Theor Chim Acta (1993) 86: 467–476

Theoretica
Chimica Acta

On the theoretical determination of the electron affinity of ozone

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Received November 4, 1992/Accepted March 24, 1993

Summary. Multiconfigurational electron correlation methods have been analyzed in order to theoretically compute the electron affinity (EA) of ozone. The near-degeneracy correlation effects, which are so important in O_3 and O_3^-, have been described using complete active space (CAS) SCF wave functions. Remaining dynamic correlation effects are computed using second-order perturbation theory (the CASPT2 method). The best calculated adiabatic value (including zero-point energy corrections), 2.19 eV, is about 0.09 eV larger than the experimental value. Comparative studies using size-consistent coupled pair functional approaches (CPF and ACPF) have also been performed. The harmonic frequencies in O_3^- have been determined to be: $\omega_1 = 992$, $\omega_2 = 572$, and $\omega_3 = 879\,\text{cm}^{-1}$, which gives a zero-point energy of 0.151 eV.

Key words: Ozone – Electron affinity – CAS – SCF

1 Introduction

Ozone and the ozonide ion play an important role in the chemistry of the ionosphere. Consequently, a large number of experimental studies have been made in order to obtain information on the properties of these compounds. Several different experimental methods have been employed for determining the electron affinity (EA) of ozone [1, 2]. The most accurate study has probably been carried out by Novick et al. [1]. The value recommended by these authors is 2.1028 ± 0.0025 eV [1]. Earlier experimental values for the EA of ozone differed significantly from one another.

These molecules have also proved difficult to study with theoretical methods. Most work has been carried out for the ozone molecule, which has turned out to be a theoretically very interesting and intriguing system. In addition to having intrinsic interest, it has provided a crucial test of the ability of different theoretical methods to calculate electron structures and properties. The reason for the difficulties encountered in some methods is closely related to the electronic structure of ozone, with its well-known mixture of ionic and diradical components. Recently, the electric properties and vibrational frequencies of ozone have been studied using a large variety of quantum chemical methods [3, 4], and have been compared with results from earlier studies [5]. It was concluded that non-dynamic and dynamic correlation effects have to be taken into account in a balanced manner in order to properly describe the properties of interest. The complete active space (CAS) SCF method in combination with a multiconfiguration second order perturbation theory (CASPT2) [6, 7] was shown to be well suited for this purpose.

The ozonide ion has been subject of more limited theoretical attention. In particular, only a few theoretical studies concerning the EA of O_3 are available [8–11]. In an early study of O_3 and O_3^-, a vertical electron affinity (VEA) of 2.12 eV [8] was obtained as the difference between natural orbital single excitation CI results for the involved species. A Green's function study gave an adiabatic electron affinity (AEA) of 2.17 eV [9]. More recently, the AEA has been determined using the unrestricted Möller–Plesset approach to fourth order (UMPn ($n = 2,3,4$)). Not surprisingly the computed EA showed a clear oscillatory behaviour (1.02 ($n = 2$), 2.00 ($n = 3$), and 1.43 eV ($n = 4$)) [10]. It was concluded that a multiconfigurational approach is needed for a proper description of the electronic structure. However, when corrections for correlation errors are applied using the Gaussian-2 procedure (G2 theory), the resulting AEA, 2.118 eV [11], is in agreement with experiment. Thus it seems that single configuration based methods can be successfully used, if the correlation treatment is carried to a high level. We cannot deduce, however, the size of the "empirical" correction applied to the end result in the G2 theory from the data given in [11].

Our purpose in this paper is to explore the effects of high level correlation contributions, in order to establish what level is required to give a quantitatively realistic description of the theoretical VEA and AEA of ozone. As will be shown below, single-reference methods can give reasonable values for the VEA. This is most probably due to the fact that the near-degeneracy effects are larger in O_3 than in O_3^-. Thus the correlation error is larger for the neutral species. The Hartree–Fock value (RHF) for the VEA is consequently much too large. Correlation corrections reduces the RHF value and can, in combination with basis set deficiencies fortuitously lead to electron affinities in good agreement with experiment. However, as will be illustrated below, some single-reference based approach completely breaks down for the anion when the geometry is optimized. Thus a multireference approach seems to be necessary for the calculation of the AEA of O_3.

First, we discuss the calculation of the VEA of ozone using different single- and multi-reference methods, which are described in the next section. Based on those findings, the AEA of ozone is computed at the CASPT2 level. It was considered to be the most suitable of the methods tested, since it includes the effects of dynamic electron correlation in a balanced way. A force field for O_3^- was determined at the same level of approximation and was used to compute the harmonic vibrational frequencies, and from them, the zero-point energy.

2 Methods and computational details

Initial calculations on the VEA of O_3 were carried out at different levels of theory. Since many electrons are correlated, single- and multireference CI methods with the property of being (nearly) size-consistent were chosen: the Coupled Pair Functional (CPF) and Average Coupled Pair Functional (ACPF) wave functions proposed by Ahlrichs and co-workers [12, 13].

The CPF approach [12] is known to give accurate results in cases where the wave function is dominated by a single configuration. The ACPF wave function [13] is an extension of the CPF method to allow more than one reference configuration. Compared to other CI techniques, the corresponding functional in these methods is modified in order to fulfil the requirement of size-consistency.

CASSCF [14] calculations were also performed, since this approach is most suited to describe the multiconfigurational character of the wave function already at the zeroth-order level. Dynamic correlation effects were then added, either using the ACPF approach or by means of second order perturbation theory (CASPT2) [6, 7].

The CASPT2 method [6, 7] computes the first-order wave function and second-order energy with a CASSCF wave function as the unperturbed wave function. The zeroth-order Hamiltonian is defined as a Fock type one electron operator such that Möller–Plesset (MP) perturbation theory is obtained in the closed-shell single determinant case. Two different partitioning of the zeroth-order Hamiltonian are possible: using only the diagonal part of the Fock matrix (called PT2D), and including also the non-diagonal elements (PT2F). Results using both formulations are provided and analyzed here. Only the non-diagonal approach is invariant to rotations of the molecular orbitals. Such invariance might be important in geometry optimizations, considered as a particular case of calculations of potential energy surfaces. Thus, the full approach is expected to be more accurate in this type of applications. However, the PT2D approach is computationally simpler, leading to cheaper calculations, and leads in most cases to results not very different from PT2F. As stated above the CASPT2 approach gives accurate results for a number of properties of the ozone molecule [3, 4]. Using basis sets of moderate size the agreement between the CASPT2 and full CI results have in different types of calibration tests been found to be satisfactory [6, 7, 15]. Similar results are obtained when the CASPT2 method is compared with the multireference CI (MRCI) method [6, 7] in calculations with more extended basis sets. These tests have included a study of the geometry and binding energies of a large number of molecules (the "G1-test") [16], and the energy barrier and exothermicity of the reaction $F + H_2 \rightarrow HF + H$ [15]. Relative energies are reproduced with errors of the order of a few kcal/mol (0.1 eV). The CASPT2 method has also been employed for calculation of electronic spectra at a quantitative level [17].

Generally contracted basis sets of the atomic natural orbital (ANO) type [18, 19] have been used, which were obtained from a (14s9p4d3f) primitive set. In order to check the convergence of the results with the basis set, two different contractions have been used: [4s3p2d] and [5s4p3d2f], hereafter labelled as BS1 and BS2, respectively. These basis sets have been constructed to optimally treat correlation and polarization effects and should be large enough to describe the electronic structure with good accuracy.

Geometries have been optimized using a 7-point grid which was fitted to a quadratic polynomial in the variables R(OO) and $<$ OOO. The procedure was iterated until no change in the variables were obtained. In the calculations of the harmonic vibrational frequencies, a larger number of grid points were used (*vide supra*).

The calculations have been performed on the IBM 9021/500-2VF computer at the University of Valencia using the MOLCAS-2 quantum chemistry software [20].

3 Results and discussion

Initial calculations were first carried out on the VEA of O_3 at different levels of theory. To be able to compare with previous work [8] the geometry was fixed at R(OO) = 2.413 au and $<$ OOO = 116.8°. The results of this calibration study are presented in Table 1. Previous theoretical findings and the most recent experimental value [1] are also included. In order to perform a meaningful comparison with the experimental (adiabatic) value, geometry optimization and the zero-point energy (ZPE) will have to be included. Since the ground state of the ozone molecule and its negative ion have similar geometries [21, 2], the difference between the VEA and AEA are expected to be small. The ZPE correction will be discussed in detail below.

We start the analysis by discussing results obtained with the BS1 basis set. This basis set includes enough basis functions to make it capable of describing the major correlation effects contributing to the EA. The Hartree–Fock configuration for the ground state of O_3, $^1A_1$, in C_{2v} symmetry can be represented by $(5a_1)^2(3b_2)^2(1b_1)^2(4b_2)^2(6a_1)^2(1a_2)^2$ where a_1 b_1 b_2 and a_2 are the standard irreducible representations of C_{2v}. For the O_3^- ground state, the extra electron appears in the $2b_1$ molecular orbital, yielding an overall symmetry of $^2B_1$ for the wave

Table 1. Calibration calculations on the vertical electron affinity (VEA) of ozone using different theoretical methods. Geometry was fixed as in [8]. Experimental (adiabatic) value: 2.10 eV[a]

Level of calculation	O_3 ($^1A_1$)	O_3^- ($^2B_1$)	VEA (eV)
BS1 basis set (4s3p2d)			
RHF	− 224.343964	− 224.447326	2.81
CASSCF	− 224.575731	− 224.564840	<0
CPF	− 225.048342	− 225.116760	1.86
π-ACPF	− 225.061593	− 225.114795	1.45
No. ref.	4	2	
w	0.9781	0.9771	
PT2D	− 225.043374	− 225.106462	1.72
w	0.9476	0.9338	
PT2F	− 225.045680	− 225.110565	1.77
w	0.9468	0.9322	
BS2 basis set (5s4p3d2f)			
RHF	− 224.358953	− 224.460918	2.77
CASSCF	− 224.589249	− 224.577546	<0
CPF	− 225.158521	− 225.232334	2.01
π-ACPF	− 225.172897	− 225.230165	1.56
No. ref.	4	2	
w	0.9776	0.9762	
PT2D	− 225.156516	− 225.224188	1.84
w	0.9440	0.9296	
PT2F	− 225.158871	− 225.228334	1.89
w	0.9431	0.9281	
Previous work			
Single excited CI[8]	− 224.226512	− 224.304537	2.12

[a] The 1*s* electrons have been kept frozen at the CPF, ACPF and CASPT2 level. *w* refers to the weight of the corresponding reference function

function (the molecule is placed in the yz plane, where z is the principal symmetry axis). The CASSCF wave function includes all configurations resulting from an unrestricted distribution of the 12 valence electrons, from the $(2p)^4$ atom configurations, among the 9 corresponding molecular orbitals. The oxygen $1s$ and $2s$ derived MOs are thus left inactive. The resultant number of configurations is 666 and 473 for the neutral and the anion, respectively.

The computed Restricted Hartree–Fock (RHF) value of the VEA is significantly larger than the experimental value indicating that valence-shell degeneracy effects are more important in the neutral species than in the anion. This result is confirmed by the CASSCF calculations. The energy lowering in ozone is about twice as large as in the anion. This is related to the well-known fact that the RHF wave function of ozone is dominated by ionic structures, in the Valence Bond (VB) sense. More advanced wave functions for ozone are more diradical in character. In order to treat the diradical and ionic structures in a balanced way, the HF configuration and the double excited $(1a_2)^2 \rightarrow (2b_1)^2$ configuration have to be treated in a balanced way, which can be accomplished, for example, by the CASSCF procedure. However, the CASSCF method itself does not give a qualitatively correct description of the VEA. The anion is not bound at the CASSCF level. Basch has in a recent study shown that the addition of the oxygen $2s$ orbitals to the active space does not lead to any appreciable improvement of this result [10]. The computed AEA is positive but very small, 0.07 eV. The remaining error is due to differences in the dynamic correlation energy between the anion and the neutral species.

The CPF calculations were carried out using the RHF MOs. In view of the preceding discussion, it is somewhat surprising to find that the single-reference VEA of ozone is rather similar to the values obtained with multiconfigurational methods. In addition, the optimal geometry (R(OO) (Å); < OOO (°)) for the neutral molecule at the CPF level (1.297; 117.4) is in reasonable agreement with the experimental data [21] (1.2717(2); 116.78(3)). However, for the anion no stable geometry could be found using the CPF method, due to strong near-degeneracy effects in the electronic structure. The trend was to larger bond distances and a smaller bond angle where the dynamic σ-polarization effects becomes increasingly important, and the single-reference based approximation breaks down.

The multireference ACPF approach was next tested for this problem. The MOs used were the ones obtained in the CASSCF calculation. The full valence π system (4 configurations for the neutral and 2 for the anion) was used as reference functions. Even if the calculations can be considered balanced in the sense that the same degree of flexibility is introduced for both systems, the computed VEA is too small. The calculation is balanced in the sense that the weight of the reference functions are the same in the neutral and the anionic species. Still, it seems that the calculation is unbalanced with a better treatment of the correlation effects in the neutral molecule. Analysis of the ACPF wave function shows that the most important remaining correlation effects are the σ–σ^* excitations coupled with π excited configurations. Thus, excitations describing the dynamic polarization of the σ system are the most important ones to be included in an extended reference space. This effect is even more pronounced for the anion. Previous experience [4] using a multireference approach for ozone has, however, shown that it is not possible to include all these type of excitations in the reference space since the calculation becomes extremely large. Truncation has somehow to be carried out, and the results will be quite sensitive to the detailed choice of reference functions.

Table 2. Calculated equilibrium geometries for the ground state of O_3 and O_3^-

	O_3 ($^1A_1$)		O_3^- ($^2B_1$)	
	R(OO) (Å)	< OOO (°)	R(OO) (Å)	< OOO (°)
BS1 basis set (4s3p2d)				
PT2D	1.304	116.5	1.387	115.6
PT2F	1.297	116.7	1.378	115.6
BS2 basis set (5s4p3d2f)				
PT2D	1.290	116.7	1.370	115.5
PT2F	1.283	116.7	1.361	115.4
Previous work[a]				
val-CASSCF[a]	1.31	116.1	1.39	115.3
MP2/6-31G*[b]	1.299	116.3		
UMP4SDTQ/6-311 + G*[b]			1.337	114.8
Exp.[21,2]	1.272	116.8	1.34 ± 0.03	113 ± 2

[a] From [10]: val-CASSCF has all valence orbitals and electrons active
[b] From [11]

Another way to include these dynamic effects, which does not suffer of such limitations, is by the CASPT2 approach. As a number of earlier test studies has shown, remaining dynamic correlation effects can be adequately described by second order perturbation theory when strong near-degeneracy effects are included in the CASSCF reference function. As shown in Table 1, this is also the case here. It should be emphasized that the in the CPF, ACPF, and CASPT2 calculations all electrons were correlated except the 1*s*. Control calculations showed that including the 1*s* electrons in the correlation treatment had no effect on the computed VEA.

The results using the BS2 set follow the same general trend as discussed for the BS1 set. Compared to the BS1 results, a general improvement, within 0.10–0.15 eV, is obtained for the VEA. Taking into consideration the advantages and limitations of the different methods discussed here, the CASPT2 approach was used in the final calculation of the AEA of ozone.

Calculated equilibrium geometries for the ground state of O_3 and O_3^- are collected in Table 2. For comparison we have also included experimental data and previous theoretical results. The comparison is with previous theoretical studies in which equilibrium geometries are available for both the neutral and the anion at a given theoretical level. Thus comparison is made with the valence CASSCF results reported by Basch [10], and the MP results obtained by Yu et al. [11] in their G2-theory study of the electron affinity of ozone. Equilibrium geometries for the ozone molecule, obtained with other theoretical methods, are available in the literature [5], but will not be further discussed here.

The CASSCF bond distances are, with a few exceptions, longer than the experimental values. This is a typical behaviour of the CASSCF approximation, which is known to overemphasize the importance of anti-bonding electron configurations. Inclusion of dynamic correlation effects reduces the error. Both the PT2D and PT2F results show a much better agreement with experiment. In fact, the equilibrium geometries show a nice convergence towards the experimental data when enlarging the basis set. The bond distance is 0.011 Å larger than experiment at the PT2F level, with the bond angle in perfect agreement. The experimental geometry for O_3^- has rather large error bars [2] and the theoretical data are here of higher quality. These results are consistent with previous experiences using the CASPT2 method [4, 16]. The equilibrium bond distance (PT2F, BS2 set) of O_3^- is greater than that of O_3 by 0.078 Å and the bond angle is smaller by 1.3°. This can be understood using simple molecular orbital arguments: due to the structure of the $2b_1$ orbital, placing electron density in it simultaneously promotes bending of the molecular bonds and weakens bonding of the terminal oxygens to the central atom.

4 The zero point energy of O_3^-

For a complete determination of the AEA of ozone, we need also to know the zero-point energy of O_3^-. The harmonic frequencies of O_3 are well known [22] and give a zero-point energy of 0.182 eV. The situation for O_3^- is, however, less clear. The laser spectroscopy measurements [1] on gaseous O_3^- yield only two of the fundamentals: the symmetric stretch ($\nu_1 = 982 \pm 30\,\mathrm{cm}^{-1}$) and the bending frequency ($\nu_2 = 550 \pm 50\,\mathrm{cm}^{-1}$). Additional information can be obtained from IR and Raman studies of matrix isolated $M^+O_3^-$ species, where M is an alkali metal atom [23]. Such studies yield ν_1 values in the range 1000–1030 cm^{-1}, ν_2 values around 600 cm^{-1}, and estimates of the anti-symmetric stretch frequency ν_3 around 800 cm^{-1}. These frequencies are, however, affected by the formation of a rather strong complex in the matrix between the ozonide ion and the positive alkali metal ion. Recently [24], the symmetric stretch frequency has been measured to be 1058 cm^{-1} for aqueous O_3^-. Again a shift is likely to result from hydrogen bond interactions with surrounding water molecules [24].

Since a complete experimental determination of the three fundamentals for a free ozonide ion is lacking, it was decided to use the CASPT2 method to compute a force field from which the harmonic frequencies could be obtained and the zero-point energy computed. We recently [4] performed such calculations for O_3 and the resulting frequencies were in good agreement with experiment. The computed zero-point energy was 0.174 eV, which is 0.008 eV smaller than the experimental value. A similar accuracy can be expected for O_3^-. The calculations were made with the BS2 basis set and with 9 active orbitals. 12 points were used to determine the symmetric (C_{2v}) force field (a third degree polynomial) and 5 points for the antisymmetric stretch coordinate (fitted to a fourth degree polynomial). For further details on these calculations we refer to the earlier study of ozone [4]. The resulting harmonic frequencies are given in Table 3. As for ozone we see pronounced effects on the frequencies from electron correlation. Thus ω_3 is imaginary at the SCF level of calculation. The effect of the dynamic electron correlation, introduced by the CASPT2 calculation, is also largest for this frequency. The

Table 3. Calculated harmonic frequencies for O_3^- (cm^{-1})

Level of calculation	ω_1	ω_2	ω_3
SCF	670.5	1297.0	imaginary
CASSCF	1003.9	579.9	688.1
PT2F	992.3	571.6	878.9

symmetric stretch and bend frequencies (PT2F) are in agreement with the gas phase data reported by Novick et al. [1]. The antisymmetric stretch frequency is, however, about 80 cm^{-1} larger than the data obtained for the $M^+O_3^-$ complexes [23]. At present we are computing the force field for LiO_3 in order to study the frequency shifts in more detail [25]. Based on the harmonic frequencies we compute a zero-point energy of 0.151 eV for the ozonide ion. The zero-point energy correction to the AEA is then + 0.023 eV. This ZPE correction is smaller than the one obtained from the G2 calculations by Yu et al., 0.069 eV [11].

5 The adiabatic electron affinity of ozone

Table 4 lists the final computed results of the electron affinity of ozone, including previous theoretical findings and the most accurate experimental value. No zero-point energy correction is included in the computed values in order to facilitate a comparison between results obtained with different methods.

The PT2D and PT2F results of the AEA and VEA are quite similar using a given basis set. The difference between the PT2F results with the two basis sets is 0.04 eV and 0.03 eV for the AEA and VEA, respectively. We consider the BS2 result converged within a few hundredths of an eV with respect to further enlargement of the basis set. Including the ZPE, the final calculated value for the AEA is 2.19 eV, which is about 0.09 eV larger than the experimental value. A large number of

Table 4. The adiabatic (AEA) and vertical (VEA) electron affinity of the ozone molecule

Level of calculation	AEA (eV)	VEA (eV)
BS1 basis set		
PT2D	2.14[e]	1.90
PT2F	2.13[e]	1.90
BS2 basis set		
PT2D	2.17[e]	1.93
PT2F	2.17[e]	1.93
Previous work		
SCI[a]		2.12
GF[b]	2.17	1.67
UMP2[c]	1.02[e]	
UMP3[c]	2.00[e]	
UMP4SDTQ[c]	1.43[e]	
G2-theory[d]	2.049[e,f]	
Exp.[1]	2.103	

[a] Single excitation CI results from [8]

[b] Green's function results from [9]

[c] UMP*n* ($n = 2,3,4$) results from [10]

[d] Results obtained with the G2-theory corrections [11]

[e] For comparison with experiment a zero point energy correction of 0.023 eV should be added

[f] The zero point energy correction of G2-theory (0.069 eV) has been subtracted from the value given in [11]

earlier tests has shown that this is a typical error obtained in CASPT2 calculations of energy differences, such as heats of reactions, excitation energies, etc.

The pattern shown by the UMP*n* series reported by Basch [10] is an indication of the need for a multireference approach. At the UMP4SDTQ level underestimation of the AEA is about 0.67 eV compared to experiment. However, the accuracy obtained by the G2-theory is impressive [11]. It seems that the applied G2-theory corrections to the total energies are capable of recovering the large errors that occur in conventional single-configurational approaches (it may be noted that the geometry of the molecule and the anion had to be, optimized at different levels of theory, MP2 for O_3 and UMP4SDTQ for O_3^-). The GF result [9] for the AEA is also in good agreement with experiment. This is probably due to a cancellation of errors due to the crude estimate of the equilibrium geometry for O_3^- together with the use of a single configuration based approach for the electron correlation.

6 Conclusion

The electron affinity and the structure of O_3 and O_3^- has been studied using multiconfigurational second-order perturbation theory. The computed value of the adiabatic electron affinity is 0.09 eV larger than the most recent experimental determination. The computed OO distance in O_3 is 0.011 Å larger than the experimental value and the bond angle is in complete agreement. The calculated equilibrium structure for O_3^- is within the error limits of the measured data. Thus, the present study provides one further test of the applicability of the CASSCF/CASPT2 approach in predicting relative energies and molecular structure with good accuracy also for systems with a complex electronic structure.

Acknowledgements. The research reported in this communication has been supported by a grant from the Swedish Natural Science Research Council (NFR), by IBM Sweden under a joint study contract, and by the Cooperación Científica of Spain.

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