

ENERGIES AND DIPOLE MOMENTS OF EXCITED STATES OF OZONE AND OZONE RADICAL CATION USING FOCK SPACE MULTIREFERENCE COUPLED-CLUSTER ANALYTICAL RESPONSE APPROACH

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Dedicated to Professors Petr Čársky, Ivan Hubač and Miroslav Urban on the occasion of their 60th birthdays.

Using the Fock space multireference coupled-cluster (FS-MRCC) analytical linear response approach, we report the dipole moments of low-lying singlet and triplet excited states of ozone. The low-lying singlet and triplet excited states are calculated at the ground-state geometry and at the adiabatic geometry for the 1A_2 and 1B_1 . For comparison we also calculate at the ground-state geometry the dipole moments of the 1A_2 , 1B_1 and 1B_2 using multireference configuration interaction (MRCI) with a bigger VQZ basis and complete active space. We also report as by-product the excitation energy values in the singles and doubles approximation. At the ground-state geometry we also report the energy and the dipole moments of the 2A_1 , 2A_2 and 2B_1 states of the ozone radical cation. The energy of the ozone cation radical is compared with the other correlated approaches. It matches well with the experimental values.

Keywords: Fock space; Multireference coupled cluster; Effective Hamiltonian; Excited states; Linear response.

The evaluation of molecular properties requires more accurate description of the wave function. The coupled-cluster response approach is the ideal method to calculate them. The linear response formalism in the single-reference coupled-cluster (SRCC) framework was proposed by Monkhorst¹ and independently by Mukherjee and Mukherjee². The application of the linear response has been extensively proven by the state-of-art calculation of the SAC-CI method of Nakatsuji and co-workers³ and the equation-of-motion (EOM) approaches of Bartlett and co-workers⁴ and, in particular,

by higher-order response properties by Jorgensen and co-workers⁵. All these methods are in the non-variational framework. The response approach in the variational and bivariational approach has been pursued by Pal and co-workers⁶. In particular, bivariational approach provides fully extensive properties of any order. Analytical linear response approach in the Fock space MRCC approach has been proposed by Pal⁷ and extended for the dynamic properties by Ajitha and Pal⁸. Slightly different response approach for the dynamic properties has been proposed and implemented by Ten-no *et al.*⁹ The linear response approach in the multireference Hilbert space approach has been applied by Bartlett and co-workers¹⁰ and Paldus and co-workers¹¹. Recently a new efficient response formalism in the Hilbert space framework was proposed by Shamasundar and Pal¹². The applications of the multireference response approach to the molecular properties is very limited. Recently Ajitha *et al.*¹³⁻¹⁶ have implemented the analytical linear-response approach in the Fock space multireference coupled-cluster (FSMRCC) framework^{7,17}. Stanton and Gauss¹⁸ have developed the gradient based on the expansion of the similarity-transformed Hamiltonian for the ionization potential. Analytical gradients using the SAC-CI has also been extensively developed and applied by Nakatsuji and co-workers¹⁹. In the present response approach, described in the paper, solution of the effective Hamiltonian and the response of the effective Hamiltonian are obtained using the Fock space method, which involves diagonalization of effective Hamiltonian obtained normally by the Bloch equation. The effective Hamiltonian can also be obtained by similarity transformation, as shown by Meissner and Bartlett²⁰, and Nooijen and Bartlett²¹. Nooijen and Bartlett²¹ have developed a similarity-transformed EOM-CC method. As the subset of the response of the excited states, we also have the response of the ground and excited states of open-shell radical cations and open-shell radical anions. It is pertinent to mention that in the FSMRCC approach the wave operator is valence-universal and in this approach the energy values of the states of interest are obtained *via* an effective Hamiltonian approach. In the analytical linear response approach, the response of the Bloch-effective Hamiltonian equation is solved in a self-consistent manner. Below we report the dipole moment of the singlet excited state of ozone and as a subset we also calculate the vertical and adiabatic excitation energy of ozone corrected with the inclusion of three-body terms of the similarity transformed Hamiltonian in the Bloch equation. We have chosen three active holes and one active particle in the model space. A brief review of valence-universal analytical linear response approach and computational details are described in the following Section.

THEORY: ANALYTICAL RESPONSE IN THE FOCK SPACE (1,1) SECTOR

Model Space

We construct the model space considering the closed-shell RHF state as the reference vacuum. We define the active orbitals as active holes and active particles with respect to the chosen RHF vacuum. The model space for the (m,n) sector consists of all determinants with m active particles and n active holes and is called the complete model space. The complete model space choice is prone to the intruder state problem leading to difficulties in obtaining the eigenvalues of the effective Hamiltonian. It has been proposed by Mukherjee and co-workers²² that for the (1,1) sector one can consider only determinants with one active particle and one active hole and the connectivity of the effective Hamiltonian is ensured if the vacuum lies outside the model space. Pal *et al.*¹⁷ have implemented this approach of using incomplete model space for the calculation of low-lying excitation energies. The model space can be considered sufficient for the low-lying states of interest. Although this is not a complete model space, it may be considered as a special type of incomplete model space. It has been shown that the model space is complete with respect to a single vacancy in the active holes and single occupancy in the active particles. It has been shown by Pal *et al.*¹⁷ that the final equations for the wave operator and the effective Hamiltonian correspond to those of the complete model space in a diagrammatic manner. The model space can be written as the combination of the chosen determinants as follows.

$$\Psi_{\mu(1,1)}^{(0)} = \sum_{ia} C_i^a \Phi_i^a, \quad (1)$$

where the summation over i spans the active holes subset a_h , and summation over a spans the active particle subset a_p

$$\Psi_{\mu(1,1)} = \Omega_{(1,1)} \Psi_{\mu(1,1)}^{(0)}. \quad (2)$$

$\Omega_{(1,1)}$, the wave operator, is valence-universal in the Fock space and is given by

$$\Omega_{(1,1)} = \{\exp(T_{(1,1)})\}. \quad (3)$$

$T_{(1,1)}$ is the cluster operator for the Fock space sector (1,1). $T_{(1,1)}$ is the cluster operator that can destroy the active holes and particles present in the model space followed by hole-particle creations depending on the rank of the cluster operator. $T_{(1,1)}$ may be decomposed as operators destroying different active holes and particles in the model space and thus may be written as

$$T_{(1,1)} = T_{(0,0)} + T_{(0,1)} + T_{(1,0)} + T_{(1,1)} \quad (4)$$

The $T_{(0,0)}$ operator is the normal hole-particle creation operator as used in SRCC theory. The $T_{(0,1)}$, $T_{(1,0)}$ and $T_{(1,1)}$ operators destroy exactly one active hole, one active particle and one pair of active hole-particle respectively. These amplitudes can be approximated to specific truncation. Specifically, we have used singles and doubles approximation.

It is pertinent to note that it is required that the Hartree-Fock determinant lies outside the model space of the single particle-hole excited determinants. Thus the wave operator contains the de-excitation operator $T_{(1,1)}$, which destroys exactly one active hole and one active particle and takes the p-h model space to the HF determinant.

In order to solve the Bloch equation for the (1,1) sector, the following set of equations is solved hierarchically.

$$\begin{aligned} P_{(k,l)}[H\Omega - \Omega H_{\text{eff}}]P_{(k,l)} &= 0 \quad \forall k,l = 0,1 \\ Q_{(k,l)}[H\Omega - \Omega H_{\text{eff}}]P_{(k,l)} &= 0 \quad \forall k,l = 0,1, \end{aligned} \quad (5)$$

where P is the projection operator onto the model space and Q is the specific operator that brings out the projection of the complement of P in the virtual space. The solution of (0,1) and (1,0) Fock space sector leads to the energies of ionized and electron attached states. The p-h model space is an incomplete model space. Mukherjee²² has shown that for such a model space, the linked nature of the effective Hamiltonian and the cluster operators can be ensured by abandoning the requirement of intermediate normalization, *i.e.*,

$$P_{(1,1)}\Omega P_{(1,1)} \neq P_{(1,1)} \quad (6)$$

Thus the P space equation is modified. In general for a (k,l) model space, this manifests as

$$P_{(k,l)}(H\Omega)_{c(k,l)}P_{(k,l)} = P_{(k,l)}(\Omega H_{\text{eff}})_{c(k,l)}P_{(k,l)} + P_{(k,l)}(\Omega\tilde{H}_{\text{eff}(k,l)})_c - P_{(k,l)}(\Omega H_{\text{eff}})_{c(k,l)}P_{(k,l)}, \quad (7)$$

where $H_{\text{eff}(k,l)}$ and $\Omega\tilde{H}_{\text{eff}(k,l)}$ have the same definitions as $T_{\sim(k,l)}$ with the lower valence subsumed. For (1,1) model space, however, there are simplifications, which lead to equations similar to the ones for the complete model space case

$$P_{(k,l)}(H\Omega)_{c(k,l)}P_{(k,l)} = P_{(k,l)}(\Omega H_{\text{eff}})_{c(k,l)}P_{(k,l)}. \quad (8)$$

Equation (7) indicates that the part $(\Omega\tilde{H}_{\text{eff}(k,l)})_c$ appearing on the right hand side must be connected. The nonvanishing scattering $P_{(1,1)}$ to $P_{(1,1)}$ could appear only from the product of $T_{1(0,0)}$ and $T_{1(1,1)}$. However, since $T_{1(0,0)}$ has lines only at the top of the vertex, it is not possible to form connected $P_{(1,1)}T_{1(0,0)}T_{1(1,1)}P_{(1,1)}$ component and thus the equations for the specific (1,1) model space are similar to the case where IN is valid (complete model space).

Since the model eigenfunctions (eigenfunctions of H_{eff}) and the exact functions obtained by the action of Ω on the model eigenfunctions are of the same spin, the operator S is spin scalar. Thus it is easy to adapt the equations to the proper spin. H_{eff} for the p-h problem is constructed by classifying the diagram as “forward” (direct) and “backward” (exchange) associated with the factors corresponding to singlet and triplet EEs respectively.

The effective Hamiltonians for the singlet excited states and the triplet states are given as

$$\begin{aligned} (H_{\text{effEE}})^S_{(ia,jb)} &= ([H_{\text{eff}(0,1)}]_{ij}\delta_{ab} + [H_{\text{eff}(1,0)}]_{ba}\delta_{ij} - \\ &\quad 2\langle ib|H_{\text{effD}(1,1)}|aj\rangle + \langle ib|H_{\text{effE}(1,1)}|ja\rangle) \\ (H_{\text{effEE}})^T_{(ia,jb)} &= ([H_{\text{eff}(0,1)}]_{ij}\delta_{ab} + [H_{\text{eff}(1,0)}]_{ba}\delta_{ij} + \\ &\quad \langle ib|H_{\text{effE}(1,1)}|ja\rangle), \end{aligned} \quad (9)$$

where H_{effD} and H_{effE} refer to the direct and exchange parts of H_{eff} , respectively.

RESPONSE EQUATIONS

The response equations are solved using the approach suggested by Pal⁷. The effective Hamiltonian is expanded as a Taylor series in terms of field strength and the response equations for the Fock space sectors are obtained as the derivatives of the Bloch equation. The subsystem embedding condition strategy, adopted for the stepwise solution of the unperturbed Bloch equation, is also used to solve the response equations. While solving the response equations and the field-perturbed amplitudes, the unperturbed amplitudes are kept fixed. This approach also neglects the orbital relaxation in the presence of field perturbation. The response equations for the (1,1) sector are given as

$$P_{(k,l)} \partial / \partial g [(H\Omega)_{c(k,l)}] P_{(k,l)} = P_{(k,l)} \partial / \partial g [(H_{\text{eff}})_{c(k,l)}] P_{(k,l)} \quad \forall k,l = 0,1 \quad (10a)$$

$$Q_{(k,l)} [\partial / \partial g (H\Omega)_{c(k,l)}] P_{(k,l)} = Q_{(k,l)} [\partial / \partial g (\Omega H_{\text{eff}})_{c(k,l)}] P_{(k,l)} \quad \forall k,l = 0,1. \quad (10b)$$

While solving the above equations, the amplitudes and the response of the amplitudes for the lower-valence sectors are kept frozen. Finally, the derivative of the effective Hamiltonian is constructed. The effective Hamiltonian derivative equations for the spin-integrated forms can be written for singlet and triplet states, respectively:

$$\begin{aligned} \partial / \partial g (H_{\text{eff(EE)}} S_{(ia,jb)}) = \partial / \partial g ([H_{\text{eff(0,1)}}]_{ij} \delta_{ab} + [H_{\text{eff(1,0)}}]_{ba} \delta_{ij} - \\ 2\langle ib | H_{\text{eff(1,1)}} | aj \rangle + \langle ib | H_{\text{eff(1,1)}} | ja \rangle) \end{aligned} \quad (11a)$$

$$\begin{aligned} \partial / \partial g (H_{\text{eff(EE)}} T_{(ia,jb)}) = \partial / \partial g ([H_{\text{eff(0,1)}}]_{ij} \delta_{ab} + [H_{\text{eff(1,0)}}]_{ba} \delta_{ij} + \\ \langle ib | H_{\text{eff(1,1)}} | ja \rangle), \end{aligned} \quad (11b)$$

where H_{effD} is the direct part and H_{effE} is the exchange part of the (1,1) sector. In the construction of H_{eff} , if we drop the closed part, we obtain the singlet and triplet EE directly on diagonalizing the $H_{\text{eff(1,1)}}$ for the singlet and triplet, respectively. The derivatives are obtained by the solution of the derivative eigenvalue equation of $H_{\text{eff(1,1)}}$.

COMPUTATIONAL DETAILS

The singles and doubles approximation of the coupled-cluster amplitudes is adopted in what is known as the MRCCSD scheme. For notational simplicity, we denote the single-similarity transformation of the electronic Hamiltonian [$\exp(-T_{(0,0)})\bar{H}\exp(T_{(0,0)})$] as \bar{H} . To construct the valence-universal wave operator Ω , \bar{H} is contracted further with amplitudes of different sectors as required by equations. In a singles and doubles truncation scheme, \bar{H} , in general, can have at most four-body open parts. However, for the FSMRCCSD equations, only up to three-body parts of \bar{H} are needed. In the earlier applications of MRCCSD for excitation energies by Pal *et al.*¹⁰, only one- and two-body parts of \bar{H} were included. In this work full \bar{H} and derivative \bar{H} containing one-, two- and three-body parts are considered. The solution of the effective Hamiltonian is obtained by diagonalizing the effective Hamiltonian, which is a double-similarity transformation of the electronic Hamiltonian. The applications of the analytical FSMRCC response approach to evaluate the dipole moments of open-shell radicals were reported by Ajitha *et al.*¹³ and Ajitha and Pal¹⁴⁻¹⁶. In the diagrammatic language, for the (1,1) sector, the Goldstone diagrams for the direct and exchange blocks of effective Hamiltonian and the terms contributing to the Bloch equations are constructed. Only two-body contribution of $T_{(1,1)}$ will be considered since the $T_{1(1,1)}$ operator does not contribute to $H_{\text{eff}(1,1)}$ or to the equation for the $T_{2(1,1)}$ amplitudes. The derivative evaluation follows similar strategy of construction. However, it is pertinent to note here that the derivative \bar{H} is constructed first for one-hole one-particle sector and all lower sectors. The storage of the one- and two-body parts of \bar{H} is less costly. Three-body contribution to \bar{H} in the singles and double approximation comes *via* the contribution to the equations determining the one valence amplitudes and the response of these. The storage of three-body \bar{H} is costly and hence it is not stored, but computed directly.

RESULTS AND DISCUSSION

Ozone has obvious importance in the environmental and the chemical fields of interest and this molecule has also been used in calibrating theoretical methods. It has been realized in the literature that high-level theoretical methods, like CCSD (T) and a very high-level basis are required for the molecular properties of ozone to be in quantitative agreement with experiment. The ground-state dipole moment has been seen to be very close to the experiment only when the cc-pVQZ basis is used at the MRCI level. Theoretical study of excited as well as electron-attached states of ozone has

been of recent interest²³. Many low-lying excited states of ozone have been probed recently by Arnold *et al.*²⁴ They have observed five low-lying states 3A_2 , 3B_2 , 3B_1 , 1A_2 , and 1B_1 below 3 eV. The only symmetry-allowed transition is from the ground 1A_1 to 1B_1 state and the transition to 1A_2 is vibronically allowed. The remaining low-lying states are triplet states. The vertical ionization leading to several low-lying states of ozone cation radical have been probed by many multi-reference approaches and we report some of them for the equilibrium ground-state geometry. EOM CC approach has also been used by Nooijen to study the cationic states of ozone²⁵. FSMRCC has also been used earlier by Vaval and Pal²⁶ for calculation of excitation energies with only one- and two-body parts of \bar{H} . In this paper, we present the vertical as well as adiabatic excitation energies with three-body parts of \bar{H} . FSMRCC response is used for presenting the dipole moments of excited states of ozone. We also report the ionization of ozone at several geometries corresponding to different O–O distances and O–O–O angles to give a rough idea of the ionization surface of ozone. For convenience, we have chosen as examples geometries of adiabatic excited states. In this paper, all geometries used are the experimentally known geometries of the relevant states. In the following, we now discuss the different sets of results.

Excitation Energies and Dipole Moments of Vertical Excited States of Ozone

The results of the vertical excitation energies are presented in Table I, which also contains comparative theoretical and experimental values. MRCI optimized geometry and DZP basis set were used for calculation. For the ground-state geometry, MRCI optimization yields O–O bond length 1.271 Å and the O–O–O bond angle 116.09°. We have used the C_{2v} geometry and chosen the configuration [core] $3a_1^2 2b_2^2 4a_1^2 5a_1^2 3b_2^2 1b_2^2 4b_2^2 6a_1^2 1a_2^2$ as the RHF vacuum. Three holes and one particle are considered active for the calculation of excited states dominated by single hole-particle determinants. We have chosen $4b_2$, $6a_1$ and $1a_2$ orbitals as active holes and $1b_1$ orbital as the active particle. All the low-lying excited states of ozone described here are dominated by single excitation from one of the three active holes to the active particle. The vertical excitation energy values reported here are compared with experimental and other theoretical numbers at the DZP basis. Out of the six states reported, five states are in the lower than 3 eV region. The lowest one is the 3B_2 state; the ordering of states is the same as reported with the earlier FSMRCC calculations with the slightly different geometry and without the inclusion of the three-body contribu-

tion of the similarity transformed Hamiltonian. 1A_2 and 1B_1 are the low-lying singlet states. In comparison with the previous FSMRCC calculations of Vaval and Pal²⁶, the present results agree better with the experimental values for 1A_2 and 1B_2 states. For the 1A_2 state, the earlier FSMRCC calculations without three-body effects in \bar{H} report 1.87 eV²⁶. MRMP calculations at a bigger basis report 1.88 eV. POL-CI values are much off from the experimental value of 1.6 eV and the result from the present case at 1.58 eV is the closest theoretical value reported for this state. For the 1B_2 state, the present calculation gives 5.13 eV corresponding to 5.32 eV without three-body effects²⁶ and thus is better in comparison with the experimental value of 4.86 eV. However, for the 1B_1 state, the value is 1.71 eV in comparison with experimental value of 2.1 eV suggesting that the 1B_1 state is very sensitive to a slight change in the geometry. These excitation energy values are obtained as the by-product of the response calculations. The excitation amplitudes are fixed while the response of the effective Hamiltonian is evaluated with respect to the field perturbation. The dipole moments of only the singlet vertical-excited states *via* the FSMRCC response approach are also reported in Table I. There are no experimental values available for the dipole moments of the excited state. The dipole moment calculated *via* the MRCI in the VQZ basis with CAS (6orb, 8e) is reported. The magnitude of the dipole moment is less than 0.2 D for the excited states in the FSMRCC approach and differs very much from the MRCI approach where the dipole moment values are obtained *via* the expectation value approach. The differ-

TABLE I

Dipole moments and excitation energies of the low-lying excited states of ozone using FSMRCC with the three-body similarity-transformed Hamiltonian terms included in the effective Hamiltonian at the singles and doubles approximation at the equilibrium geometry

State	Excitation energy, eV			Dipole moment, D	
	MRCC	POL-CI	Experiment	FSMRCC	MRCI
1A_2	1.58	2.34	1.6	0.105	0.296
1B_1	1.71	2.41	2.1	0.218	-0.040
1B_2	5.13	6.12	4.86	0.041	0.475
3A_2	1.36	2.09			
3B_1	1.26	2.01			
3B_2	0.80	1.60			

ences suggest that the level of basis set is more crucial for molecular properties than for energetics and the role of non-dynamic correlation is observed to be substantial for the case of the dipole moment as the ground-state dipole of the MRCI is close to experiment and the dipole moment at the CCSD in the single reference with the DZP basis differs drastically from experiment. It is pertinent to mention here that these results also include the three-body terms of similarity-transformed electronic Hamiltonian ($\exp -T_{(0,0)} H \exp T_{(0,0)}$). We note that the energy obtained with the MRCC method at the DZP basis is lower than the MRCI at the VQZ basis suggesting the role of dynamic correlation recovered by the MRCC. We report the total energy of the states at the MRCC and MRCI levels at the equilibrium geometry.

Vertical Ionization Energies of 1A_1 State and Dipole Moments of Vertically Ionized $^2A_1, ^2A_2, ^2B_2$ States of Ozone Cation Radical

The FSMRCC theory provides the results at the lower FS sectors. Hence, in calculating the vertical EE of the model space of the (1,1) sector, we also obtain the one-valence hole and one-valence particle results. Valence hole results correspond to the ionized states and valence particle results give the electron-attached states. The ionized results are of interest. Thus, we also report ionization energies in this paper to produce three vertically ionized states $^2A_1, ^2B_2, ^2A_2$ at the equilibrium geometry of the ground 1A_1 state of ozone. These are compared with earlier FSMRCC results without the three-body effects in \bar{H} , results from propagator calculation as well as with experimental results. These are presented in Table II. The agreement of the results with the experimental results is satisfactory, considering that the basis set is not extensive. Experimental values are slightly larger than the FSMRCC results, while there is no fixed trend with the propagator values. The responses of the ionized states are also reported as the by-product in Table II. They reflect the dipole of the low-lying states of the ozone cation radical.

Adiabatic Singlet Excited States 1A_2 and 1B_1 and Dipole Moments

We report in this subsection the EE and dipole moments for the adiabatic singlet excited states 1A_2 and 1B_1 (Table III). For the description of adiabatic excited states, the corresponding experimental geometry of the excited state 1A_2 and 1B_1 is used. At these experimental geometries, the dynamic and non-dynamic correlation are evaluated by the FSMRCC approach and

thus the total energy of the state of interest is calculated. The energy of the ground state is subtracted to get the adiabatic excitation energy and thus, for each state, a set of calculations have to be carried out. For adiabatic calculations, thus the advantage of evaluation of direct excitation energies of several states in one single calculation is lost.

Vertical Ionization Energies of 1A_1 and 1A_2 and 1B_2 and Dipole Moments of 2A_1 , 2A_2 , 2B_2 at Different Geometries

We report in this subsection the vertical ionization energies of 1A_1 and 1A_2 and 1B_2 states at different geometries (Table IV). We also report the dipole moments of the corresponding ionized states 2A_1 , 2A_2 , 2B_2 at these geometries, which are presented in Table V. We observe that the three vertical ionizations of 1A_1 state are not maximum at the equilibrium geometry of 1A_1 state. The dipole moments of the doublet states change on moving away from the equilibrium 1A_1 geometry of ozone. For the 2A_1 and 2A_2 state the dipole moment lowers on going from the vertical to the adiabatic 3B_1 geometry. For the 2B_2 state the dipole moment is lower at the vertical geometry. Both the ionization energy and the dipole show a sharp change in the energy/energy-response vs the distance/ angle curves.

TABLE II
Vertical ionization energies (in eV) of low-lying states of ozone

State	Experimental	FSMRCC	Propagator approach (ccpvdz) ^a
2A_1	12.73	12.41	12.10
2B_2	13.00	12.46	12.29
2A_2	13.54	13.15	13.27

^a Ref.²⁷

TABLE III
Adiabatic FSMRCC dipole moments of 1A_2 and 1B_1 states of ozone

State	Adiabatic excitation energy, eV	Dipole moment, D
1A_2	1.736	-0.104
1B_1	1.195	0.014

TABLE IV
Ionization energies (in eV) of low-lying states of ozone at different geometries

State	Geometry		Ionization energies of doublet states, a.u.		
	O-O, Å	O-O-O, °	2A_1	2B_2	2A_2
Vert	1.271	116.1	0.457	0.456	0.483
3B_1	1.351	101.5	0.477	0.435	0.472
1A_2	1.362	116.2	0.459	0.460	0.480
3B_2	1.360	108.3	0.469	0.448	0.476
1B_1	1.343	121.3	0.464	0.453	0.482

TABLE V
Dipole moments of low-lying states of ozone at different geometries

State	Geometry		Dipole moments of doublet states, a.u.		
	O-O, Å	O-O-O, °	2A_1	2B_2	2A_2
Vert	1.271	116.1	0.374	0.286	0.353
3B_1	1.351	101.5	0.370	0.291	0.340
1A_2	1.362	116.2	0.432	0.503	0.434
3B_2	1.360	108.3	0.397	0.464	0.407
1B_1	1.343	121.3	0.412	0.341	0.369

CONCLUSIONS

In this paper we report the energies and dipole moments of the singlet and triplet vertical excited states of ozone, adiabatic excitation energy and dipole moments of singlet excited states of ozone. Ionization energy of the ozone doublet states and response of the doublet excited states of the ozone cation radical are also reported at the ground state and different other geometries of ozone. The excitation energy values include the three-body contribution of the similarity transformed Hamiltonian contribution to the energy and the response calculations. The excitation energy values match well with experiment.

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