlation at the high order required for the accurate determination of weak intermolecular forces and usually suffer of size extensivity problems. Very recently, we have performed²⁶ a detailed *ab initio* study aimed at the investigation of strategies to circumvent this problem. We expect that in the near future this effort yield reliable singlet and triplet PESs which, together with the quintet one, will be able to be tested against a variety of experimental data.^{19,20,30–32}

ACKNOWLEDGMENTS

The authors acknowledge financial support by MEC (Spain, Grant No. CTQ2007-62898-BQU), by CONACYT (Mexico, Grant No. 44117F), and by binational CSIC-CONACYT program (2005MX0025). M.B. was supported by the “Juan de la Cierva” program of the MEC. We also thank SESIC-SEP-FOMES2000 for unlimited time on the IBM p690 supercomputer at UAEM.

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