

THEORETICAL RESULTS FOR THE EXCITED STATES OF OZONE ‡

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Received 4 February 1972

On the basis of ab initio calculations (configuration interaction and generalized valence bond), we find eight excited states of ozone with vertical excitation energies less than 7 eV. Using these results the various experimental transitions are assigned. One state has an equilateral triangle as the minimum energy geometry (1.5 eV above the ground state).

There is only a meager understanding of the excited states of ozone from either experimental knowledge [1, 2] or theoretical calculations. We report here the preliminary results of a series of ab initio calculations on ozone using the generalized valence bond (GVB)†† [3] and configuration interaction (CI) methods††† (using a minimum basis set (MBS) of contracted gaussians) [4] ‡.

We find eight excited states with vertical excitation energies less than 7 eV, as listed in table 1 and illustrated in fig. 1. These states are classified by the number of electrons in π orbitals.

Transitions between states with differing numbers of π electrons should be weak because they correspond

to $n \rightarrow \pi^*$ transitions. Thus, the only strong transition should be ${}^1B_2 \leftarrow {}^1A_1$, which we identify with the Hartley band at 2200–3000 Å. Upon optimizing the bond length, we find that the 1B_2 state drops 1.4 eV, which is about the separation between the bottom of the Huggins band (3.6 eV) and the peak in the Hartley band (4.9 eV). Thus the Huggins band is just the non-vertical part of ${}^1B_2 \leftarrow {}^1A_1$ that leads to too low an energy to dissociate to $O_2({}^1\Delta_g) + O({}^1D)$. Of the other dipole-allowed transitions, the (${}^1B_1 \leftarrow {}^1A_1$) should be weak, as mentioned above, and we identify it with the weak Chappuis band that has peak absorbances at 6020 and 5770 Å. The transition ($2 {}^1A_1 \leftarrow 1 {}^1A_1$) should be extremely weak since it is $6\pi \leftarrow 4\pi$ and hence requires exciting two orbitals (very small components of 6π character get mixed into the $1 {}^1A_1$ wavefunction). It is possible that this transition is responsible for the change in character of the Huggins band at around 3400 Å (Chalonge–Lefèbvre band). Mulliken [6] also assigned the Hartley and Chappuis bands as ${}^1B_2 \leftarrow {}^1A_1$ and ${}^1B_1 \leftarrow {}^1A_1$, respectively.

The ${}^1A_2 \leftarrow {}^1A_1$ transition, although dipole-forbidden, becomes vibronically allowed (for antisymmetric stretch) and should thus correspond to the extremely weak progressions from 6000–10 000 Å in the Wulf band.

Of the triplet states, $1 {}^3B_2 \leftarrow {}^1A_1$ should be strongest since the orbitals correspond closely (both states are 4π). The vertical transition is calculated to

‡ Partially supported by a grant (PF-013) from the President's Fund of the California Institute of Technology.

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‡‡‡ Partially supported by a grant (GP-15423) from the National Science Foundation.

† Contribution No. 4400.

†† In these calculations a single valence bond configuration is used and the orbitals are solved for self-consistently, keeping orbitals in different pairs orthogonal.

††† The configuration interaction started with the GVB wavefunction having three pairs split and included all single and double excitations from these pairs.

‡ Hartree–Fock calculations on ozone have been reported in ref. [5].

Table 1
Excitation energies for the electronic states of ozone (eV)

State	GVB			CI (vert)	Experimental ^{a)}	
	Vert	0-0	R_{\min} (Å)		ΔE	$\epsilon(\text{cm}^{-1})$
$1^1A_1(4\pi)$	—	—	1.35	—	—	—
$1^3B_2(4\pi)$	0.51	0.22	1.38	1.11	1.2 ^{b)}	0.00003 ^{b)}
$^3A_2(5\pi)$	1.04	0.67	1.39	1.79	—	—
$^1A_2(5\pi)$	1.15	0.73	1.38	1.96	1.2–2.0	0.001 ^{b)}
$^3B_1(5\pi)$	—	—	—	2.02	—	—
$^1B_1(5\pi)$	—	—	—	2.24	2.0–2.3	0.055
$2^3B_2(6\pi)$	2.09	1.39	1.40	3.20	—	—
$2^1A_1(6\pi)$	2.26	1.28	1.41	3.50	[3.6–4.1]	[3.3]
$^1B_2(4\pi)$	8.05	6.65	1.44	6.70	4.1–5.6	131.8

a) Refs. [1, 2]; b) ref. [7].

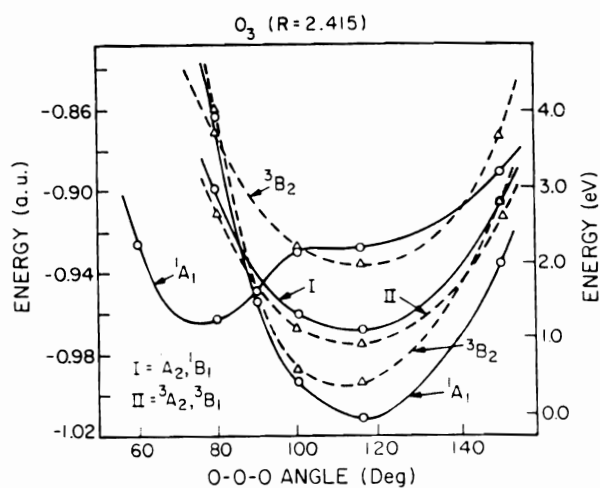
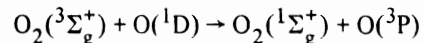


Fig. 1. The energy curves (GVB) for the excited states of ozone. In these calculations the O–O bond length was kept fixed and only the angle varied.

be at 1.11 eV, which is quite close to the 1.2 eV band sometimes considered to be the 0–0 transition of the Wulf band. The 1.2 eV transition is about 30 times weaker ($\epsilon = 0.00003 \text{ cm}^{-1}$) [7] than the stronger vibrational components of the Wulf band and is different in character in that rotational levels are resolved [8]. Thus the 1.2 eV transition may well be the $1^3B_2 \leftarrow 1^1A_1$ transition.

Photochemical evidence for other triplet states

comes from the work of Jones and Wayne [9] who concluded that for $\lambda = 3340 \text{ \AA}$, $O_2(^1\Delta_g \text{ or } ^1\Sigma_g^+) + O(^3P)$ is produced[†]. This process would involve a crossing from the excited singlet state to one of the 5π or 6π triplet states. The extremely rapid reaction [11]



may involve a complex related to an excited state of O_3 . A 5π triplet state is most reasonable, and hence the 3B_1 state should be involved here.

As indicated in table 1, the excited states have increasingly larger bond lengths (with the 1B_2 state having a bond length 0.1 Å longer than the ground state). All states have minima in the region $100^\circ < \theta < 130^\circ$ (θ is the central bond angle) except the 2^1A_1 state^{††}. This state has a minimum for $\theta = 60^\circ$ (that is, an equilateral triangle) with a computed energy

[†] DeMore and Raper [10] established earlier that $O(^3P)$ is produced.

^{††} As shown in fig. 1, the GVB wavefunctions of the 4π and $6\pi A_1$ states cross. We refer to the $4\pi A_1$ state as 1^1A_1 and the 6π state as 2^1A_1 even though 2^1A_1 is the lowest state for $\theta < 90^\circ$. The configuration interaction leads to a weak coupling of these states near $\theta = 90^\circ$ and the CI energy curves split apart ($\approx 0.3 \text{ eV}$) so that the lowest state changes continuously but rapidly from essentially all 4π for $\theta > 90^\circ$ to essentially all 6π for $\theta < 90^\circ$. However, this coupling is small enough that in many dynamic processes what we have labeled as 2^1A_1 and 1^1A_1 should behave as two different weakly coupled states.

1.5 eV† above the 1^1A_1 ground state. The 1^1A_1 and 2^1A_1 curves cross near $\theta = 90^\circ$ with an energy about 2.2 eV above the 1^1A_1 minimum. Since the mixing of these states is very small (splitting about 0.3 eV at the crossing point), they would act as essentially two different states, 1^1A_1 dissociating to $O_2(^3\Sigma_g^-) + O(^3P)$ and 2^1A_1 dissociating to $O_2(^1\Delta_g) + O(^1D)$. It is likely that, once formed, the 2^1A_1 state would be quite long-lived; however, it may be difficult to form this state since the reactants [$O_2(^1\Delta_g) + O(^1D)$] should both be in excited states ††. The resulting ring state of O_3 should be transparent in the visible and near ultraviolet.

Similar ring (small-angle) states are expected for

† This result is obtained from calculations using a larger basis set ($9s5p \rightarrow [4s2p]$). The MBS is biased towards the 60° state (2^1A_1) and places it very nearly equal in energy to the 116° state (1^1A_1). The MBS calculations may also lead to too large a bond length. Hartree-Fock calculations lead to a very poor treatment of the 1^1A_1 (open) state, placing it above the 3B_2 state and (for smaller basis sets) placing it above the 2^1A_1 (ring) state.

†† A possible means of forming and detecting this state would be to place purified ozone (no O_2 or N_2) into a cold matrix (rare gas) and photolyze in the Hartley band (2500 Å). The ozone would decompose into the appropriate states of O_2 and O, and if nothing is around to quench the $O(^1D)$ [such as $O_2(^3\Sigma_g^-)$ or N_2] these states may recombine (occasionally) in the 2^1A_1 state (60°). After collisional stabilization, this state would not absorb in the Hartley band and hence sufficient concentrations might accumulate to detect with infrared absorption.

many other molecules including CO_2 , NO_2 , N_2O , SO_2 , and C_3 .

More extensive calculations using large basis sets with polarization functions are in progress to obtain more quantitative estimates of the bond lengths, angles, and energies of the excited states of ozone.

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