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## Study of Singlet–Triplet Transitions in the Ozone Molecule Using the Multiconfigurational Self-Consistent Field Theory

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**Abstract**—The intensities and dipole moments of the lower singlet–triplet transitions  ${}^3A_2 \leftarrow X^1A_1$  and  ${}^3B_1 \leftarrow X^1A_1$  in the ozone molecule were calculated by the multiconfiguration self-consistent field theory with the quadratic response function. The results of calculations of the intensities of singlet–triplet transitions using different basis sets and complete active spaces were compared. The assignment of the  ${}^3A_2 \leftarrow X^1A_1$  transition in the ozone spectrum to the Wulf band is discussed.

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A wealth of attention has been given in the last years to spectroscopy and photochemistry of ozone, as well as to the reactions of its photocatalytic degradation in the atmosphere. In our studies, we focus on the role of the lower excited triplet states in the absorption spectrum of ozone. Excited triplet states of chemically stable molecules are of interest not only from the standpoint of their spectroscopic and photochemical properties but also for understanding the chemical reactivity of molecules and the phenomenon of spin catalysis [1, 2]. The first excited triplet term  $T_1$  in the ozone molecule always lies below the first excited singlet state  $S_1$  on the energy scale. Therefore, the nonradiative transition  $S_1 \rightarrow T_1$  between the neighboring excited states is more likely than the radiative transition  ${}^1S \rightarrow S_0$  and most excited molecules exist in the metastable triplet state.

The triplet excited states in the  $O_3$  molecule are bonding. A knowledge of the intensity of  $S$ – $T$  transitions is necessary for a deeper understanding of the electronic structure of molecular excited states [3, 4]. In addition, a detailed study of the intensity of  $S$ – $T$  transitions and the role of the lower excited  $T$  states in the absorption spectrum of ozone will make it possible to predict the picture of spin-selective photoprocesses in the recombination and degradation reactions of this molecule, which are the key point in understanding atmospheric photochemistry.

Triplet states have three spin sublevels, which are split even in the absence of an external magnetic field. Each spin sublevel has its own intrinsic probability for radiative transition to the ground  $S_0$  state. The mixing of  $S$  and  $T$  states by spin–orbit coupling is the major factor in the enhancement of spin-forbidden  $S$ – $T$  transitions. Zero field splitting (ZFS) is primarily due to spin–orbit coupling and is determined in part by its anisotropy (in

the second-order perturbation theory). The selectivity of the spin sublevels of  $S$ – $T$  transitions and the ZFS parameters can be obtained from the rotational structure of the gas-phase spectrum [5–7], as well as from ESR spectra in crystals. The vibronic models of  $S$ – $T$  transitions also provide conceptual information on spin-selective processes and about the dependence of spin–orbit coupling on vibrational motion.

Mixed  $S$ – $T$  absorption and the emission spectrum of the ozone molecule were analyzed on the basis of results of ab initio calculations. In this work, we present the probabilities of  $S$ – $T$  transitions to individual spin sublevels as calculated for two lower excited triplet terms of the  $O_3$  molecule by the multiconfiguration self-consistent field (MC SCF) method using the quadratic response theory.

Singlet–triplet transitions in the ozone molecule have been a subject of numerous experimental [5–8] and theoretical [3, 4, 9–14] studies in the last decade. This interest is explained by the fact that the  $T$  states of ozone are involved in the kinetics of the formation and dissociation processes  $O_2 + O \rightleftharpoons O_3$  and, thus, are important for atmospheric chemistry [8, 9, 11, 12].

It should be noted that the electronic structure of the ground state  $X^1A_1$  of the ozone molecule is similar to that of the biradical state in which two unpaired electrons on the outermost oxygen atoms form a weakly bound singlet state [15]. Therefore, the triplet states of ozone have a low energy. The contribution of the biradical structure is considerable and, as such, results in a number of excited triplet biradicals:  ${}^3A_2$ ,  ${}^3B_1$ , and  ${}^3B_2$ . The first two are  $\sigma\pi^*$  in nature, and the last is  $\pi\pi^*$ —an analogue of the ground state. The vertical excitation from the ground state  ${}^3B_2 \leftarrow X^1A_1$  has a lower energy than the vertical transitions to other triplet states  ${}^3A_2$ ,

$^3B_1 \leftarrow X^1A_1$  and  $^3B_2 \leftarrow X^1A_1$ . In view of this, Nordfors et al. [16] tentatively assigned  $^3B_2 \leftarrow X^1A_1$  transitions to weak absorption by the  $O_3$  molecule in the near IR region, the so-called Wulf band. However, semiempirical calculations with allowance for spin–orbit coupling including vibronic perturbation for the deformation mode showed that the  $^3B_2 \leftarrow X^1A_1$  transition is polarized along the  $x$  axis with a relatively low intensity ( $f = 10^{-8}$ ) [16]. Until 1993 [17], the Wulf band had been assigned to the forbidden singlet–singlet transition  $^1A_2 \leftarrow X^1A_1$ . In [10, 11], the possibility that the weak absorption in the near IR region is due to the forbidden  $S$ – $T$  transition  $^3A_2 \leftarrow X^1A_1$  caused by spin–orbit coupling was examined using quantum-chemical calculations. This theoretical prediction was corroborated by experimental data [7]. An analysis of the rovibrational structure of the Wulf band at a relatively high resolution [7] confirms its assignment to the  $S$ – $T$  transition associated with the  $A''$  symmetry ( $^3A_2$  state).

The results of ab initio calculations for this  $S$ – $T$  transition [10, 13] and experimental studies [5–8] agree with the assignment of the  $^3A_2 \leftarrow X^1A_1$  transition in the  $O_3$  absorption spectrum to the Wulf band. A rather weak  $^3B_2 \leftarrow X^1A_1$  transition was also detected among other vibronic bands in the Wulf absorption region [7]. In this work, we calculated the intensities of two lower forbidden singlet–triplet transitions  $^3A_2 \leftarrow X^1A_1$  and  $^3B_2 \leftarrow X^1A_1$  in the ozone molecule and compared the obtained results using different basis sets and complete active spaces (CASs).

## CALCULATION PROCEDURE

The  $S$ – $T$  transition matrix elements were calculated using the full Breit–Pauli spin–orbit operator, including the one- and two-electron expressions [18]. To calculate the probabilities of two types of  $S$ – $T$  transition, we used the cc-pVTZ, 6-311G\*\*, and i6-311++G(3df, 3pd) basis sets. For the irreducible representations  $a_1$ ,  $b_1$ ,  $a_2$ , and  $b_2$  in the symmetry group  $c_{2v}$ , we selected an inactive space (4020) (Table 1), which includes 12 electrons in all complete active spaces. The simplest active space (4331) denoted as CAS-1 gives 53484 determinants for the extension of the ground state. The active space CAS-2 (4332) contains 157016 determinants. In this case, the inclusion of the unoccupied orbital  $a_2$  has a significant effect on results; therefore, the results of calculations using CAS-2 will not be considered further. CAS-3 (4341) and CAS-4 (4342) give 213640 and 736464 determinants, respectively. CAS-5 (5342) includes about two million determinants. Such a large active space requires the 6-311++G(3df, 3pd) basis set, which gives many lower unoccupied orbitals, and the active spaces that we have selected are compatible with smaller basis sets.

**Table 1.** Electron population of orbitals in different complete active spaces

$a_1$	$b_1$	$b_2$	$a_2$	CAS
4	0	2	0	Inactive space
4	3	3	1	CAS-1; 53484
4	3	3	2	CAS-2; 157016
4	3	4	1	CAS-3; 213640
4	3	4	2	CAS-4; 736464

We performed calculations by the quadratic-response MC SCF method with CAS-1 on a greater number of points encompassing a wide range of bending and stretching vibrations. The experimental geometry of the ground state ( $r_{O-O} = 1.278$  Å,  $\angle OOO = 116.8^\circ$ ) of  $O_3$  is reproduced fairly well in all methods. The results of computation of the geometry and vibronic frequencies for three lower triplet states of ozone agree well with published data [4].

Note that the ground-state term of the ozone molecule is predissociative in character and has an open shell. Therefore, the Hartree–Fock method cannot be used in calculations on ozone, and the results of calculation by the quadratic-response MC SCF method depend to a considerable extent on the CAS and basis set selected.

## RESULTS AND DISCUSSION

The moments and intensities of the lower vertical transition  $^3A_2 \leftarrow X^1A_1$  as given below were calculated with the use of different CASs and basis sets. Let us begin an analysis of the calculation results from the  $^3A_2 \leftarrow X^1A_1$  transition, since the  $^3A_2$  state relates to the most important excited triplet term that determines in most part the intensity of the Wulf band. Therefore, the intensity of the vertical transition  $^3A_2 \leftarrow X^1A_1$  in the ozone molecule should correspond to a maximum in the bending progression ( $2_0^2$  band). This long progression covering the spectral region from 9500 to 15000  $\text{cm}^{-1}$  was analyzed by Anderson and Mauersber [8] and its assignment was confirmed by means of high-resolution spectroscopy [5–7]. An analysis of the cross sections of the least broadened rotational lines gave a value of 0.2 picoseconds for the radiative lifetime [7]. This implies that all upper vibronic levels are predissociative and the effective lifetime of the  $^3A_2$  state must be much shorter.

An analysis of the data presented in Table 2 shows a significant dependence of the results of MC SCF calculations on the selected CAS and basis set. For example, the energy change during the  $^3A_2 \leftarrow X^1A_1$  transition is in the range of 1.1–1.9 eV. Other methods [7] gives the energy difference within 1.6–2 eV; however, the relative intensities of  $S$ – $T$  transitions to different spin sub-

**Table 2.** Intensities of vertical transition  ${}^3A_2 \leftarrow X^1A_1$  in ozone molecule as calculated using different basis sets

Method, basis set	$\Delta E$	$M_y(T^y)$	$M_x(T^x)$	$M_z(T^z)$	$K_y$	$K_x$	$K_z$	$\tau$	$f \times 10^{-7}$
CAS-1 6-311G*	1.43	0.00192	-0.00024	0.00135	11.50	0.19	5.69	0.06	1.96
CAS-1 cc-pVTZ	1.17	0.00138	-0.00029	0.00361	3.22	0.14	21.85	0.04	4.28
CAS-1 6-311++G (3df, 3pd)	1.05	0.00230	-0.00025	0.00135	10.88	0.19	5.45	0.06	1.91
CAS-3 6-311G*	1.91	0.00684	-0.00005	0.000158	344.8	0.02	0.18	0.00	21.9
CAS-3 cc-pVTZ	1.92	0.01269	-0.00015	0.000088	1205	0.17	0.05	0.001	75.7
CAS-4 cc-pVTZ	1.89	0.00432	-0.00023	0.00011	133.7	0.37	0.09	0.007	8.67

Note:  $\Delta E$  in eV is the transition energy;  $M_i(T^j)$  in a.u. is the transition moment along the axis  $i$  to spin sublevels;  $i, j = x, y, z$ ;  $K_i$  in  $s^{-1}$  are the Einstein coefficients of spontaneous emission polarized along the  $i$ th axis ( $i = x, y, z$ );  $\tau$  is the radiative lifetime of the corresponding excited state, in s; and  $f$  is the oscillator strength of  $S \rightarrow T$  transition.  $f$ ,  $K_i$ , and  $\tau$  were calculated without consideration for the Franck-Condon factors.

**Table 3.** Intensities of vertical transition  ${}^3A_2 \leftarrow X^1A_1$  in ozone molecule as calculated using different basis sets at different bond angles

Method, basis set	$\Delta E$	$\angle OOO$	$M_y(T^y)$	$M_x(T^x)$	$M_z(T^z)$	$K_y$	$K_x$	$K_z$	$\tau$	$f \times 10^{-7}$
CAS-1 6-311G*	1.07	110°	0.002107	-0.00026	0.00076	5.86	0.09	0.77	0.15	1.34
CAS-1 cc-pVTZ	0.96	110°	0.000655	-0.00026	0.00128	0.40	0.06	1.52	0.49	0.50
CAS-1 6-311G*	1.31	115°	0.00228	-0.00025	0.00078	12.42	0.15	1.47	0.07	1.89
CAS-1 cc-pVTZ	1.16	115°	0.000429	-0.00027	0.00153	0.31	0.13	3.91	0.23	0.74
CAS-1 6-311G*	1.50	120°	0.00243	-0.00021	0.00082	21.42	0.16	2.47	0.04	2.44
CAS-1 cc-pVTZ	1.32	120°	0.00011	-0.00028	0.00197	0.03	0.19	9.49	0.10	1.29
CAS-1 6-311G*	1.82	130°	0.002603	-0.00076	0.00084	43.52	3.76	4.59	0.02	8.11
CAS-1 cc-pVTZ	1.51	130°	0.002778	-0.00025	0.00359	28.49	0.23	47.72	0.10	7.67

Note:  $R_{O-O} = 1.3 \text{ \AA}$  was selected as a fixed value corresponding to the  $r$ -centroid.

levels agree well with one another. The most important quantity is the moment  $M_y$  of the  ${}^3A_2 \leftarrow X^1A_1$  transition to the  $T^y$  spin sublevel, which is about 0.0043 a.u. in CAS-4 (Table 2); in CAS-1 and CAS-3, this value is substantially different. Calculation in CAS-1 give a somewhat underestimated and those in CAS-3 give a considerably overestimated value of the transition moment. To reproduce the cross section of the Wulf absorption band, Braunstein and Pack [3] fitted the dipole transition moment to a value of 0.0047 a. u., which agrees with the value calculated in CAS-4 (Table 2). Note that the measured cross section of the least broadened rotational lines at a sufficiently high resolution [5–7] give a somewhat smaller value of the transition moment than we calculated using the cc-pVTZ basis set (CAS-4). Thus, the results of MC SCF calculations are reliable enough, although an analysis of the  $M_z(T^z)$  component of the  ${}^3A_2 \leftarrow X^1A_1$  transition moment, which is of great importance in CAS-1 (Table 2), points to a drawback in quadratic-response MC SCF calculations. The  $M_y(T^y)/M_z(T^z)$  ratio is 0.37 with the cc-pVTZ basis set, whereas the analysis of rotational lines by Bouvier et al. [7], Anderson and Mauersber [8], Minaev and Bilan [9] gives a value close to 10.

The  ${}^3B_2 \leftarrow X^1A_1$  transition turns out to be very weak, a finding that agrees with the data reported in [10, 13] and experimental results [5–8]. The  $M_x(T^x)$  component of the moment of this transition turned to be stronger than  $M_z(T^z)$ , namely,  $M_x(T^x) = 1.6 \times 10^{-4}$  a.u. for the vertical excitation  ${}^3B_2 \leftarrow X^1A_1$  in CAS-4 with the cc-pVTZ basis set while  $M_z(T^z) = 2 \times 10^{-6}$  a.u. Similar results were obtained using other calculation methods.

Based on the results of calculations, it may be concluded that the  ${}^3A_2 \leftarrow X^1A_1$  and  ${}^3B_1 \leftarrow X^1A_1$  absorption bands of  $O_3$  are rather intense and the Wulf system of absorption bands should be assigned exclusively to these two transitions [7], with the  ${}^3A_2 \leftarrow X^1A_1$  transition contributing mainly to the long-wavelength region of the Wulf absorption band.

We studied the dependence of the moments of two lower  $S \rightarrow T$  transitions on the angle  $\angle OOO$  (Tables 3, 4) in view of a large change in the equilibrium angle upon excitation (from  $-18^\circ$  for  ${}^3A_2$  to  $+7^\circ$  for  ${}^3B_1$  states). To obtain the intensity of the  ${}^3A_2 \leftarrow X^1A_1$  transition in the  $\omega_2$  bending progression (with a change in frequency

**Table 4.** Intensities of vertical transition  ${}^3B_1 \leftarrow X^1A_1$  in ozone molecule as calculated using different basis sets at different bond angles

Method, basis set	$\Delta E$	$\angle OOO$	$M_z(T^y)$	$M_y(T^z)$	$K_z$	$K_y$	$\tau$	$f \times 10^{-7}$
CAS-3 6-311G*	1.86	110°	0.00067	0.00329	3.09	73.72	0.01	5.14
CAS-1 6-311G*	1.78	110°	0.00076	0.00151	3.47	13.75	0.06	1.21
CAS-1 cc-pVTZ	1.80	110°	0.000679	0.00039	2.87	0.95	0.26	0.27
CAS-1 6-311G*	1.64	115°	0.000716	0.00123	2.40	7.2	0.10	0.82
CAS-1 cc-pVTZ	1.65	115°	0.000654	0.00053	2.07	1.37	0.29	0.29
CAS-1 6-311G*	1.48	120°	0.00066	0.00096	1.51	3.21	0.21	1.11
CAS-1 cc-pVTZ	1.49	120°	0.00062	0.00091	1.36	2.95	0.23	0.97
CAS-1 6-311G*	1.12	130°	0.000484	0.00043	0.35	0.28	1.59	0.26
CAS-1 cc-pVTZ	1.13	130°	0.000498	0.00213	0.37	6.91	0.14	1.33

Note:  $R_{O-O} = 1.3 \text{ \AA}$  was selected as a fixed value corresponding to the  $r$ -centroid.

from  $705 \text{ cm}^{-1}$  in the ground state to  $530 \text{ cm}^{-1}$  in the  ${}^3A_2$  state and the corresponding increase in the bond length from  $1.278$  to  $1.345 \text{ \AA}$ , we used an intermediate value of length,  $r_{O-O} = 1.3 \text{ \AA}$ , in the  $r$ -centroid qualitative approximation. The results presented in Table 3 and 4 show that the outcome of MC CSF calculations depends on the choice of CAS and a basis set; e.g., as the  $M_y(T^z)$  value for the  ${}^3B_1 \leftarrow X^1A_1$  transition at an angle  $\angle OOO = 110^\circ$  (Table 4). Similar results were obtained for the important  $M_y(T^y)$  component of the  ${}^3A_2 \leftarrow X^1A_1$  transition, they substantially differ at different angles ( $110^\circ$ ,  $115^\circ$ ,  $120^\circ$ ) in quadratic response MC SCF calculations. Furthermore, the  $M_y(T^y)/M_z(T^z)$  ratio obtained by the MC SCF method differs for the 6-311G\* and cc-pVTZ basis sets (Table 3), wherein the latter set gives erroneous results as follows from analysis of the rotational spectrum [5–7]. The  $M_y(T^y)/M_z(T^z)$  value in the 6-311G\* basis set is 3, which differs insignificantly from the experimental value [7]. The rotational analysis of the vibronic bands  $0_0^0$ ,  $2_1^1$ , and  $2_0^1$  [5–7] shows that the  $M_y(T^y)/M_z(T^z)$  ratio increases with an increase in the bond angle, namely from 6.4 at  $\angle OOO = 110^\circ$  to 14.7 at  $\angle OOO = 120^\circ$  (Table 3).

To summarize, the complex molecule of  $O_3$  and its  $S$ – $T$  absorption spectrum are reproduced well using the MC SCF theory with the 6-3111G\* basis set. This method also describes well the permanent dipole moment of the ground-state molecule, giving a value of  $0.60 \text{ D}$  in good agreement with the experimental value  $0.53 \text{ D}$ . The intensities of two lower  $S$ – $T$  transitions in the ozone molecule as obtained by MC SCF calculation using the 6-311G\* basis set also agree with experimental results. Our calculations confirm the assignment of the Wulf weak absorption band in the ozone spectrum primarily to the  ${}^3A_2 \leftarrow X^1A_1$  transition, suggesting that this transition determines to a great extent the band intensity and makes a main contribution to its long-wavelength part.

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