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Citation: *J. Chem. Phys.* **113**, 9562 (2000); doi: 10.1063/1.1321311

View online: <http://dx.doi.org/10.1063/1.1321311>

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Three-dimensional *ab initio* potential energy surface for He–O₂

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(Received 10 July 2000; accepted 8 September 2000)

An interaction potential with vibrational coordinate dependence is presented for the He–O₂(X³Σ_g[−]) van der Waals complex. The interaction is calculated with the partially spin-restricted open-shell single and double excitation coupled cluster method with perturbative triples [RCCSD(T)] in the supermolecule approach, with correction for the basis set superposition error. The augmented correlation consistent polarized triple zeta basis set is used with an additional set of bond orbitals. The single reference configuration method breaks down at an O–O separation of $r \approx 3.5 a_0$. No points with $r > 3.1 a_0$ are used in the construction of the potential surface. A high quality 120 parameter fit to 754 *ab initio* points is presented. Special attention is given to the extraction of the long range coefficients. © 2000 American Institute of Physics. [S0021-9606(00)30845-5]

I. INTRODUCTION

Recent success in the cooling and trapping of atoms that led to the creation of gaseous atomic Bose–Einstein condensates has generated much interest in low energy atomic and molecular collisions. Ultracold molecules may provide an opportunity for high resolution spectroscopy, accurate determination of intermolecular potentials, and the study of reactive and inelastic collisions at ultralow temperatures. These prospects have attracted considerable attention recently.^{1,2}

Several methods have been proposed for creating translationally cold molecules with thermal or nonthermal vibrational excitation.^{3–5} They rely on removing kinetic energy from molecules one way or another. Of these, the buffer gas loading technique of Doyle and co-workers³ was successfully demonstrated by trapping CaH in a magnetic trap.⁶ Here, a cold buffer gas of ³He is used to cool molecules to a temperature of about 240 mK. Molecules, slowed down by elastic collisions with the buffer gas, are trapped in an inhomogeneous magnetic field.

At low translational energy the vibrational and rotational relaxation cross sections must satisfy Wigner's threshold law which states that they increase as the inverse of the velocity and that the corresponding rate constants are finite and non-zero in the limit of zero translational energy. Studies carried out on H–H₂ and He–H₂ systems^{7,8} showed unusual temperature dependence of the rate constants for translational kinetic energies lower than the van der Waals well depth. The He–O₂ system appears to be an ideal candidate for low translational energy scattering studies as O₂ is paramagnetic and hence suitable for the magnetic trapping method of Doyle *et al.* Indeed, Doyle *et al.* have developed a model³ for trapping O₂ in which they emphasized the importance of accurately determining the elastic cross sections for He–O₂ collisions at low energies. We report the first He–O₂ inter-

action potential with explicit dependence on the O₂ stretch so that vibrational relaxation of O₂ by He can be studied.

The He–O₂ interaction potentials available in the literature treat O₂ as a rigid rotor. For example, empirical two-dimensional anisotropic potentials were constructed by Keil *et al.*,⁹ Faubel *et al.*,¹⁰ and Beneventi *et al.*¹¹ These potentials were derived mainly by fitting to scattering data^{9–11} and also second virial data.¹¹ The surfaces of Refs. 10 and 11 give good representations of the existing experimental data. Note that there is no spectroscopic data on the van der Waals levels of the He–O₂ complex, in contrast with Ne–O₂¹² and Ar–O₂.¹³ The first *ab initio* studies on the two-dimensional surface were performed by van Lenthe and van Duijneveldt¹⁴ and by Jaquet and Staemmler.¹⁵ These studies overestimated, respectively, underestimated, the interaction energies for reasons well understood. A more recent *ab initio* study by Cybulski *et al.*¹⁶ is in good agreement with the empirical surfaces for at least the global minimum with T-shaped geometry. In all the *ab initio* studies a local minimum was found for the linear geometry in contrast with all the empirical studies. However, extracting accurate information on the anisotropy from scattering data is difficult and therefore simple functional forms with monotonic angular dependence were used in the empirical surfaces. Clearly, a state-of-the-art *ab initio* potential, possibly with slight scaling, could be more accurate than the purely empirical surfaces. However, the points in the Cybulski study were not all computed at the same level of theory for all geometries and no analytic fit was provided. Recently, there has been considerable interest in rotational alignment and cooling in seeded supersonic expansions of, amongst other systems, O₂ in He.^{17–19} Extensive computational studies of this effect^{18,19} were done employing the empirical potential of Beneventi.¹¹ The present work opens up the possibility of a full *ab initio* study on this effect. Also, rovibrational-spin calculations²⁰ employing the potential of Faubel *et al.*¹⁰ may be reconsidered.

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FIG. 1. The coordinates for He–O₂. The “X” indicates the position of the bond functions.

II. AB INITIO CALCULATIONS

The potential is calculated with the partially spin-restricted open-shell single and double excitation coupled cluster method^{21,22} with perturbative triples²³ [RCCSD(T)] as implemented in the MOLPRO 98 package.²⁴ The O(1s) orbitals are kept doubly occupied. We use the augmented correlation consistent triple zeta (aug-cc-pVTZ) basis set^{25–27} for the He and O atoms. Added to this is the set of (3s3p2d1f) bond functions defined by Tao and Pan.²⁸ The bond functions are placed on the intersection of the vector **R**, connecting the center of mass of the O₂ molecule and the He atom, and an ellipse as shown in Fig. 1. The ellipse is chosen such that the bond functions are centered at the midpoint of **R** for the T-shaped geometry and at the midpoint between the He atom and the nearest O atom for the linear geometry of the complex. This procedure prevents the bond functions from getting too close to an O atom for large values of the vibrational coordinate of O₂. We correct for the basis set superposition error (BSSE) with the Boys and Bernardi counterpoise procedure.²⁹

A well known problem in calculations on He–O₂ is the instability of the Hartree–Fock wave function of O₂ with respect to breaking of the *D*_{∞h} symmetry.¹⁴ To avoid this problem we obtain the molecular orbitals to be used in the RCCSD(T) calculation as the natural orbitals of a complete active space multiconfigurational self consistent field (CAS-MCSCF) wave function. The active space consists only of the π orbitals of O₂: $7a'(\pi_u)8a'(\pi_g)1a''(\pi_u)$ and $2a''(\pi_g)$. We use the MCSCF program^{30,31} included in the MOLPRO package.

After the calculations were finished a new version of the MOLPRO package became available in which a minor mistake in the RCCSD(T) program was corrected.²² The interaction energy was recalculated for several geometries and the correction was found to be too small to warrant a complete recalculation. For example, near the equilibrium geometry the interaction energy was decreased by about 0.4 μE_h .

III. THE GRID AND THE FUNCTIONAL FORM

The interaction energy is calculated for 754 geometries. The vibrational coordinate *r* is varied between 1.9 and 3.1

(all distances are given in *a*₀). The angle θ only needs to be varied between 0° and 90°, because of symmetry. We distinguish three regions of *R*:

- (1) In the short range ($3.05 \leq R < 5.05$) we use equally spaced grids with $\Delta_R = 0.50$, $\Delta_r = 0.24$, and $\Delta_\theta = 10^\circ$;
- (2) In the intermediate range ($5.05 \leq R < 8$), we use $\Delta_R = 0.35$, $\Delta_r = 0.24$, and $\Delta_\theta = 10^\circ$;
- (3) In the long range ($8 \leq R \leq 15$) a logarithmically spaced grid is used for *R*, with $R_{i+1}/R_i = 1.11$. For *r* an equally spaced grid is used with $\Delta_r = 0.4$. The number of angular points is linearly dependent on *R* with eight points for *R* = 8 to three points for *R* = 15.

Points where the interaction energy is larger than 0.1 *E_h* are not used in the fit.

We fit the interaction potential with the function

$$V(R, \theta, r) = V_{sr}(R_a, \theta_a, r) + V_{sr}(R_b, \theta_b, r) + V_{lr}(R, \theta, r). \quad (1)$$

The coordinates $R_i, \theta_i, i = a, b$, as defined in Fig. 1, are known to be efficient for representing anisotropic potentials.^{32,33} The short range part of the function is further expanded as ($i = a, b$)

$$V_{sr}(R_i, \theta_i, r) = \sum_{l=0}^2 e^{-\beta R_i} P_l(\cos \theta_i) s_l + \sum_{n=0}^3 \sum_{k=0}^3 \sum_{l=0}^3 R_i^n e^{-\beta R_i} P_l(\cos \theta_i) r^k e^{-\beta r^3} s_{nlk} \quad (2)$$

and the long range part is expanded as

$$V_{lr}(R, \theta, r) = - \sum_{n=6}^{12} \sum_{l=0}^{n-4} \frac{f_n(\beta R)}{R^n} P_l(\cos \theta) c_{nl}(r), \quad (3)$$

in which both *n* and *l* must be even and where the *r* dependent long range coefficients are defined as

$$c_{nl}(r) = c_{nl}^{(0)} + \sum_{k=0}^{k_{\max}(n)} r^k e^{-\beta r^3} c_{nlk}, \quad (4)$$

with $k_{\max}(6,8) = 1$ and $k_{\max}(10,12) = 2$. The functions f_n are Tang-Toennies damping functions,³⁴

$$f_n(x) = 1 - e^{-x} \sum_{k=0}^n \frac{x^k}{k!}. \quad (5)$$

The total number of linear parameters ($s_l, s_{nlk}, c_{nl}^{(0)}, c_{nlk}$) is 118 and there are two nonlinear parameters (β and β_r).

IV. THE FIT PROCEDURE

In order to obtain the most reliable fit, in particular for the long range part of the potential, we follow a two-step procedure. In the first step, we fit the *ab initio* points with $R > 10 a_0$ using only the $n = 6, 8$, and 10 terms of the long range function V_{lr} , with the damping function set to one. In this step the coefficients $c_{nl}^{(0)}$ and c_{nlk} are determined in a weighted linear least squares fit using the weight function $w_\infty(R) = R^6$. In the second step, we fix the long range coefficients for $n = 6$ and $n = 8$ and we determine all other linear parameters (including the $n = 10$ and $n = 12$ long range coef-

ficients) in a linear least squares fit. The choice of the non-linear parameters is discussed at the end of this section. Since we want to fit *ab initio* points that vary from the order of $1 \mu E_h$ around $R=15 a_0$ to about $0.1 E_h$ in the repulsive region we carefully construct a weight function $w(R, \theta, r)$ such that $w(R, \theta, r)V(R, \theta, r)$ is of the order of 1 everywhere. Both in the short and the long range $w=|V|^{-1}$ would actually work well, but in the intermediate range the interaction potential may go through zero. We factorize the weight function $w = w_{sr} \times w_{lr}$ and choose factors such that

$$w_{sr} \sim \begin{cases} \frac{V_0}{V} & \text{for small } R (V \rightarrow \infty) \\ 1 & \text{for large } R (V \rightarrow 0), \end{cases} \quad (6)$$

$$w_{lr} \sim \begin{cases} \frac{1}{V_0} & \text{for small } R (V \rightarrow \infty) \\ \frac{R^6}{C_6} & \text{for large } R (V \rightarrow 0). \end{cases} \quad (7)$$

In particular we take

$$w_{sr} = [\ln(e^{V/V_0} + e - 1)]^{-1} \quad (8)$$

$$w_{lr} = \left[1 + \left(\frac{R}{R_0} \right)^6 \right] V_0^{-1}, \quad (9)$$

where $V_0 = C_6/R_0^6$. This parameter determines where the short range factor of the weight function effectively “switches on” and we set it equal to $V_0 = 5|E_0|$, where $E_0 = -153 \mu E_h$ is the most attractive point on the grid. The choice of C_6 is not critical and we take the rounded value of $C_6 = 10$ (see next section) which gives $R_0 = 4.85 a_0$.

The nonlinear parameters β and β_r , as well as the upper limits in the summations (i.e., the degrees of the polynomials), and the power of r in the exponential factors were determined by extensive experimentation. In order to judge the quality of the fit in each experiment we considered the relative error for points where $V > V_0$, the absolute error for points with $V < 0$, and the relative error for points with $R > 7 a_0$. This test was done not only for the 754 geometries mentioned before, but also for an additional 27 random geometries that were not used in the fit. For very small values of R , the potential may become unphysical (i.e., negative). Therefore, in each numerical experiment we also took into consideration the barrier to the unphysical region. We found that the easiest way to determine nonlinear parameters β and β_r that minimize the error while keeping the barrier as high as possible is to start with a functional form that includes only low degree polynomials. Once a reasonably good fit is obtained the nonlinear parameters are kept fixed and the order of the polynomials is increased step by step as long as it gives substantial improvements of the fit.

With $\beta = 2.15$ and $\beta_r = 0.055$ we finally obtain a fit with the following properties:

- The largest relative error for all points with $V > V_0$ (i.e., in the short range) is 2.36%;
- The largest absolute error for all points with $V < 0$ is $0.71 \mu E_h$;

FIG. 2. A cut through the potential for $r = 2.282 a_0$. In this figure $Y_{He} = 0$ corresponds to the linear geometry.

- The largest relative error for all points with $R > 7 a_0$ is 0.39%;
- The barrier to the unphysical region is larger than $0.1 E_h$.

V. RESULTS AND DISCUSSION

In order to compare our potential with results from the literature we first look at a two-dimensional cut for a fixed O–O separation of $r = r_e = 2.282 a_0$ (see Fig. 2). We find a global minimum at the T-shaped geometry for $R = 6.0 a_0$ with $D_e = 127.1 \mu E_h$. This is in close agreement with the results of Cybulski *et al.*¹⁶ who report, for almost exactly the same geometry, a D_e of $126.4 \mu E_h$ at the unrestricted Møller–Plesset perturbation theory of fourth order (UMP4) level of theory. For the local minimum at the linear geometry our well depth is $116.7 \mu E_h$ for $R = 6.9 a_0$, which also agrees very well with the $116.4 \mu E_h$, $R = 7.0 a_0$ reported by Cybulski *et al.* The saddle point is located at $R = 6.8 a_0$, $\Theta = 49^\circ$ and the energy is $36.8 \mu E_h$ above the global minimum. Cybulski *et al.* determined the saddle point at the UMP2 level of theory and find a barrier of $34 \mu E_h$ at 6.5 – $7.0 a_0$ and $\Theta = 60^\circ$.

In Table I we compare the long range coefficients in our

TABLE I. Comparison of the long range coefficients $C_{nl}(r = 2.282 a_0)$ in E_h/a_0^n with the MC-TDCHF results of Hettema *et al.* (Ref. 35) (Table VIII for $n = 6$ and Table VII for $n = 8$; notice the extra factor $\sqrt{2l+1}$ in their definition).

n	l	C_{nl}	MC-TDCHF
6	0	9.17	9.21
6	2	1.41	1.43
8	0	194.53	170.83
8	2	160.68	168.70
8	4	−9.70	−9.80

FIG. 3. The $V_{OO}(r)$ potential curve calculated with the RCCSD(T) method (dashed line) and the semiempirical curve of Refs. 36 and 37 (solid line).

fit for $r = 2.282 a_0$ with the results of Hettema *et al.*,³⁵ who computed directly the long range coefficients in the multipole approximation with the multiconfigurational time-dependent coupled Hartree–Fock (MC-TDCHF) method. The surprisingly good agreement suggests that our *ab initio* calculations as well as our fit procedure are also reliable in the long range part of the potential.

We now turn to the vibrational coordinate dependence of the potential. The calculation of the O₂ potential [$V_{OO}(r)$], i.e., without the He, with the RCCSD(T) method diverges for $r > 3.5 a_0$. This is not surprising since one cannot expect to properly describe the dissociation of O₂ ($^3\Sigma_g^-$) into two O(3P) atoms with a single reference configuration method. In Fig. 3 we show the $V_{OO}(r)$ curve (the dashed line) together with the best available semi-empirical curve (the solid line).^{36,37} In this figure we also show how the potential is sampled by the $v = 14$ vibrational level computed for the RCCSD(T) curve. The first 15 vibrational levels are computed with the sinc-function discrete variable representation (DVR) method.^{38,39} In Table II we compare these vibrational energy levels with the experimental values. For $v \leq 12$ the

TABLE II. Comparison of $G(v) \equiv \epsilon(v) - \epsilon(0)$ with experiment (Ref. 41).

v	Experiment (mE_h)	RCCSD(T) (mE_h)	Error (%)
0	0.00	0.00	
1	7.09	7.09	−0.08
2	14.08	14.08	0.00
3	20.95	20.97	0.08
4	27.73	27.77	0.17
5	34.39	34.48	0.26
6	40.96	41.10	0.35
7	47.42	47.63	0.44
8	53.77	54.06	0.54
9	60.02	60.41	0.65
10	66.17	66.68	0.76
11	72.22	72.85	0.88
12	78.16	78.94	1.00
13	84.00	84.95	1.13
14	89.74	90.87	1.26

FIG. 4. The r -dependence of the interaction potential.

errors are at most 1%. The semiempirical potential^{36,37} reproduces all experimental values to better than 0.04% (not shown in the table). Based on these results for the O₂ potential we decided not to attempt to compute the He–O₂ interaction potential with the RCCSD(T) method beyond $r = 3.1 a_0$.

In Fig. 4 we show the dependence of the interaction potential on the O–O stretch coordinate around the local and the global minimum of the surface. Due to the interaction with the He atom the O–O equilibrium distance shortens by about $7 \times 10^{-5} a_0$ for the T-shaped geometry. In Table III the $n=6,8$ long range coefficients are given for three values of r . Together with Fig. 2 these data give an impression of the shape of the interaction potential. A Fortran 77 code to generate the interaction potential $V(R, \Theta, r)$, as well as the empirical potential $V_{OO}(r)$ is made available as an EPAPS document.⁴⁰ In this document, also the full data set of RCCSD(T) points can be found.

VI. CONCLUSION

We presented the first three-dimensional He–O₂ interaction potential. A single-reference configuration method was used, which limits the largest value of the O–O distance for which the potential could be calculated reliably to about $3.1 a_0$. A flexible, 120 parameter functional form was chosen to fit the potential. A special 2-step fit procedure was developed to extract good long range coefficients and to obtain a high quality global fit. For the O₂ equilibrium distance the interaction potential is in good agreement with the best literature

TABLE III. Vibrational coordinate dependence of C_{nl} .

n	l	$r = 2.0$	$r = 2.5$	$r = 3.0$
6	0	8.35	9.78	10.98
6	2	0.80	1.92	3.04
8	0	206.26	201.31	252.98
8	2	195.81	141.46	121.82
8	4	−21.15	−4.06	−0.37

calculations for the global and the local minimum, as well as with the best long range interaction coefficients computed in the multipole expansion.

ACKNOWLEDGMENTS

We thank Ad van der Avoird and Paul E. S. Wormer for useful discussions and for carefully reading the manuscript. We thank N. Balakrishnan for suggesting the problem. I.M.S. gratefully acknowledges support by the Socrates program of the European committee.

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