

THEORETICAL EVIDENCE FOR BOUND ELECTRONIC EXCITED STATES OF OZONE[‡]

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Received 20 September 1973

Extensive configuration interaction calculations (up to 1532 spin eigenfunctions) have been carried out on ozone with both minimal and extended bases. Vertical and adiabatic excitation energies to 14 excited states are reported, including seven states with vertical excitation energies less than 4 eV. Our calculations indicate that in addition to the ground state there are four other states of ozone (3B_2 , 3A_2 , 1A_2 and 3B_1) bound with respect to dissociation to ground state O_2 and O (by 0.4, 0.3, 0.1 and 0.0 eV, respectively). With such small bonding energies, the current results cannot be said to show definitively (except perhaps for 3B_2) these four states to be bound with respect to $O_2 + O$. However, the theoretical evidence is sufficiently strong as to warrant careful experimental studies. Such bound excited electronic states could play important roles in the chemistry of the upper atmosphere and in the chemistry of oxygen discharge systems. One (or more) of these states may be responsible for the short-lived intermediate ('ozone precursor') recently observed in oxygen radiolysis.

1. Introduction

In 1972 we reported [1] the first extensive ab initio theoretical studies of the excited states of O_3 . Seven excited electronic states were found to have vertical excitation energies less than 4 eV on the basis of configuration interaction (CI) calculations (197 to 382 determinants) using a minimum basis set (MBS). Optimum bond lengths and energy curves as a function of angle were obtained from generalized valence bond calculations. Although these studies were expected to yield reasonable vertical excitation energies for the

first seven excited states, they were not adequate for determining the adiabatic excitation energies to the various states.

We have now carried out extensive CI calculations for the various states as a function of bond length and bond angle using both minimal and extended basis sets. This allows much more accurate estimates of the vertical and adiabatic excitation energies and of the equilibrium geometries of the excited states. In particular we find that in addition to the ground state of ozone, there are three excited electronic states that appear to be bound with respect to dissociation to ground state O_2 and O.

[‡] This work was supported in part by the National Science Foundation (GP-15423) and the Caltech President's Fund (PF-013).

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[‡] Contribution No. 4756.

2. Calculations

In these calculations we used two bases: (1) a minimal basis set (MBS) consisting of STO-4G functions

[2]; (2) a double-zeta (DZ) basis of contracted gaussian basis functions [3].

For ozone a full CI with 30 basis functions (DZ) requires $\approx 10^{14}$ determinants, a completely impractical number. In order to obtain a high quality CI wavefunction with far fewer terms, we have first carried out generalized valence bond (GVB) calculations [4, 5] to determine the optimum orbitals for incorporating molecular correlation effects. A CI calculation based on these GVB orbitals requires only $\approx 10^3$ terms for an adequate wavefunction. This approach is similar to the MC SCF approach used by Wahl and co-workers [6] and the first-order wavefunction of Schaefer and Bender and coworkers [7], although our basic method differs from theirs.

The GVB spatial wavefunction for the ground state (1^1A_1) of ozone has the form

$$(1a_1)^2(1b_2)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(5a_1)^2(3b_2)^2(1b_1)^2 \chi^{\text{GVB}}, \quad (1)$$

where

$$\chi^{\text{GVB}} = (\sigma_{1\ell} \sigma_{2\ell} + \sigma_{2\ell} \sigma_{1\ell}) \times (\sigma_{1r} \sigma_{2r} + \sigma_{2r} \sigma_{1r})(\pi_{\ell} \pi_r + \pi_r \pi_{\ell}), \quad (2)$$

and where (1) is to be multiplied by an appropriate spin function and antisymmetrized. These 15 GVB orbitals are all solved for self-consistently [8]. The remaining 15 orbitals are referred to as virtual orbitals and can play an important role in readjusting the GVB orbitals to describe excited states. The CI calculations were carried out using configurations that are symmetry adapted (space and spin); a maximum of six open shells was allowed so that each spin eigenfunction is composed of up to 20 determinants for singlet states and up to 15 determinants for triplet states. Three types of CI calculations were carried out: (1) MBS CI: Using an MBS basis [2] all configurations that can be obtained by up to quadruple excitations from the HF configuration of the ground state were included, with the restriction that the O 1s and O 2s-like orbitals were kept doubly occupied[†]. This led, for example, to 795 spin eigenfunctions for 1^1A_1 (4π) and 1058 spin eigenfunctions for 3^1B_1 (5π). For the calculations as a function

[†]Our previous MBS CI studies, ref. [1], included all single and double excitations from the dominant configurations (usually two) of each excited state. The current calculations are more complete but the excitation energies are quite similar.

of θ the highest lying O 2s-like orbital was also included in the CI (this orbital correlates with $1\pi_u$ orbital at 180°). (2) GVB CI: Only the 15 GVB orbitals from the DZ calculations [3] on the ground state were used. From the previous calculations we found that all states involve from two to four dominant configurations (CI coefficients greater than 0.2). We included in the CI these configurations plus all single and double excitations within the GVB space with the restriction that the O 1s-like orbitals were kept doubly occupied. This led to 579 spin eigenfunctions for 1^1A_1 (4π) and 1036 spin eigenfunctions for 3^1B_1 (5π). (3) Polarization CI (POL CI): In addition to the configurations included in GVB CI, single and double excitations from the dominant configurations of (1) to the full DZ basis were included with the restriction that at most one virtual orbital be occupied and that the 1s- and 2s-like orbitals remain doubly occupied. In addition, for POL CI, we screened the configurations by computing an energy contribution using perturbation theory and eliminated configurations with an energy contribution $\Delta E < 0.00001$ h. This led to 2472 spin eigenfunctions (1048 after screening) for the 1^1A_1 (4π) state and 4826 spin eigenfunctions (1532 after screening) for the 3^1B_1 (5π) state. The POL CI wavefunction is essentially the same as the first-order wavefunction of Schaefer et al. [7].

3. Results

In columns 1–3 of table 1 we report the vertical excitation energies for 14 excited states. We have classified these states in terms of the number of electrons in π orbitals and in terms of the overall charge distribution for the GVB form of the wavefunction. The states denoted as covalent involve essentially four electrons in 2p-like orbitals on each O atom (in addition to two in 1s and two in 2s-like orbitals). The states denoted as ionic involve significant charge transfer character. Only two excited states are known experimentally [9, 1] (see column 4). The POL CI theoretical results are the most reliable and for the covalent states are expected to be within 0.2 eV of the exact value.

Using $\theta = 116.8^\circ$ we obtained for the 1^1A_1 (4π) state, $R_{\text{opt}} = 2.62, 2.61$ and $2.60 a_0$ from the MBS CI, GVB CI, and POL CI calculations. The experimental

Table 1
Excitation energies for ozone. All energies are in eV

State		Vertical excitation energies ($R = 2.415 a_0, \theta = 116.8^\circ$)			Nonvertical excitation energies						
		CI calculations			optimum R , fixed θ (116.8°)			variable θ , fixed R ($2.6 a_0$)			
		MBS	DZ	exp. a)	CI calculations			CI calculations			
			GVB CI	POL CI	MBS	DZ		MBS	DZ	GVB CI	exp. b)
ionic π^4	2^3A_1	9.50	9.96		5.93 ^{d,e)}	6.59 ^{e)}					
	1^3A_1	9.02	9.23		5.18 ^{d,e)}	5.86 ^{e)}					
ionic π^5	2^1B_1	8.33	7.71	7.23	5.64	5.15	5.09				
	2^1A_2	8.12	7.56	6.93	5.64	5.33	5.06				
	2^3B_1	7.13	7.00		4.77	4.42	4.16 ^{b)}				
	2^3A_2	7.08	6.89		4.78		4.25 ^{b)}				
ionic π^4	3^1A_1	7.91	8.33	8.14	5.45	5.76	5.52				
	1^1B_2	6.50	6.93	5.60	4.13– 5.64	5.04	4.92	4.36	5.04		3.45
covalent π^6	2^1A_1	4.16	4.51	4.18	2.22	2.49	2.43				
	2^3B_2	3.80	4.19	3.86	1.97	2.22	2.17	1.81			
covalent π^5	1^1B_1	2.18	2.32	2.06	2.03– 2.26	1.22	1.36	1.29	1.22		
	1^1A_2	1.97	2.32	1.98		1.17	1.33	1.22	0.85	1.10 ^{f)}	} (1.2)
	1^3A_2	1.80	2.11	1.80 ^{b)}		1.07	1.18	1.10 ^{b)}	0.72	0.93 ^{f)}	
	1^3B_1	1.94	1.97	1.74 ^{b)}		1.07	1.13	1.10 ^{b)}	1.09		
covalent π^4	1^3B_2	1.20	1.69	1.47	0.60	0.77	0.77	0.47			
	1^1A_1	0.0 ^{c)}	0.0 ^{c)}	0.0 ^{c)}	0.0 ^{c)}	0.0 ^{c)}	0.0 ^{c)}	0.0 ^{c)}	0.0 ^{c)}	0.0 ^{c)}	0.0
column number		1	2	3	4	5	6	7	8	9	10

a) See refs. [9, 10].

b) The POL CI calculations on these states were not carried out at all R . To obtain adiabatic excitation energies the GVB CI potential curves were scaled to match the calculated POL CI points. POL CI excitation energies at $R = 2.601 a_0$ are 1.22, 1.74, 4.81 and 4.87 eV for 1^3B_1 , 1^3A_2 , 2^3A_2 , and 2^3B_1 , respectively.

c) Energies for the 1^1A_1 state are -223.13048 , -224.45066 , -224.50365 , -223.16065 , -224.46264 , -224.51478 , -223.16179 , and -224.46264 for columns 1–3, 5–9 respectively (energies in hartree).

d) Calculated at $R = 2.8 a_0$.

e) For the ground state geometry the dominant configuration of 1^3A_1 involves an excitation in the π system while the dominant configuration for 2^3A_1 is an excitation of the σ system. For the optimum R the 1^3A_1 and 2^3A_1 states have opposite character.

f) Calculated at $R = 2.74 a_0, \theta = 100^\circ$.

value is $2.415 a_0$ so that the error here is very large ($0.2 a_0 = 0.1 \text{ \AA}$) considering that a DZ basis and a very extensive CI was used. It is expected that the major source of the error here is the lack of O 3d functions in the basis. The optimum R calculated (with POL CI) for the other states follow (in bohr): $1^3B_2 = 2.72$, $1^3A_2 = 2.74^\dagger$, $1^1A_2 = 2.75$, $1^3B_1 = 2.73^\dagger$, $1^1B_1 = 2.72$, $2^3B_2 = 2.80$, $2^1A_1 = 2.81$,

$1^1B_2 = 2.82$, $3^1A_1 = 2.83$, $2^1B_1 = 2.82$. These values are expected to be about $0.2a_0$ too large, just as for the ground state.

Using $R = 2.601 a_0$ and a minimum basis set, we calculated the states as a function of angle θ (see column 8 of table 1), leading to optimum angles of:

[†]These numbers are based on GVB CI rather than POL CI.

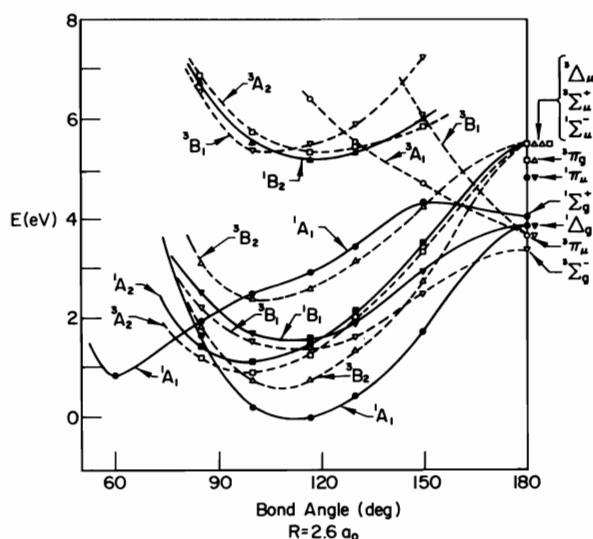


Fig. 1. Potential curves of the lower excited states of ozone. MBS CI using $R_{OO} = 2.601 a_0 \perp$.

$1^1A_1 = 112^\circ$, $1^3B_2 = 110^\circ$, $1^3A_2 = 100^\circ$, $1^1A_2 = 101^\circ$, $1^3B_1 = 114^\circ$, $1^1B_1 = 112^\circ$, $2^3B_2 = 107^\circ$, $2^1A_1 = 60^\circ$, $1^1B_2 = 117^\circ$. The corresponding potential curves are shown in fig. 1. These calculated bond angles are expected to be within about two degrees of the correct values. Calculations were also carried out at $R = 2.74$ and $\theta = 100^\circ$ to obtain adiabatic excitation

energies for the 3^1A_2 states.

The smaller bond angle of the lowest A_2 states as compared with the B_1 states can be understood from an examination of the dominant configurations

$$(6a_1)^2(4b_2)^1(1a_2)^2(2b_1)^1$$

and

$$(6a_1)^1(4b_2)^2(1a_2)^2(2b_1)^1, \quad (3)$$

respectively, since the $6a_1$ orbital is bonding between terminal atoms while $4b_2$ is antibonding.

The adiabatic excitation energies in tables 1 and 2 are obtained from the calculated optimum geometries. However, as mentioned above the MBS and DZ bases yield bond lengths too long by $\approx 0.2 a_0 = 0.1 \text{ \AA}$. Upon adding O 3d basis functions, the calculated bond lengths should decrease to the experimental value. We are now carrying out such studies; indications are that the calculated adiabatic excitation energies will increase.

Using experimental geometry and carrying out GVB CI calculations, we find the following ordering of positive ion states [energies relative to $1^1A_1(4\pi)$]: $2^1A_1(4\pi) = 12.9 \text{ eV}$, $2^3B_2(4\pi) = 13.0 \text{ eV}$, $2^1A_2(3\pi) = 13.5 \text{ eV}$, $2^3B_1(5\pi) = 14.5 \text{ eV}$, $2^1A_2(5\pi) = 15.3 \text{ eV}$, $2^2A_1(4\pi) = 16.6 \text{ eV}$, $2^2B_2(4\pi) = 16.6 \text{ eV}$, $2^3B_1(3\pi) = 16.6 \text{ eV}$. The first ionization potential is in agreement with the experimental value [9] of 12.8 eV. Use of Koopmans theorem leads to the following ion states: $2^1A_2(3\pi) = 13.43 \text{ eV}$, $2^1A_1(4\pi) = 15.28 \text{ eV}$,

Table 2

Best estimates of spectroscopic properties of bound states of ozone. POL CI results used unless otherwise indicated. All energies in eV

State	Excitation energy from ground state		Bond dissociation energy to $O_2(^3\Sigma_g^-) + O(^3P)$	First strong absorption		Lowest vertical ionization potential	
	vertical	adiabatic ^{a)}		upper state	$\Delta E^{c)}$	ion state	ΔE
1^1A_1 4 π	0	0	(1.13) ^{b)}	$1^1B_2(4\pi)$	4.7	$2^1A_1(4\pi)$	12.9
3^3B_2 4 π	1.47	≈ 0.7	≈ 0.4	$2^3A_1(4\pi)^{d)}$	5.8 ^{e)}	$2^1A_2(3\pi)$	≈ 12.8
3^3A_2 5 π	1.80	≈ 0.8	≈ 0.3	$2^1B_1(5\pi)$	4.0 ^{e)}	$2^1A_1(4\pi)$	≈ 12.1
1^1A_2 5 π	1.98	≈ 1.0	≈ 0.1	$2^1B_1(5\pi)$	3.8	$2^1A_1(4\pi)$	≈ 11.9
3^3B_1 5 π	1.74	≈ 1.1	≈ 0.0				

a) Probably lower limits, obtained from table 1 by using various results to predict the POL CI adiabatic excitation energies.

b) Experimental value (corrected for differences in zero point energies); ref. [11].

c) Using calculated optimum R at $\theta = 116.8^\circ$.

d) At the calculated R it is the second 3^3A_1 state that should lead to the strong transition from 1^3B_2 .

e) GVB CI.

${}^2B_2(4\pi) = 15.77$ eV; that is Koopmans theorem leads to energies off by as much as 2.8 eV and to the wrong ordering of the ion states.

4. Discussion

4.1. Bound electronic states

From table 1, columns 8 and 9, we see that there are four excited electronic states with calculated adiabatic excitation energies less than 1.13 eV, the experimental value of the dissociation energy [11][‡]. Thus we expect[†] these states to be bound with respect to dissociation to O_2 and O. All previous studies (see, for example, the extensive review by Johnston [13] and the review by Schiff [14]) of the kinetics and chemistry of oxygen-ozone systems have assumed that

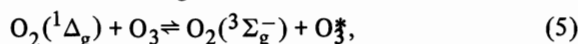


yields only the ground state O_3 . Now we must, in addition, include the possibility of exothermic formation of excited states of ozone (O_3^*) in (4). The excited states have a much weaker O_2 -O bond and hence may lead to much larger reaction rates with various atoms and molecules [some important cases for the lower and upper atmosphere might be the reactions of O_3^* with O, O_3 , O_2 (${}^1\Delta_g$), NO, NO_2 , CO,

[‡]We have taken the bond dissociation energy appropriate for 0° K [$D(O_2 - O) = 1.049$ eV] and corrected for the difference in zero point energies in order to obtain the value [$D_e(O_2 - O) = 1.13$ eV] to be compared with the theoretical results.

[†]The use of an extensive CI in conjunction with an extended basis is expected to lead to quite comparable correlation errors for the various covalent states and should yield adiabatic excitation energies within 0.1 or 0.2 eV. However, the direct calculation of the dissociation energy as $D = E(O_3) - E(O_2) - E(O)$ involves a comparison of very different geometries and can lead to much larger errors (e.g., with POL CI and DZ we calculate $D_e(O-O) = 4.65$ eV for O_2 whereas the experimental value is 5.21 eV). Thus we have calculated the dissociation energies for the excited states of O_3 by subtracting the calculated adiabatic excitation energy from the experimental dissociation energy of the ground state [11]. Wilson and Wahl [12] have recently carried out SOVC calculations (using a comparable basis) on the $X {}^1A_1$ and 3B_2 states of ozone, finding results in reasonable agreement with our GVB CI calculations.

CO_2 , OH, and H_2O]. The lifetime of these excited states (and hence their importance to the chemistry) will depend upon the pressure; for example, they may be very important at pressures of 1 torr while of little consequence at atmospheric pressures. Particularly interesting are the possible energy transfer processes between $O_2({}^1\Delta_g)$ and O_3^*



which can set up an equilibrium between O_3^* and $O_2({}^1\Delta_g)$, strongly affecting, for example, the apparent rate constants one might measure for various species [e.g., O with $O_2({}^1\Delta_g)$]^{☆☆}.

Recent studies on the radiolysis of oxygen have indicated the presence of some new species associated with the formation of ozone [16, 17]. In particular, Riley and Cahill [16] found that a species was formed with a broad absorption peak at about 3.9 eV (obtained by subtraction of the known Hartley absorption from the observed spectrum). This species, which they considered to be a precursor in the formation of ozone, exhibited a lifetime of ≈ 5 μ sec (at atmospheric pressure). The bound excited states 3B_2 and 3,1A_2 are excellent candidates as the ozone precursor. Our estimated excitation energies (see table 2) for the A_2 states are quite consistent with the observed absorption at 3.9 eV.

From these results we assign the Wulf and Chappuis transitions [9, 10] as arising from $1 {}^1B_1(5\pi) \leftarrow 1 {}^1A_1(4\pi)$ [with possible contributions from $1 {}^1A_2(5\pi) \leftarrow 1 {}^1A_1(4\pi)$] and the Hartley and Huggins bands [9, 10] as arising from $1 {}^1B_2(4\pi) \leftarrow 1A_1(4\pi)$.

4.2. The ring state

The $2 {}^1A_1(6\pi)$ state favors a small bond angle of 60°. We previously reported [1] GVB (1) calculations with a DZ basis suggesting that the ring state is about 1.2 eV above the normal open ground state of ozone. We have now carried out POL CI calculations on the ring state (DZ basis), obtaining an energy of -224.44682 h, which is 1.57 eV above the POL CI energy for the ${}^1A_1(4\pi)$ state (using the experimental geometry for ${}^1A_1(4\pi)$ and $R_{OO} = 2.737 a_0$, $\angle OOO = 60^\circ$

^{☆☆}This might for example have affected the rate constants measured by Clark and Wayne [15].

for the ring state[†]).

Some time after our [1] DZ calculations on the ring state were reported, Wright [18] reported two configuration MBS calculations indicating that the ring state might be below the open form and suggested that this ring state might be the ozone precursor observed in oxygen radiolysis experiments [16, 17]. However, we found that large basis sets lead to the ring state about 1.5 eV above the open form, and hence formation of the ring state from O plus O₂ in their ground states should be quite unfavorable [1]. (We do find a ¹E'' state at 4.37 eV above the cyclic ¹A₁ state. Although dipole-forbidden, a weak absorption could be vibronically allowed.) In summary, the theoretical studies indicate that the ring state is not a good candidate for the role of 'ozone precursor'[‡].

5. Summary

We present evidence from extensive CI calculations that the low-lying excited electronic states of O₃ may be bound with respect to dissociation. Although these calculations are among the most extensive ever reported for a molecule, the predicted adiabatic excitation energies (0.7 to 1.0 eV) are sufficiently close to the ground state dissociation energy (1.1 eV) that these calculations cannot be said to provide definitive proof of the existence of bound excited states (they are in any case low-lying). Such definitive proof from theoretical calculations must await the incorporation of 3d basis functions. However, we hope that our current results will stimulate and guide experimental investigations of both the spectroscopy and kinetics of ozone.

[†] $R = 2.737 a_0$ is the optimum value from HF DZ calculations on the ring state.

[‡]Hochandel et al. [17] and Bair [19] suggested that the 'ozone precursor' is just vibrationally excited ozone. However, Riley and Cahill [16] show that the absorption spectrum of the 'precursor' peaks at 0.82 eV below the absorption peak (Hartley band) of ground state ozone and that the spectrum of the precursor does not change with time.

Acknowledgement

We thank Dr. David C. Cartwright for help with the GVB calculations and Dr. I. Shavitt for the use of his CI programs.

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