

Frequency-dependent polarizabilities of O₂ and van der Waals coefficients of dimers containing O₂

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We report frequency-dependent dipole and quadrupole polarizabilities of the oxygen molecule in its $^3\Sigma_g^-$ ground state. These properties are obtained by means of the multiconfiguration self-consistent field method and used for the computation of the van der Waals coefficients of (O₂)₂ and the O₂-Rg dimers, where Rg is He, Ne, Ar, and Kr. The required frequency-dependent polarizabilities of the rare gases were computed earlier by means of second-order many body perturbation theory.

I. INTRODUCTION

Potential energy surfaces of the O₂ molecule in interaction with atoms and molecules are of great interest for the spectroscopy of van der Waals molecules containing O₂, such as the complexes He-O₂, Ne-O₂, Ar-O₂, and O₂-O₂.¹⁻⁴ The solid state of O₂ also requires an accurate potential energy surface for the theoretical study of its dynamical behavior.⁵

The long-range part of the potential energy surfaces can be obtained by first computing the polarizabilities of the monomers as a function of imaginary frequency and by subsequently integrating the product of monomer polarizabilities along the imaginary axis.⁶ In this manner we get the van der Waals dispersion coefficients, which describe the multipole-expanded potential energy. This expansion is valid in the region where the electronic wave functions of the different monomers have negligible overlap and exchange effects can be neglected. The induction energy, another term in the second-order long range intermolecular potential energy, is quite easily obtained from the static polarizabilities and the multipole moments of the monomers.

Electron correlation usually affects computed monomer polarizabilities quite considerably. For closed-shell systems, one can use the Møller-Plesset (MP) theory to compute correlation effects on the energy. The second-order MP (MP2) formalism has been extended to the computation of frequency-dependent polarizabilities^{7,8} and yields good results for complexes containing the noble gases⁹ and a number of diatomics.¹⁰

The computations of correlation effects in open-shell systems is at present not possible by MP theory, but such calculations are feasible by a multiconfigurational approach: either CI or MCSCF.

In an earlier study Rijks, van Heeringen, and

Wormer¹¹ computed the frequency dependent dipole polarizabilities for the O₂ molecule by a single-double-triple configuration interaction (SDT-CI) method. They obtained the wave function perturbed by a monochromatic electric field in the space spanned by the single, double and selected triple excitations constructed from unperturbed orbitals. Prior to this work a similar procedure was explored in a paper by Visser, Wormer, and Jacobs,¹¹ but no triple excitations were included in the CI wave function. A subsequent analysis by Wormer and Rijks¹³ showed that in SD-CI certain unlinked clusters yield large contributions to the polarizability, which are cancelled by inclusion of triples. This analysis showed also that the use of orbitals that are relaxed in the external time-dependent field avoids the occurrence of these unlinked clusters.

The O₂ molecule is one of the earliest to which the multiconfigurational time-dependent coupled Hartree-Fock (MCTDHF)¹⁴⁻¹⁶ method was applied. The method was used for a computation of *inter alia* the dipole polarizability tensor on the real axis.^{15,16} It was shown by Albertsen, Jørgensen and Yeager^{15,16} that the component along the axis of the molecule is too high in the TDCHF approximation and that correlating the wave function with even a small active space lowers the computed polarizability by about 35%, so that the use of a correlation method is essential.

In this paper we will use the MCTDHF method to compute the dipole and quadrupole polarizability tensors of the O₂ molecule. Since our approach is based on Cauchy moments, we may obtain the linear response properties on the whole complex plane by Padé approximant type methods.^{17,18} Our calculation of the frequency-dependent quadrupole polarizability of oxygen is—as far as we are aware—the first one to date. We will report the van der Waals coefficients of complexes involving O₂ up to and including

C₈. We employ three different active spaces: an empty one (HF), a normal valence CAS (2*p*-CAS), and a restricted active space devised to include some of the dynamic correlation effects.

II. METHOD AND COMPUTATIONAL DETAILS

We will first discuss the computational method. The theory of the calculation of polarizabilities in the MCTD-CHF approximation has been discussed in a paper by Olsen and Jørgensen,¹⁴ to which we refer for further details. The computational implementation has been discussed by Jørgensen, Jensen and Olsen.^{19,20} The method we use is essentially the same as the one given by Fowler *et al.*,²¹ and was inspired by the method of Visser *et al.*²²

A. Method

In order to compute the van der Waals coefficients by the Casimir–Polder integral, we have to evaluate the multipole polarizability on an integration grid of several imaginary frequencies. Details on the grid and the numerical integration are given by Rijks *et al.*²³ We define a multipole operator by $Q_m^l = \sum_\alpha Z_\alpha S_m^l(\mathbf{r}_\alpha)$, where $S_m^l(\mathbf{r}_\alpha)$ is a real solid harmonic in Racah normalization and the sum runs over electrons and nuclei.

We consider the linear response function (polarization propagator²⁴) for two arbitrary multipole operators Q_m^l and $Q_{m'}^{l'}$

$$\begin{aligned} \alpha_{mm'}^{ll'}(\omega) &= \sum_{n>0} \langle 0 | Q_m^l | n \rangle \langle n | Q_{m'}^{l'} | 0 \rangle \\ &\times \left[\frac{1}{E_n - E_0 + \omega} + \frac{1}{E_n - E_0 - \omega} \right] \\ &\equiv - \langle \langle Q_m^l ; Q_{m'}^{l'} \rangle \rangle_\omega = \mathbf{Q}_m^{lT} (\mathbf{E}^{[2]} - \omega \mathbf{S}^{[2]})^{-1} \mathbf{Q}_{m'}^{l'}, \end{aligned} \quad (1)$$

where the matrices $\mathbf{E}^{[2]}$, $\mathbf{S}^{[2]}$ and the vector \mathbf{Q}_m^l , related to the perturbation operator, $V(t) = F_m^l Q_m^l \cos(\omega t)$, are defined in Ref. 14. The linear response function is minus the multipole polarizability.

We make an expansion of this expression in powers of ω to get

$$(\mathbf{E}^{[2]} - \omega \mathbf{S}^{[2]})^{-1} = \mathbf{E}^{[2]-1} \sum_{n=0}^{\infty} \omega^n (\mathbf{S}^{[2]} \mathbf{E}^{[2]-1})^n \quad (2)$$

from which we may rewrite the response function in powers of ω

$$\begin{aligned} \alpha_{mm'}^{ll'}(\omega) &= \mathbf{Q}_m^{lT} \mathbf{E}^{[2]-1} \mathbf{Q}_{m'}^{l'} + \omega \mathbf{Q}_m^{lT} \mathbf{E}^{[2]-1} \mathbf{S}^{[2]} \mathbf{E}^{[2]-1} \mathbf{Q}_{m'}^{l'} \\ &+ \omega^2 \mathbf{Q}_m^{lT} \mathbf{E}^{[2]-1} \mathbf{S}^{[2]} \mathbf{E}^{[2]-1} \mathbf{S}^{[2]} \mathbf{E}^{[2]-1} \mathbf{Q}_{m'}^{l'} + \dots, \end{aligned} \quad (3)$$

which is the same as Eq. (9) in the paper by Fowler *et al.*²¹ It can be shown from the block structure of the matrices that terms of odd power in ω vanish, as is to be expected since $\alpha_{mm'}^{ll'}(\omega)$ is a symmetric function of ω . The expansion can also be written in terms of Cauchy moments $S_{mm'}^{(-2k-2)}$,

$$\alpha_{mm'}^{ll'}(\omega) = \sum_{k=0}^{\infty} S_{mm'}^{(-2k-2)} (\omega^2)^k, \quad (4)$$

where we suppressed in the notation the dependence of the Cauchy moments on the indices l and l' . This series converges for real ω less than the lowest excitation energy of the system. By the use of the Cauchy moments in a Padé approximant the polarizability may be continued analytically on the whole complex plane.^{17,18,22} It is known that this procedure converges very fast, low order Padé approximants give already a very good description of the frequency-dependent polarizabilities.

In this method of computing the frequency-dependent polarizabilities, Cauchy vectors are defined recursively by,^{21,22}

$$\lambda^{[k]} = \mathbf{S}^{[2]} \mathbf{E}^{[2]-1} \lambda^{[k-1]} \quad (5)$$

with $\lambda^{[0]} = \mathbf{Q}_m^l$ initiating the recursion. The computational implementation of this procedure is easy: The first step consists of determining the solution vector \mathbf{X} of the linear equation

$$\mathbf{E}^{[2]} \mathbf{X} = \lambda^{[0]} \quad (6)$$

after which $\lambda^{[1]}$ is determined by multiplying \mathbf{X} by $\mathbf{S}^{[2]}$. The higher vectors are determined in the same fashion. Further details concerning this algorithm have been given in the papers by Jørgensen, Jensen, and Olsen^{19,20} and Fowler *et al.*²¹

The van der Waals coefficients were computed only for the equilibrium internuclear distance. We performed 2*p*-CAS multipole moment and static dipole polarizability calculations at four additional internuclear distances, which allows us to estimate the vibrational effects. We follow the work of Pandey and Santry,²⁵ who wrote the electronic energy as a double Taylor series in the field F and the internuclear distance R . They retained the terms up to and including F^2 and R^2 and used the field-independent, harmonic, terms as the zeroth order potential in the nuclear motion problem. The remaining terms in the electronic energy were used as a perturbation in first and second order perturbation theory. The perturbation energy terms quadratic in F are nuclear contributions to the dipole polarizability. Assuming that the molecule is in its vibrational ground state they arrived at the following expression for a vibrational correction on the polarizability, which is correct to second order,

$$(\alpha)_v = \frac{1}{m\omega_0} \left[\frac{1}{4} \left(\frac{\partial^2 \alpha}{\partial R^2} \right)_{R_0} + \frac{1}{\omega_0} \left(\frac{\partial \mu}{\partial R} \right)_{R_0}^2 + \frac{1}{8m\omega_0^2} \left(\frac{\partial^2 \mu}{\partial R^2} \right)_{R_0}^2 \right], \quad (7)$$

where ω_0 is the frequency of the harmonic vibration, m is the reduced mass of the oxygen molecule, and μ is the dipole moment. Since for homonuclear molecules the electronic dipole and its derivatives with respect to R vanish, only the first term survives.

TABLE I. Exponents of the polarization functions.

<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>
0.125 892 5	0.125 892 5	0.125 892 5	0.316 227 8	0.501 187 2
0.047 863 0	0.050 118 7	0.050 118 7	0.125 892 5	
0.015 135 6	0.019 952 6			
0.006 025 6				

B. Computational details

Our van der Waals coefficient calculations were performed at an internuclear distance of 2.2819 a.u., which was the distance used by Rijks *et al.*¹¹ and Visser *et al.*¹² Two additional multipole moment and static polarizability calculations were performed at steps of 0.05 a.u. on either side of this point in order to create a five-point grid for estimating vibrational effects.

We used the correlation consistent polarization valence triple zeta (cc-pVTZ) basis set substrate of Dunning²⁶ which consists of a set of (10*s*,5*p*,2*d*,1*f*) primitive functions, which are contracted using a general contraction to [4*s*,3*p*,2*d*,1*f*]. This basis set was then augmented with diffuse functions, according to the recipe used by Chong and Langhoff in their study of the OH⁻ ion.²⁷ Our basis set consists of 164 functions for O₂. The polarization functions are given explicitly in Table I.

We performed calculations at the Hartree-Fock (HF) level and at the MCSCF level with two active spaces. The first active space consists of all 2*p* orbitals with eight electrons active. It will be denoted 2*p*-CAS. The second active space was a restricted active space (RAS) consisting of the 2*s*-shell σ -orbitals in RAS1, the 2*p*-shell σ and π orbitals in RAS2, and finally the 3-shell (σ , π , δ) orbitals with the 3 σ_u excluded in RAS3 with a total of 12 active electrons. We allowed single and double excitations from RAS1 and single and double excitations to RAS3. This calculation will be denoted RAS. This choice of active spaces allows us to estimate the effects of dynamic correlation, i.e., the improvement of RAS on the 2*p*-CAS calculation.

For reliable polarizability calculations, one must have a good convergence of the original (time-independent) wave function. In all cases, the MCSCF wave function was converged to at least 10⁻⁷. The algorithm to compute the frequency dependent polarizabilities as a function of imag-

inary frequency $i\omega$ outlined above is stopped when the frequency-dependent polarizabilities have converged. In all cases, the polarizabilities have converged to within 10% of the value at the largest $i\omega$ quadrature point. Since the polarizability at this grid point contributes about 10% to the van der Waals coefficients and $\alpha(i\omega)$ goes monotonically to zero for large $i\omega$, we estimate the errors resulting from the convergence of our algorithm to be of the order of 1%.

III. RESULTS AND DISCUSSION

A. Multipole moments and static polarizabilities

Our energies and multipole moments are given in Table II. Our RAS energy lies close to the estimated full-CI limit of Ahlrichs *et al.*,²⁸ and the recent value of McLean *et al.*²⁹ Our 2*p*-CAS quadrupole Q_0^2 is close to the one computed by Visser *et al.*,¹² who used SD-CI. Our RAS Q_0^2 value lies below the 2*p*-CAS value and below the experimental value of Buckingham *et al.*,³⁰ but approaches the experimental value of Cohen and Birnbaum³¹ and is not far from the SDT-CI calculation of Rijks *et al.*¹¹ Looking at the different experimental and computed quadrupole values in Table II, we conclude that the RAS value of -0.264 a.u. has the highest credibility. The hexadecupole moment Q_0^4 is also close to the previously calculated value of Rijks *et al.*¹¹ These multipole moments enter the expressions for the induction energies, in the manner given in Ref. 32.

Our static polarizabilities are given in Table III, where they are compared to other calculations and experiment. From earlier MCSCF calculations,^{15,16} it is known that the static dipole polarizability α_{zz} is too high in the HF approximation. The value is considerably changed by going from HF to 2*p*-CAS, and changes little by going from CAS to RAS. Our best values for the dipole polarizabilities, obtained in the RAS calculation, are very close to the values $\bar{\alpha}=10.78$ and $\Delta\alpha=7.43$ measured at 632.8 nm by Bridge and Buckingham.³⁴ At this frequency we obtain (with the RAS wave function) $\bar{\alpha}=10.39$ a.u. and $\Delta\alpha=7.447$ a.u. Our agreement with $S(-2)$ values from constrained DOSD data³⁵ is of the same quality. The differ-

TABLE II. Energies and multipole moments of O₂.

	HF	2 <i>p</i> -CAS	RAS	Literature
$E(\text{MCSCF})$	-149.655 714	-149.754 885	-150.045 401	-150.101 987 ^a ; -150.089 19 ^b ;
$(Q_0^2)^c$		-0.315 392	-0.264 063	-0.271 37 ^d ; -0.3146 ^e -0.299 ^f ; -0.25 ^g
$(Q_0^4)^h$		+4.402 622	+4.408 699	4.384 66 ^d

^aReference 29.

^bReference 28.

^cNuclear contribution $Q_0^2=4R^2=20.828$ 27.

^dReference 11.

^eReference 12.

^f Experimental value; Ref. 30.

^g Experimental value; Ref. 31.

^h Nuclear contribution $Q_0^4=R^4=27.1136$.

TABLE III. Static polarizabilities of O₂. Definitions: $\bar{\alpha} = (\alpha_{xx} + 2\alpha_{yy})/3$ and $\Delta\alpha = \alpha_{xx} - \alpha_{yy}$.

	HF	2p-CAS	RAS	Literature	
$\bar{\alpha}$	11.914	9.68	10.22	9.76 ^a	9.25 ^b
$\Delta\alpha$	13.272	7.09	7.157	10.66 ^c	10.59 ^d
α_{00}^{22}	62.11	60.92			
α_{22}^{22}	29.94	28.51			
α_{11}^{22}	74.01	71.27			

^aReference 11.^bReference 15.^cRefractivity measurement of Ref. 33.^d $S(-2)$ value from constrained DOSD, Ref. 35.

ence between our values and the older MCTDCHF values of Albertsen *et al.*¹⁵ (who also performed a 2p-CAS calculation) must be attributed to our improvements in the basis set. The effects of electron correlation are much less significant for the quadrupole polarizabilities, where the values change by no more than 5% upon including electron correlation.

B. Frequency dependent polarizabilities

Rather than giving the dipole polarizabilities for some selected frequencies, we have chosen to present the Cauchy moments as these can be compared directly with the constrained DOSD values of Zeiss and Meath.³⁵ In Table IV Cauchy moments at the 2p-CAS and RAS level are listed. We have converged only the lowest Cauchy moments, so that the higher moments can be expected to be represented more poorly. Also the three lowest moments calculated with the RAS wave function, however, are too low: they differ from the experimental values by 3.5%, 8.8%, and 15.5%. This indicates that the frequency dependence of

TABLE IV. Cauchy moments from the 2p-CAS and RAS wave functions. Digits in brackets indicate powers of 10. The experimental values are from Ref. 35. See Eq. (4) for the definition of the Cauchy moments.

k	$S_{xx}^{(-2k)}$	$S_{zz}^{(-2k)}$	$S_{av}^{(-2k)}$	Expt.
2p-CAS				
1	7.322 186(0)	1.440 986(1)	9.684 745(0)	1.059(1)
2	1.165 057(1)	6.186 600(1)	2.838 905(1)	3.475(1)
3	2.912 646(1)	4.696 688(2)	1.759 739(2)	2.371(2)
4	9.472 423(1)	4.165 410(3)	1.451 619(3)	2.196(3)
5	3.761 511(2)	3.826 784(4)	1.300 671(4)	2.276(4)
6	1.762 656(3)	3.545 022(5)	1.193 425(5)	2.475(5)
7	9.396 835(3)	3.291 100(6)	1.103 298(6)	2.768(6)
k	$S_{xx}^{(-2k)}$	$S_{zz}^{(-2k)}$	$S_{av}^{(-2k)}$	Expt.
RAS				
1	7.833 918(0)	1.499 286(1)	1.022 023(1)	1.059(1)
2	1.398 818(1)	6.704 004(1)	3.167 213(1)	3.475(1)
3	3.982 573(1)	5.209 946(2)	2.002 153(2)	2.371(2)
4	1.516 403(2)	4.680 275(3)	1.661 185(3)	2.196(3)
5	7.225 343(2)	4.335 768(4)	1.493 425(4)	2.276(4)
6	4.050 470(3)	4.043 599(5)	1.374 870(5)	2.475(5)
7	2.512 308(4)	3.777 239(6)	1.275 828(6)	2.768(6)

TABLE V. Coefficients in the [3/4] Padé approximants of the O₂ quadrupole polarizabilities (a.u.), cf. Eq. (8). Digits in brackets indicate powers of 10.

	α_{00}^{22}	α_{11}^{22}	α_{22}^{22}
a values			
0	6.092 169 19(1)	7.126 881 41(1)	2.851 092 53(1)
1	-3.251 979 98(2)	-1.109 424 56(3)	-1.777 661 44(2)
2	4.851 071 78(2)	4.510 828 12(3)	3.032 880 86(2)
3	-1.740 950 32(2)	-4.120 058 59(3)	-1.229 845 58(2)
b values			
1	-6.453 473 09(0)	-1.881 150 82(1)	-7.697 872 16(0)
2	1.343 127 44(1)	1.005 994 57(2)	1.874 928 28(1)
3	-9.914 637 57(0)	-1.634 024 81(2)	-1.571 488 76(1)
4	1.880 464 55(0)	5.931 881 71(1)	3.194 822 31(0)

our results will differ from the DOSD frequency dependence. This will also have its effects on the calculated van der Waals coefficients.

Since this is the first time the frequency-dependent components of the quadrupole polarizability are calculated, we have chosen to present them in the easy accessible form of [3/4] Padé approximants,

$$\alpha_{mm}^{22}(\omega) \approx \frac{\sum_{i=0}^3 a_i \omega^{2i}}{1 + \sum_{i=1}^4 b_i \omega^{2i}}, \quad (8)$$

see Table V for the parameters a_i and b_i .

C. van der Waals coefficients

All van der Waals coefficients are presented in the *LLL* convention, i.e., they pertain to an expansion in

TABLE VI. O₂-O₂ dispersion coefficients at the different levels of approximation.

L_A	L_B	L	n	HF	2p-CAS	RAS	SDT-CI ^a
0	0	0	6	64.740	54.598	58.659 ^b	58.49
0	2	2	6	32.642	20.315	21.176	21.97
2	0	2	6	32.642	20.315	21.176	21.97
2	2	0	6	1.776	0.767	0.768	0.836
2	2	2	6	4.747	2.051	2.054	2.234
2	2	4	6	51.271	22.150	22.180	24.14
0	0	0	8	1735.9	1565.5		
0	2	2	8	2586.2	2450.0		
0	4	4	8	-306.2	-171.9		
2	0	2	8	2586.2	2450.0		
2	2	0	8	66.2	46.5		
2	2	2	8	-201.0	-181.5		
2	2	4	8	1493.9	1150.0		
2	4	2	8	-12.6	-5.2		
2	4	4	8	-29.1	-13.7		
2	4	6	8	-686.3	-277.9		
4	0	4	8	-306.2	-171.9		
4	2	2	8	-12.6	-5.2		
4	2	4	8	-29.1	-13.7		
4	2	6	8	-686.3	-277.9		

^aReference 11.^bOther literature values are $C_6=62.01$, from constrained DOSD in Ref. 35; $C_6=45.9 \pm 6.9$, from Ref. 37; $C_6=44.2$ from refractivity data, Ref. 38.

TABLE VII. Dispersion coefficients of O₂ with the noble gases. O₂ is computed on the 2*p*-CAS level, the polarizabilities of the noble gases are computed at the MBPT level (Ref. 9).

<i>L</i>	<i>n</i>	He	Ne	Ar	Kr	Xe
0	6	8.8962	18.577	59.091	84.838	124.79
2	6	3.2081	6.436	22.684	33.344	50.58
0	8	170.83	397.25	1591.3	2535.3	4450.4
2	8	377.21	805.32	2608.6	3807.3	5803.3
4	8	-25.93	-50.34	-197.0	-298.0	-469.0

spherical harmonics, which are coupled to a rotational invariant by a 3*j* symbol. Details concerning these conventions may be found in a paper by Visser, Wormer, and Stam.³⁶ We present the O₂-O₂ van der Waals coefficients in Table VI. In comparison to the constrained DOSD value our calculated value for the isotropic C₆ coefficient is 4.6% too low, which is consistent with the discrepancy found in the Cauchy moments. Our RAS value for the isotropic C₆ is very close to the extrapolated value of Rijks *et al.*,¹¹ who used a different method, but a much smaller basis: the remaining discrepancy with the DOSD values must be due to a too approximate a treatment of electron correlation effects in the two computational methods, or to inaccuracies in the DOSD approach. The anisotropy values also compare very well to the results of Rijks *et al.*¹¹ The old value of Langhoff, Gordon and Karplus³⁷ for the isotropic C₆ is very close to the recent estimate of Hohm and Kerl,³⁸ but since these authors used only a one-term approximation to the van der Waals coefficients, their result should be interpreted as a first estimate.

We present the van der Waals coefficients of O₂ in interaction with the noble gases in Tables VII and VIII. The frequency-dependent polarizabilities of the noble gases were taken from earlier work,⁹ and are calculated at the MP2 level. In Table VII the results are derived from O₂ polarizabilities calculated at the 2*p*-CAS level, whereas Table VIII is based on RAS polarizabilities.

Prospective users of our results are advised to take the C₆ values from Table VIII instead of from Table VII, because the RAS results are generally more reliable. Note that in atom-diatom complexes it is common to write the interaction in a Legendre expansion. Our dispersion coefficients must be divided by (-1)^{*L*}√2*L*+1 to adapt them to such an expansion.

TABLE IX. Energies, multipole moments and dipole polarizabilities of O₂ at several internuclear distances calculated with the 2*p*-CAS wave function.

<i>R</i>	<i>E</i>	Q ₀ ²	Q ₀ ⁴	α _{xx}	α _{zz}	$\bar{\alpha}$
2.1819	-149.749 409 01	-0.4552	4.210	7.151	13.43	9.243
2.2319	-149.753 310 32	-0.3852	4.287	7.236	13.91	9.461
2.2819	-149.754 884 53	-0.3154	4.403	7.322	14.41	9.685
2.3319	-149.754 545 87	-0.2460	4.554	7.410	14.91	9.911
2.3819	-149.752 643 97	-0.1771	4.739	7.498	15.42	10.14

TABLE VIII. Dispersion coefficients of O₂ with the noble gases. O₂ is computed on the RAS level, the polarizabilities of the noble gases are computed at the MBPT level (Ref. 9).

<i>L</i>	<i>n</i>	He	Ne	Ar	Kr	Xe
0	6	9.2078	19.196	61.326	88.139	129.83
2	6	3.2069	6.436	22.680	33.345	50.60

D. Vibrational contributions

We present the 2*p*-CAS multipole moments and the polarizabilities at several internuclear distances in Table IX. These data allow us to estimate the effects of vibrational averaging and the vibrational contributions to the multipole moments and polarizabilities.

The five energies may be fitted to a parabola with a minimum at *R* = 2.302 a.u. The root mean square deviation of the fit is on the order of 10⁻⁸ a.u. We obtain a value of ω = 0.007 26 a.u. (1593.4 cm⁻¹), which compares well to the experimental value of 1580.2 cm⁻¹.³⁹ The vibrational contributions to the multipole moments and polarizabilities are for ¹⁶O₂ (with a reduced mass of 14 578 amu, computed from the data in Ref. 40) (Q₀²)_v = -0.0004, (Q₀⁴)_v = 0.0337, (α_{zz})_v = 0.0011, (α_{xx})_v = 0.0071, where the second derivatives of the properties are also obtained by a fit to a parabolic form. With the exception of (Q₀⁴)_v, these values are an order of magnitude smaller than the effects of the dynamic correlation as can be seen from the difference in the 2*p*-CAS and RAS values in Tables II and III. In all cases we can conclude that the vibrational contributions are at most on the order of 1% of the total correlation effects.

IV. SUMMARY AND CONCLUSIONS

Our calculations show good agreement with the previous calculations of Rijks *et al.*¹¹ Since these authors used an entirely different method, the source of remaining errors is due to either the approximate treatment of electron correlation, or inaccuracies in the experimental values, or to both. Dynamic correlation effects change the value of the calculated van der Waals coefficients by about 10% in the O₂-O₂ case, but still our van der Waals coefficients differ from the DOSD values by a few percent. The first calculations of the C₈ coefficients are reported. The effects of the vibrational contributions to properties are estimated to be negligible.

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