ELECTRONIC SPECTRA AND IONIZATION POTENTIALS OF HALOGEN OXIDES USING THE FOCK SPACE COUPLED-CLUSTER METHOD

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Dedicated to Professor Josef Paldus on the occasion of his 70th birthday.

The ionization potentials and excitation energies of halogen monoxides and dihalogen oxides are studied using fully size-extensive Fock space version of multi-reference coupled-cluster theory. The low-lying excited states of ClO^-, FO^-, Cl_2O and F_2O are obtained along with the ionization spectra of Cl_2O and F_2O. The adiabatic electron affinity of ClO, FO and the vertical detachment energy of ClO^- and FO^- are also presented.

Keywords: Multireference coupled-cluster method; Ionization potentials; FSCCDS; Excitation energies; Halogen monoxides; Dihalogen oxides; Atmospheric chemistry; *Ab initio* calculations.

In the last decade, halogen oxides have proved to be an important family of compounds particularly in atmospheric chemistry. Neutral halogen oxides are formed in stratosphere from the reaction of the halogen with ozone[1–3]. Due to the environmental importance of ozone, a lot of experimental[4,5] and theoretical[6–8] investigations have been performed on the spectroscopic properties and photochemical reactions of halogen–oxygen containing compounds present in the stratosphere. ClO [9], ClO_2 [10], Cl_2O and ClOOCl [11] are few of the important halogen–oxygen compounds. Despite early studies of ClO and BrO by electronic spectroscopy[12] and by gas-phase electron paramagnetic resonance (EPR)[13], the FO radical remained elusive. The first experimental detection of the FO radical was made by McKellar[14] in 1979 through the observation of its infrared spectrum. Most of the theoretical work[15–18] has focused on predicting bonding character, bond lengths, electron affinity and dipole moments of halogen oxides. F_2O, difluorine monoxide, chemically and structurally closely related to Cl_2O, on the other hand, did not receive so much attention. The potential energy surfaces of

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Cl_2O and F_2O were first recorded by Cornford et al.[19], Brundle et al.[20] by using a He I 584 Å radiation source. More recently Motte-Tollet et al.[21], again using He I, presented more accurate and vibrationally resolved measurements of the four outermost bands of Cl_2O up to 13.0 eV. For F_2O, several theoretical approaches[22,23] have been applied to the outer valence ionization potentials. There are various experimental observations[24,25] and theoretical predictions[17,18] for the electron affinity of ClO ranging from 1.6 ± 0.2 to 2.16 eV. In the present paper we present theoretical calculation of ionization and excitation spectra of Cl_2O and F_2O. We also report the vertical detachment energy and the lowest singlet and triplet excited states of XO^- (X = Cl, F) as well as adiabatic electron affinity (AEA) of ClO, and FO.

The Fock space coupled-cluster (FSCC)[26–28] method has now been well established as a tool to study the direct difference energies[29–32]. Traditionally, FSCC has been used for direct difference energies. However, recently it has also been used to obtain adiabatic difference energies[32]. In the latter case, it is no longer a direct calculation. The multi-reference model space enables efficient inclusion of non-dynamic electron correlation inherent in the excited or ionized states. The Fock space version of the theory is based on a common vacuum concept with respect to which the model space contains a set of m active particles and n active holes, called the (m,n) model space. A valence-universal wave-operator, correlating the above model space and all other spaces of lower active particles and holes, ensures size-extensivity. Subsystem embedding conditions are followed to solve for the wave-operator. Using a (1,1) model space and a singles and doubles approximation of the cluster amplitudes, the method (FSCCSD) has been well studied to calculate excitation energies[31,32] and ionization potentials (IP)[29,30]. For the evaluation of IP/EA, a suitable one active hole or one active particle model space is sufficient. Although, a general (1,1) model space is an incomplete model space, it can be considered as "quasi-complete" model space and the complete model space conditions can be used. There have been few reports of inclusion of approximate triples in the FSCC for IP as well as EE [30]. Kaldor and co-workers[33] first reported full inclusion of triples in the FSCC for ionized states. Piecuch and Kowalski[34] have done full equation of motion coupled-cluster singles and doubles (EOMCCSD) and a selected set of triples defined through active orbitals for excited states. Recently Bartlett and co-workers[35] have implemented full triples for excitations energies. They have also implemented full triples for IP-EOMCCSDT [36] and EA-EOMCCSDT [37] which provide results equivalent to Fock space for principal ionizations and electron attached states.

FOCK SPACE COUPLED-CLUSTER THEORY

The valence-universal coupled-cluster theory has been discussed extensively previously[26–28]. However, we summarize the important features of the FSCC theory very briefly in this section. In the FSCC method, a convenient single determinant, usually the N electron restricted Hartree–Fock (RHF), is chosen as a vacuum, which defines holes and particles. These holes and particles are further subdivided into active and inactive set of orbitals. The model space, in general, is a linear combination of important determinants, with m active particles and n active holes. Such a model space is said to belong to the (m,n) sector, where the first index denotes the number of active particles and the second refers to the number of active holes.

$$\left|\Psi_{\mu}^{(0)(m,n)}\right\rangle = \sum_{i} C_{i\mu}\left|\Phi_{i}^{(0)(m,n)}\right\rangle \tag{1}$$

where $C_{i\mu}$s are the model space coefficients and $|\Phi_i\rangle$s are the model space determinants with m active particles and n active holes. The valence-universal wave operator can be expressed as

$$\Omega^{(m,n)} = \{\exp \tilde{T}^{(m,n)}\} \tag{2}$$

where curly bracket denotes the normal ordering of operators enclosed in it.

$$\tilde{T}^{(m,n)} = \sum_{k=0}^{m}\sum_{l=0}^{n} T^{(k,l)}. \tag{3}$$

The Fock space Bloch equation is solved using the subsystem embedding condition (SEC) by projecting it to the model space (P) and the virtual space ($Q = 1 - P$) to obtain the effective Hamiltonian (H_{eff}) and the cluster amplitudes.

$$P^{(k,l)}[H\Omega - \Omega H_{\text{eff}}]P^{(k,l)} = 0 \tag{4}$$

$$Q^{(k,l)}[H\Omega - \Omega H_{\text{eff}}]P^{(k,l)} = 0 \tag{5}$$

where, $H_{\text{eff}} = P\Omega^{-1}H\Omega P$.

Normal ordering in Ω ensures that in the equation for (0,0) sector the $T^{(k,l)}$ amplitudes do not occur. In the equation for higher valence sector, the $T^{(0,0)}$ amplitudes appear as constant quantities. The SEC and normal ordering thus ensure a hierarchical decoupling of the equations of various Fock space sectors. For details one can refer to the review by Mukherjee and Pal[26]. The low-lying N electron excited states are dominated by one particle-one hole states and hence an appropriate model space may consist of singly excited determinants within a pre-chosen active subspace with respect to N-electron Hartree–Fock determinant. This one hole-one particle model space is a special incomplete model space. It is complete in occupation of one hole or one particle. Such model space is known as quasi-complete model space. For this model space the cluster operator can be decomposed as,

$$\tilde{T}^{(1,1)} = T^{(0,0)} + T^{(0,1)} + T^{(1,0)} + T^{(1,1)} \qquad (6)$$

where the cluster operator $T^{(0,0)}$ acts only on the RHF determinant. The operators $T^{(0,1)}$ and $T^{(1,0)}$ destroy one hole and one particle, respectively. $T^{(1,1)}$ operator destroys both one active hole and one active particle. Each of these cluster operators can be decomposed into one, two, and higher body cluster operators. We have used the singles and doubles approximation at each Fock space sector in what is known as the FSCCSD approximation. The de-excitation $T_1^{(1,1)}$ operator, while acting on the (1,1) model space, leads to the Hartree–Fock determinant, which is outside the model space. For incomplete model space it is known that, intermediate normalization has to be abandoned in order to maintain the linked diagram theorem[27]. However, Pal et al.[31] showed that for the special one particle one hole model space there are simplifications and, the P space equation remains unchanged. Further, the $T_1^{(1,1)}$ operator does not contribute to the effective Hamiltonian and to the corresponding excited state energies, though it is present in the actual wave function. The situation is very similar to the EOMCC method[38] where the de-excitation operators are not included. In both the cases it is easy to show that to get the excited state energies it is sufficient to get the eigen values of $Q\bar{H}Q$ where $Q = 1 - |\Phi\rangle\langle\Phi|$ and $\bar{H} = (H \exp (T^{(0,0)}))_{\mathrm{conn}}$. If the closed part of $\bar{H}$, denoted as $(\bar{H})_{\mathrm{cl}}$ is dropped, the direct vertical difference energies may be obtained. Open part of $\bar{H}$, known as $(\bar{H})_{\mathrm{op}}$ has one, two, and higher body terms. In our calculation we have truncated $(\bar{H})_{\mathrm{op}}$ to the one and two body parts denoted as $\bar{F}$ and $\bar{V}$. Following SEC, Eqs (*4*) and (*5*), we also obtain IP and EA in the process of calculating EE. The effective Hamiltonian $H_{\mathrm{eff}}^{(1,1)}$ has two blocks the direct part denoted as $H_{\mathrm{eff}}^{\mathrm{D}(1,1)}$ and the exchange part denoted as $H_{\mathrm{eff}}^{\mathrm{E}(1,1)}$.

Finally, to evaluate the singlet and triplet excited states, the following spin integrated matrices are constructed and diagonalized to obtain vertical singlet and triplet excited state energies.

$$(H_{\mathrm{EE}}^{\mathrm{S}})_{\alpha p\beta q} = (H_{\mathrm{eff}}^{(0,1)})_{\alpha\beta}\,\delta_{pq} + (H_{\mathrm{eff}}^{(1,0)})_{qp}\,\delta_{\alpha\beta} - 2\langle \alpha q | H_{\mathrm{eff}}^{\mathrm{D}(1,1)} | \beta p\rangle + \langle \alpha q | H_{\mathrm{eff}}^{\mathrm{E}(1,1)} | \beta p\rangle \tag{7}$$

$$(H_{\mathrm{EE}}^{\mathrm{T}})_{\alpha p\beta q} = (H_{\mathrm{eff}}^{(0,1)})_{\alpha\beta}\,\delta_{pq} + (H_{\mathrm{eff}}^{(1,0)})_{qp}\,\delta_{\alpha\beta} + \langle \alpha q | H_{\mathrm{eff}}^{\mathrm{E}(1,1)} | \beta p\rangle \tag{8}$$

COMPUTATIONAL DETAILS

We have used two different basis sets in our calculations. The Dunning augmented correlation consistent polarized valence triple zeta (aug-cc-pVTZ) basis set[39a] for ClO and FO is one of the basis. The other basis set consists of triple zeta valence plus two polarization functions (TZV2P)[39b]. TZV2P basis set was augmented with additional set of f function and one set of diffuse s and p functions. (TZV2P+ f + diff). The TZV2P + f basis set was formed by adding a set of f functions with orbital exponents $\alpha_f(\mathrm{Cl}) = 0.7$, $\alpha_f(\mathrm{O}) = 1.4$ in ClO; $\alpha_f(\mathrm{F}) = 0.5$, $\alpha_f(\mathrm{O}) = 0.724$ in FO. The exponents of the diffuse function were $\alpha_s(\mathrm{Cl}) = 0.05541$, $\alpha_p(\mathrm{Cl}) = 0.04531$, $\alpha_s(\mathrm{O}) = 0.08993$ and $\alpha_p(\mathrm{O}) = 0.0584$, and $\alpha_s(\mathrm{F}) = 0.09158$, $\alpha_p(\mathrm{F}) = 0.07361$, $\alpha_s(\mathrm{O}) = 0.07376$ and $\alpha_p(\mathrm{O}) = 0.059740$. The equilibrium bond distances for the ground states of ClO($^2\Pi$) and ClO$^-$($^2\Sigma^+$) were considered to be 1.5768 and 1.704 Å, respectively[42]. Similarly for FO and FO$^-$ the bond distances considered were 1.37337 and 1.4758 Å. During the calculation of spectroscopic properties, two core orbitals were frozen. The model space consist of 2 active particles and 1 active particle.

For the calculation of spectroscopic properties the FSCC method is used. The excitation energies reported in this paper are vertical excitation energies (VEE). Calculation of AEA of XO (X = Cl, F) is a two step procedure. First energy of XO$^-$ is calculated using Coupled cluster singles and doubles (CCSD) approximation[40,41] at the optimized or experimental geometry of the XO$^-$. To obtain the total energy of the XO we perform the calculations for XO$^-$ at the optimized geometry of XO, followed by the CCSD and ionization potential energy calculations using the FSCC theory. This together gives the total energy of XO. The difference between the total energies of XO and XO$^-$ gives the AEA of the XO. Thus, we lose the advantage of the FSCC method of getting multiple roots at a time.

Vertical excitation and ionization potentials (VIP) of $\mathrm{Cl_2O}$ and $\mathrm{F_2O}$ are investigated using cc-pVTZ basis with the FSCC method. The bond distances and angles used in the calculations were: $R_{\mathrm{Cl–O}} = 1.7319$ Å, $\angle$Cl–O–Cl =

111.61° and $R_{F–O}$ = 1.4053 Å, ∠F–O–F = 103.4°. Both the geometries were taken from ref.[48]. During the calculation of spectroscopic properties, two core holes were frozen for Cl_2O and three core holes were frozen for F_2O. Model space for these calculations consists of 4 active holes and 2 active particles. Our results were compared with the other theoretical as well as experimental where ever possible.

RESULTS AND DISCUSSION

Table I reports spectroscopic properties of ClO and ClO^- using the FSCC method in both basis sets. We compare our results with the equation of motion coupled-cluster singles and doubles (EOMCCSD)[42] as well as with experimental[43] results where ever available. As we go from the TZV2P + f + diff basis set to the aug-cc-pVTZ basis, VIP and AEA are enhanced by electron correlation. However, VEEs are reduced by electron correlation. In general, the IP and EA values match with the EOMCCSD results in the same basis set. The difference between the FSCC and EOMCC for excitation energies (EE) is large, as for two valence sector both the theories have no analogy unlike in the one valence problem.

TABLE I
Spectroscopic energies of ClO and ClO^-

Spectroscopic energy	FSCC[a]	CCSD(T)[b]	Expt
TZV2P + f + diff			
Adiabatic EA of ClO	2.08	2.03	2.278
IP of ClO^-	2.27	2.19	2.17
EE of $^1\Pi$ state of ClO^-	4.20	3.21	
EE of $^3\Pi$ state of ClO^-	3.88	2.51	
Aug-cc-pVTZ			
Adiabatic EA of ClO	2.17	2.19	2.278[c]
IP of ClO^-	2.38	2.38	2.17
EE of $^1\Pi$ state of ClO^-	3.72	3.11	–
EE of $^3\Pi$ state of ClO^-	3.43	2.90	–

[a] All values in eV; two core holes frozen during FSCC calculations, model space consist of 2 active holes and 1 active particle. [b] See ref.[42]. [c] See ref.[43]

Table II presents AEA of FO, VIP and singlet and triplet EEs for FO^-. FO is isovalent with ClO. No theoretical or experimental results are available for FO except for the adiabatic electron affinity. Haaland[44] performed QCISD/6-31+G* calculations and reported AEA to be 2.08 ± 0.2 eV. Experiments[45] have predicted the AEA for FO to be 2.272. Since the AEA is dependent on geometry the little discrepancy in the aug-cc-pVTZ basis can be explained. Comparing the ionization potential and excitation energies of FO and ClO, it can be seen that the IP and EE values of FO are towards higher energy side in comparison with those of ClO.

Dichlorine monoxide is a gaseous compound with C_{2v} symmetry. The HF configuration is written as

$[\text{core}]\ 6a_1^2\ 5b_1^2\ 7a_1^2\ 2b_2^2\ 6b_1^2\ 8a_1^2\ 2a_2^2\ 9a_1^2\ 7b_1^2\ 3b_2^2|10a_1^0\ 8b_1^0.$

Table III reports the ionization potential for the four states of Cl_2O. We compare our results with He I experiments[20,21] as well as with the one obtained using the Symmetry adapted cluster configuration interaction (SACCI) method[46]. SACCI is a greatly truncated and approximate version of EOMCC method. Since three IPs corresponding to $7b_1$, $9a_1$ and $2a_2$ lie within half eV, a very accurate method is required to predict them correctly. It can be seen that in general the results are in good agreement with the SACCI as well as experimental values. The difference between FSCC and

TABLE II
Spectroscopic energies of FO^-

Spectroscopic energy	FSCC[a], eV	Expt/Theory, eV
TZV2P + f + diff		
Adiabatic EA of FO	2.06	2.08[b], 2.272[c]
IP of FO^-	2.31	–
EE of $^1\Pi$ state of FO^-	4.33	–
EE of $^3\Pi$ state of FO^-	3.76	–
Aug-cc-pVTZ		
Adiabatic EA of FO	2.16	2.08[b], 2.272[c]
IP of FO^-	2.47	–
EE of $^1\Pi$ state of FO^-	4.5	–
EE of $^3\Pi$ state of FO^-	3.96	–

[a] All values are in eV; two core holes frozen during FSCC calculations, model space consist of 2 active holes and 1 active particle. [b] See ref.[44] (QCISD(T)/6-31+G*). [c] See ref.[45]

other methods is less than 0.2 eV. It is also interesting to note that the separation between the three ionized states $7b_1$ (12.31 eV), $9a_1$ (12.53 eV) and $2a_2$ (12.81 eV) is also in good agreement with SACCI results.

Table IV reports the EEs of Cl_2O for first eight singlets as well as triplet states. We compare our results with EOMCCSD(T) [47], CASSCF-MRCI [48], and experimental values[49]. Unfortunately, most of these studies except MRCI [50] report only singlet excitation energies. We observe that in general all the methods are in good agreement with each other. For triplet excitation energies we will compare our results with MRCI values. We observe that MRCI gives slightly higher values compared with FSCC.

Table V reports ionization potentials difluorine monoxide. F_2O is isovalent with Cl_2O and belongs to the C_{2v} point group. The HF configuration is

[core] $4a_1^2\ 1b_2^2\ 5a_1^2\ 3b_1^2\ 1a_2^2\ 4b_1^2\ 6a_1^2\ 2b_2^2|7a_1^0\ 5b_1^0$.

We compare our results with the SACCI, MRCI [51], OVGF [52] as well as He I experimental results. He I spectrum[21] of F_2O consists of vibrationally resolved first band around 13.0 eV, then a composite band between 16 and 17 eV. An important issue in the F_2O photoelectron spectrum was whether this band should contain two or three ionized states. CI calculations and experiments reported only two states. In order to confirm the assignments made in previous calculations we carried out FSCC calculations for the seven valence states of F_2O.

The first peak was obtained at 13.11 eV which is in close agreement with experimental (13.26 eV) and previous studies using SACCI (12.99 eV), MRCI (13.43 eV) and OVGF (13.06 eV). For the second band, our calculations gave three ionized states corresponding to $4b_2$, $6a_1$ and $1a_2$ whose IPs were 16.03, 16.26 and 16.60 eV. This ordering matched well with the SACCI results giving 16.27, 16.48 and 16.84 eV for the same states, respec-

TABLE III
Ionization potentials (in eV) of Cl_2O

State	He I[a]	He I[b]	SACCI[c]	FSCC[d]
$3b_1$	11.02	10.97	11	10.86
$7b_2$	12.37	12.3	12.43	12.31
$9a_1$	12.65	12.59	12.62	12.53
$2a_2$	12.79	12.74	12.88	12.81

[a] See ref.[19] [b] See ref.[21] [c] See ref.[46] [d] cc-pVTZ basis; two core holes were frozen during FSCC calculations, model space consist of 4 active holes and 2 active particles.

tively. Thus, our calculations also confirm previous studies of Tomasello et al.[46] that in this band apart from $4b_2$ and $6a_1$ ionized states $1a_2$ state also exists. For the higher energy band we have three peaks corresponding to the ionized states of $1b_1$ (18.75 eV), $5a_1$ (19.73 eV) and $3b_2$ (21.01 eV). These assignments are in good agreement with previous theoretical as well as experimental studies.

TABLE IV
Excitation energies (in eV) of Cl_2O

Character	Excitation energies				
	Expt[a]	SACCI[b]	MRCI[c]	EOMCC[d]	FSCC[e]
Singlet					
$2a_2 \rightarrow 10a_1$	–	5.69	5.88	5.01	5.57
$2a_2 \rightarrow 8b_1$	–	8.25	–	–	7.21
$9a_1 \rightarrow 10a_1$	4.88	4.81	5.45	4.66	4.81
$9a_1 \rightarrow 8b_1$	7.25	7.55	7.98	–	7.55
$7b_1 \rightarrow 10a_1$	4.20	4.42	4.98	4.23	4.46
$7b_1 \rightarrow 8b_1$	–	7.14	–	–	6.92
$3b_2 \rightarrow 10a_1$	2.90	2.92	3.42	2.82	2.84
$3b_2 \rightarrow 8b_1$	–	4.57	4.97	4.23	4.21
Triplet					
$2a_2 \rightarrow 10a_1$	–	–	5.62	–	5.28
$2a_2 \rightarrow 8b_1$	–	–	–	–	6.62
$9a_1 \rightarrow 10a_1$	–	–	5.45	–	3.69
$9a_1 \rightarrow 8b_1$	–	–	6.55	–	5.95
$7b_1 \rightarrow 10a_1$	–	–	4.16	–	3.62
$7b_1 \rightarrow 8b_1$	–	–	6.4	–	6.07
$3b_2 \rightarrow 10a_1$	–	–	2.63	–	2.04
$3b_2 \rightarrow 8b_1$	–	–	4.02	–	3.26

[a] See ref.[49] [b] See ref.[46]; [6s5p1d] of McLean and Chandler for Cl and Rydberg functions of double zeta quality were added. [c] cc-pVTZ basis see ref.[50] [d] See ref.[47] [e] cc-pVTZ basis set used, two core holes were frozen during FSCC calculation, model space consist of 4 active holes and 2 active particles.

TABLE V
Ionization potentials (in eV) of F_2O

State	Expt[a]	OVGF[b]	MRDCI[c]	SACCI[d]	FSCC[e]
$2b_1$	13.26	13.06	13.43	12.99	13.11
$4b_2$	16.17	16.46	16.36	16.11	16.03
$6a_1$	16.47	16.37	16.17	16.21	16.26
$1a_2$	–	16.95	–	16.63	16.60
$1b_1$	18.68	18.85	17.41	18.49	18.75
$5a_1$	19.50	19.49	19.52	19.51	19.73
$3b_2$	20.09	20.57	20.49	20.74	21.01

[a] See ref.[9] [b] See ref.[52] [c] See ref.[51]; DZP basis augmented with Rydberg type functions. [d] See ref.[46]; [5S3P] GTOs of Huzinaga–Dunning and d type polarization functions of ζ_d = 0.90 and 0.85 for F and O atoms. [e] cc-pVTZ basis set; three core holes were frozen during FSCC calculation, model space consist of 4 active holes and 2 active particles.

TABLE VI
Excitation energies (in eV) of F_2O

Character	SACCI[a]	MRDCI[b]	FSCC[c]
Singlet			
$1a_2 \rightarrow 7a_1$	9.08	8.41	8.17
$1a_1 \rightarrow 5b_1$	9.86	10.81	9.21
$4b_1 \rightarrow 7a_1$	8.17	8.24	7.43
$4b_1 \rightarrow 5b_1$	10.33	–	9.54
$6a_1 \rightarrow 7a_1$	8.52	8.29	7.89
$6a_1 \rightarrow 5b_1$	11.43	11.46	11.16
$2b_1 \rightarrow 7a_1$	5.36	5.58	4.56
$2b_1 \rightarrow 5b_1$	6.05	5.62	4.99
Triplet			
$1a_2 \rightarrow 7a_1$	–	7.60	7.34
$1a_1 \rightarrow 5b_1$	–	8.68	8.65
$4b_1 \rightarrow 7a_1$	–	6.90	6.54
$4b_1 \rightarrow 5b_1$	–	8.20	7.68
$6a_1 \rightarrow 7a_1$	–	6.50	6.36
$6a_1 \rightarrow 5b_1$	–	6.40	7.03
$2b_1 \rightarrow 7a_1$	–	4.20	3.21
$2b_1 \rightarrow 5b_1$	–	4.10	4.12

[a] See ref.[21]; [5S3P] GTOs of Huzinaga–Dunning and d type polarization functions of ζ_d = 0.90 and 0.85 for F and O atoms. [b] See ref.[51]; DZP basis augmented with Rydberg type functions. [c] cc-pVTZ basis set was used, three core holes were frozen during FSCC calculations, model space consist of 4 active holes and 2 active particles.

Table VI reports the excitation spectra of F_2O. There are no experimental studies for the excitation spectra of F_2O. Valenta et al.[51] studied the vertical ionization as well as excitation spectra using MRCISD in the DZP basis augmented by Rydberg type functions. Tomasello et al.[50] studied the valence spectra using the CASCI method in triple zeta quality basis augmented by polarized functions. Compared to Cl_2O, each state in F_2O is blue-shifted by 2 to 3 eV. In general, SACCI as well as MRCI overestimate the excitation energy value compared to FSCC. However, in general there is good agreement of all the three methods.

CONCLUSIONS

The ionization potential and excitation energies of XO^- (X = Cl, F) as well as Cl_2O and F_2O are calculated using Fock space coupled-cluster method. We compare our results with the experimental as well as theoretical results. In general, results are in good agreement with other theoretical results. For the second band of F_2O our calculations gave three ionized states corresponding to $4b_2$, $6a_1$ and $1a_2$ states. This ordering matches well with the SACCI results.

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