Theoretical investigation on the valence ionization spectra of Cl_2O, ClOOCl, and F_2O by correlation-based configuration interaction methods

Pasquale Tomasello[a]
Dipartimento di Fisica e Astronomia, Università di Catania, INFM and INFN, Via S. Sofia 64, I-95123 Catania, Italy

Masahiro Ehara and Hiroshi Nakatsuji
Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

We report on theoretical valence ionization spectra of molecules relevant in the stratosphere photochemistry obtained by all-electron SAC–CI (symmetry-adapted-cluster–configuration-interaction) calculations. Vertical ionization energies and pole strengths of the one- and two-electron processes of Cl_2O and F_2O were calculated beyond the energy region so far explored in the few other available theoretical and experimental studies to interpret the electronic structure of these molecules. Early and recently proposed incomplete assignments of the available He I photoelectron spectra are discussed and completed at least up to 20–21 eV binding energy on firmer grounds relying on valuable and accurate results based on different basis sets and an adequate treatment of electron correlations. Our theoretical data predict satellite states of Cl_2O starting already in the outer-valence region because of strong correlation effects; the $(2b_1^{-1})$, $(8a_1^{-1})$, and $(6b_2^{-1})$ states interact with the two-electron processes and they split into more-than-two peaks. On the other hand, Koopmans' picture is valid for the main peaks of F_2O and no prominent satellites with strong intensity were found in the outer-valence region. The $(4b_2^{-1})$, $(6a_1^{-1})$, and $(1a_2^{-1})$ were attributed to the second band of F_2O, for which different assignments or orderings of the states have previously been proposed in some experimental and theoretical works. Differences of the valence-ionization spectra of Cl_2O and F_2O for the appearance of the satellites in the intermediate energy region have been discussed with the aid of the calculated ionization potentials and excitation energies. For ClOOCl, we have presented the first theoretical low-energy ionization spectrum and discussed the character of the calculated states referring to the available ionization spectra of ClO radical. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Electronic structure of chlorine, or dichlorine, monoxide and its peroxide (Cl_2O and ClOOCl) has recently attracted increasing attention among experimentalists and computational chemists,[1–17] in order to clarify in some details the photochemistry of these compounds, as they are directly or indirectly involved in the chain reactions occurring in the high terrestrial atmosphere supposedly leading to the ozone depletion. Therefore recent work on these molecules has mainly been devoted to electronic excitation energies, structural and bonding properties and energetics of various kind of chlorine oxides and peroxides.[12–17] F_2O, difluorine monoxide, a chemically and structurally closely related to Cl_2O compound, on the other hand, has been long neglected both experimentally and theoretically, in spite of its simplicity and importance. Its experimental absorption spectrum, to date, remains still unknown while its photoelectron spectrum

(PES) has only been investigated in the outer-valence region three decades ago,[18,19] and since then have never been revisited.

The PES of Cl_2O and F_2O were first recorded by Cornford *et al.*[18] and Brundle *et al.*[19] by using He I 584 A radiation source and therefore limited up to about 21 eV. More recently Motte-Tollet *et al.*,[20] again using the He I PES, presented more accurate and vibrationally resolved measurements of the four outermost bands of Cl_2O up to about 13 eV. These four peaks and their vibrational spectrum were also theoretically investigated in details by CASSCF and QCISD calculations of Wang *et al.*,[21] however, the valence-ionized states in the intermediate energy region above 15 eV were not studied therein. For F_2O, several theoretical approaches[22–26] have been applied to the outer-valence region ionization potentials (IPs). However, the ensuing assignments were controversial for the second band; the energy's ordering of the third and fourth states was different from one another and even the number of the states attributed to it was different. As to the dichlorine peroxide, experimental and theoretical investigations have been limited to the first IP only by Schwell *et al.*[27] It is the scope and motivation of the

[a]Author to whom correspondence should be addressed. Electronic mail: pasquale.tomasello@ct.infn.it

present work to fill this lacking of information on the main peaks and satellites of the aforementioned molecules, as well as to build up on more firm grounds the previous assignments for the valence ionization spectra of Cl_2O and F_2O, let alone that of ClOOCl.

The SAC[28]/SAC–CI[29–33] method has now been well established as a useful quantum-chemical method for studying molecular ground, excited, ionized, and electron attached states of molecules from singlet to septet spin-multiplicities.[34] For ordinary single electron excitation and ionization processes, we use the SAC–CI SD (singles and doubles)-R method. For multiple-electron processes, like those involved in shake-up satellite and correlation peaks, the SAC–CI general-R method[35–38] has been shown to be a powerful theoretical tool to study electronic structures. By the general-R method, we cannot only describe accurately the multiple electron processes, but even also calculate a larger number of states appearing in the ionization spectra[39,40] unavailable in the previous one. Recently, we have applied systematically the general-R method into the outer- and inner-valence ionization spectra of several molecules.[40–46] The method has been shown to be useful for the detailed characterizations of the satellite peaks as well as to handle the occurrence of the MO picture break down of the ionization event, traditionally studied by the Green's function approach[47,48] and MRCI methods.[49]

In our recent work we have investigated the excitation spectra of Cl_2O, F_2O, and ClOOCl by the SAC–CI method.[17] Absorption spectra of these molecules were accurately reproduced and the detailed assignments were proposed for both the UV and VUV regions. In the present work, we present the detailed theoretical ionization spectra of these molecules in the outer- and intermediate-valence region and interpret satellite lines and non-Koopmanns' structures of the spectra with the aid of the calculated IPs of the main peaks and of the previously calculated excitation spectra.

In the next section we give the computational details of the used methods and basis sets. Section III is devoted to discuss the results we have obtained for each molecule in comparison with experiments and previous theoretical studies. The last section concludes this work giving a resumè and conclusive remarks.

II. COMPUTATIONAL DETAILS

To study the vertical IPs of the main peaks for Cl_2O, F_2O, and ClOOCl, we first used the SAC–CI SD–R method. Then, to investigate the appearance of the secondary valence-ionized states (satellite lines, correlation states), we adopted the general-R method. We first examined the effect of the molecular geometries and the basis sets for calculating the IPs of the valence-ionized states by the SD–R method as discussed in the Appendix. On the basis of these examinations, the ground-state experimental geometries were adopted for the final calculations; namely, R_{ClO} = 1.695 87 Å and <ClOCl = 110.886° (Ref. 50) for Cl_2O, R_{FO} = 1.4053 Å and <FOF = 103.4° (Ref. 51) for F_2O, both in C_{2v} structure, and R_{ClO} = 1.704 Å, R_{OO} = 1.426 Å, <ClOO = 110.1° and ClOOCl = 81.9° (dihe. angl.)[52] in C_2

TABLE I. SAC–CI dimensions for the ionized states of Cl_2O, F_2O, and ClOOCl.

	Singles	Doubles	Triples	Total
		Cl_2O		
A_1	4	1127	78 915	80 046
A_2	1	981	59 754	60 736
B_1	2	986	65 461	66 449
B_2	3	1133	80 838	81 974
		F_2O		
A_1	4	1124	84 587	85 715
A_2	1	966	60 889	61 856
B_1	2	984	69 347	70 333
B_2	3	1110	76 771	77 884
		ClOOCl		
A'	7	4686		4693
A''	6	4673		4679

structure for ClOOCl. Basis set of the triple-zeta quality were used; namely $(13s10p)/[6s5p]$ GTOs of McLean and Chandler[53] augmented with d-type polarization function of $\zeta_d = 0.514$ for Cl atom,[54] and $[5s3p]$ GTOs of Huzinaga–Dunning[55] plus d-type polarization functions of $\zeta_d = 0.90$ and 0.85 for F and O atoms,[56] respectively. The resultant SCF MOs dimensions were 71, 57, and 90 for Cl_2O, F_2O, and ClOOCl, respectively. These basis sets are flexible enough to describe electron correlations of the shake-up states in the outer-valence region.

The detailed satellite spectra of Cl_2O and F_2O were calculated by the SAC–CI general-R method in outer-valence region. From the preliminary calculations, most of the shake-up states were shown to be dominantly described by two-electron processes in this energy region, and therefore the R operators were included up to triple excitations. For ClOOCl, for which only the first IP has been reported in the literature, only the SAC–CI/SD-R method was applied to see the position of the main peaks. The $1s$, $2s$, and $2p$ orbitals of Cl and the $1s$ orbitals of O and F were kept as frozen core and all the other MOs were included in the active space; the SAC–CI active space consisted of 10 occupied and 50 unoccupied MOs for Cl_2O, 10 occupied and 44 unoccupied MOs for F_2O, and 13 occupied and 65 unoccupied MOs for ClOOCl.

To reduce the computational effort, perturbation selection[57] was performed in the state-selection scheme. The threshold of the linked terms for the ground state was set to $\lambda_g = 1 \times 10^{-6}$. The unlinked terms were described as the products of the important linked terms whose SD–CI coefficients were larger than 0.005. For ionized states, the thresholds of the linked doubles and triples were set to $\lambda_e = 1 \times 10^{-7}$ and $\lambda_e = 1 \times 10^{-6}$, respectively. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC–CI method were set to 0.05 and 1×10^{-8} for the R and S operators, respectively. The resultant SAC–CI matrix dimensions were summarized in Table I.

The ionization cross sections were calculated within the monopole approximation[58,59] to evaluate the relative intensities of the peaks. For the calculations of monopole intensities, the correlated SAC/SAC–CI wave functions were used

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for the ground and ionized states to include both initial- and final-state correlation effects.

The SAC/SAC–CI calculations were performed using the SAC–CI96 program system,[60] which has been incorporated into the development version of the Gaussian suite of programs.[34]

III. RESULTS AND DISCUSSION

The IPs of Cl$_2$O and F$_2$O, mainly in the outer-valence region, are closely related to each other. Besides the different shell quantum number of the halogen, which makes the IPs of F$_2$O higher by about 2–3 eV, the MOs originating them are structurally and symmetrically very similar. He I experimental spectra of dihalo-monoxides exhibit therefore close kinship with each other. ClOOCl photoelectron spectrum, on the other hand, should on the whole look quite different from that of the dihalo-monoxides; many more congested bands are expected. Nevertheless the first IP of the ClOOCl seems essentially to be equal to those of Cl$_2$O and ClO.[27] In particular, the whole spectrum should show evidence of the fact that this molecule is a weakly bound dimer of the ClO radical.

A. Cl$_2$O

The He I experimental spectrum of Ref. 18 showed two band systems vibrationally active below 14 eV, which was much better resolved in the more accurate measurements of Ref. 20. These two bands, compressed and redshifted relatively to those of F$_2$O, are believed to contain in increasing energy order the $3b_1$, $7b_2$, $9a_1$, and $2a_2$ ionizations. Their assignment, though grounded on the partially resolved vibrational structure, required the high level CASSCF and QCISD calculations of Wang *et al.*[21] to be confirmed. These calculations, however, aimed to reproduce mainly vibrational band profiles. In particular the second band, involving three ionized states within a spread of ~1 eV, calls for calculations of very good quality. Thus, we have performed SAC–CI calculations and summarized the selected results together with experimental data in Table II.

It is seen from the listed results therein, that SAC–CI SD–R method performs quite well in agreement with the experimental data within 0.2 eV for most of the outer-valence ionizations, and confirms thus the previous assignment with greater accuracy. It is worth here to notice, not only the excellent agreement with the experiment on absolute scale, but also the energy separation between the three ionized states $(7b_2^{-1})$, $(9a_1^{-1})$, and $(2a_2^{-1})$, inside the second band, all lying within 1 eV. This feature of our results is independent from the basis sets and geometry we adopted. Passing from the optimized geometry to the experimental one, for instance, significant changes on the calculated IPs appear in the higher-energy ionizations only. The slightly shrunken experimental geometry seems to produce results higher by 0.3–0.8 eV relatively to those of the optimized geometry, and in better agreement with the experimental IPs. Then, we assign the three weak to medium intensity features of the experimental He I spectrum at 15.9, 16.65, and 17.68 eV, to single-hole or main ionization out of the $2b_1$, $8a_1$, and $6b_2$ MOs relying on our SAC–CI SD–R results.

The greater sensitivity to ClO bond distance of these ionizations can be rationalized by the bonding character of the originating MOs. On the other hand, their energy range is just where one could well expect the appearance of the satellite states. Indeed, the experimental PES shows between 13 and 20 eV first a flat almost vanishing intensity up to 15.5 eV, which thereafter arises slowly but continuously creating three broad prominences containing vibrational structure and/or satellite lines, and above 19 eV again sharply rising up to about 21 eV. For this energy region, though the SD–R method provides qualitative description of the ionized states, we need the general-R method for a detailed picture, whose results are reported in Table II and in Fig. 1. Therein experimental data and the whole spectrum of Ref. 18 is compared with our findings. The general-R results show interesting features. First of all they corroborate the SD–R based assignment discussed above, but only for the lowest four ionized states. The general-R results for these states appear to match the values of the SD–R method by 0.1 eV, which is nice for building good confidence on our data, so that the relative ordering of the ionized states as well as their energy separations is consistently preserved. The calculated relative intensities of the first four ionized states, $(3b_1^{-1})$, $(7b_2^{-1})$, $(9a_1^{-1})$, and $(2a_2^{-1})$, show that these states are main peaks or Koopmans' lines. Satellite states originating from these latter states have very weak intensity, smaller than 0.01.

Satellite states start to appear just above the highest main peak, the $^2A_2$ state at 13.83 eV, even though with very small relative intensity (4×10^{-4}). Below 15 eV, where the very low recorded intensity starts to increase, we have calculated two secondary states at 14.54 and 14.73 eV of A_2 and B_1 symmetry whose summed intensity amounts to 0.14, a value absolutely not negligible and which can make contribution to the spectral intensity. Above 15 eV, we should expect according to the SD–R results first a strong intensity of $(2b_1^{-1})$ ionized state, and thereafter around 16.5 eV, the $(8a_1^{-1})$ ionized state. The general-R results instead indicate a collapse of the supposed "main" states $(2b_1^{-1})$ and $(8a_1^{-1})$ into several strong correlation-dominated secondary states. For the $2b_1$ ionization, besides the shake-up state at 14.73 eV before mentioned, we have calculated three states at 15.22, 15.86, and 16.57 eV with relative intensity of 0.31, 0.22, and 0.10, respectively; whereas for the $8a_1$ ionization we realize the separation of the single-hole intensity mainly into two states. First we encounter an $^2A_1$ state, originating from the $(8a_1^{-1})$ but weakly coupled to the $9a_1$ single-hole state, at 15.69 eV with 0.40 of relative intensity and 1 eV below the expected main line at 16.65 eV, which is again calculated at 16.56 eV even though with a wildly reduced intensity of 0.39. Other satellites originating from the $9a_1$, $8a_1$, and $7a_1$ ionizations are found at higher energy around 19, 21, and 24 eV, respectively, but with relatively small intensity of 0.01–0.02.

Another break-down of the one-electron model occurs for the $6b_2$ ionization. Calculated by SD–R at 17.88 eV, it is now obtained by general-R split again into two strong lines, separated by each other less than 0.3 eV at 17.50 eV (0.41) and 17.77 eV (0.34). These states are characterized as the $(6b_2^{-1})$ and $(3b_1^{-1}10a_12a_2^{-1})$ configurations. Thus, we realize that the general-R calculation has preserved the main

TABLE II. Ionization potentials (in eV), monopole intensities, and main configurations of the valence ionized states of Cl_2O.

State	He I UPS[a] IP	He I UPS[b] IP	RCC SD(T)[c] IP	SAC–CI SD–R IP	SAC–CI General-R IP	SAC–CI General-R Intensity	SAC–CI General-R Main configuration ($|C|>0.4$)
B_1	11.02	10.97	11.20	10.93	11.00	0.83	$0.88(3b_1^{-1})$
B_2	12.37	12.30	12.37	12.40	12.43	0.84	$0.89(7b_2^{-1})$
A_1	12.65	12.59	12.90	12.69	12.62	0.83	$0.89(9a_1^{-1})$
A_2	12.79	12.74	12.85	12.99	12.88	0.79	$0.86(2a_2^{-1})$
A_2					14.54	0.02	$8.84(3b_1^{-1}10a_17b_2^{-1})-0.74(7b_2^{-1}10a_13b_1^{-1})$
B_1					14.73	0.12	$-0.33(2b_1^{-1})+0.76(9a_1^{-1}10a_13b_1^{-1})+0.71(3b_1^{-1}10a_19a_1^{-1})$
B_1					15.22	0.31	$0.54(2b_1^{-1})+0.49(3b_1^{-1}10a_19a_1^{-1})$
A_2					15.33	0.01	$0.55(7b_2^{-1}10a_13b_1^{-1})-0.40(3b_1^{-1}10a_17b_2^{-1})$
A_1					15.69	0.40	$0.62(8a_1^{-1})-0.47(9a_1^{-2}10a_1)+0.46(7b_2^{-2}10a_1)$
B_1	15.90			15.75	15.86	0.22	$0.45(2b_1^{-1})+0.46(9a_1^{-1}10a_13b_1^{-1})$
A_1	16.65			16.47	16.56	0.39	$0.61(8a_1^{-1})-0.45(7b_2^{-2}10a_1)+0.42(9a_1^{-2}10a_1)$
B_1					16.57	0.10	$0.67(7b_2^{-1}8b_23b_1^{-1})+0.53(3b_1^{-1}8b_27b_2^{-1})$ $+0.47(7b_2^{-1}10a_12a_2^{-1})$
A_2					16.65	0.02	$0.60(9a_1^{-1}8b_23b_1^{-1})+0.60(3b_1^{-1}8b_29a_1^{-1})$ $+0.56(2a_2^{-1}10a_19a_1^{-1})+0.56(9a_1^{-1}10a_12a_2^{-1})$
B_2					16.70	0.04	$0.61(7b_2^{-1}10a_19a_1^{-1})-0.40(9a_1^{-1}10a_17b_2^{-1})$
B_2					17.49	0.01	$0.67(9a_1^{-1}10a_17b_2^{-1})+0.60(7b_2^{-1}10a_19a_1^{-1})$ $-0.46(7b_2^{-1}10a_18a_1^{-1})+0.44(9a_1^{-2}8b_2)$
B_2	17.68			17.88	17.50	0.41	$0.64(6b_2^{-1})-0.40(3b_1^{-1}8b_22b_1^{-1})$
B_1					17.68	0.01	$0.66(2a_2^{-1}10a_17b_2^{-1})-0.52(3b_1^{-1}10a_18a_1^{-1})$ $+0.46(2a_2^{-1}8b_29a_1^{-1})$
B_2					17.77	0.34	$0.58(6b_2^{-1})+0.42(3b_1^{-1}10a_12a_2^{-1})$
B_1					18.43	0.01	$0.56(7b_2^{-1}10a_12a_2^{-1})+0.48(9a_1^{-1}8b_22a_2^{-1})$
B_2					18.52	0.02	$0.66(7b_2^{-2}8b_2)-0.42(9a_1^{-2}8b_2)+0.41(9a_1^{-1}10a_17b_2^{-1})$
A_1					18.86	0.01	$0.53(7b_2^{-1}8b_29a_1^{-1})-0.40(9a_1^{-1}8b_27b_2^{-1})$
B_2					20.18	0.01	$0.54(7b_2^{-1}10a_18a_1^{-1})$
A_1					21.46	0.02	$0.56(7b_2^{-1}10a_16b_2^{-1})-0.55(8a_1^{-1}10a_19a_1^{-1})$ $+0.43(9a_1^{-1}8b_26b_2^{-1})-0.43(9a_1^{-1}10a_18a_1^{-1})$
B_2					22.10	0.01	$0.49(2b_1^{-1}10a_12a_2^{-1})+0.47(2a_2^{-1}10a_12b_1^{-1})$ $-0.43(7b_2^{-2}2b_26b_2^{-1})-0.41(9a_1^{-1}10a_16b_2^{-1})$
A_1					22.69	0.06	$0.39(7b_2^{-1}10a_16b_2^{-1})+0.39(7b_2^{-1}8b_28a_1^{-1})$
B_2					22.83	0.03	$0.41(7b_2^{-1}8b_26b_2^{-1})+0.41(7b_2^{-1}10a_18a_1^{-1})$
A_1					23.72	0.02	$0.60(8a_1^{-1}8b_27b_2^{-1})$
B_2					23.88	0.02	$0.75(6b_2^{-1}10a_19a_1^{-1})$
A_1					24.06	0.04	$0.72(6b_2^{-1}10a_17b_2^{-1})$
B_2					24.12	0.02	$0.60(8a_1^{-1}8b_29a_1^{-1})$
A_1					24.76	0.33	$0.55(7a_1^{-1})+0.44(9a_1^{-1}8b_26b_2^{-1})+0.40(6b_2^{-1}8b_29a_1^{-1})$
B_2					25.18	0.02	$0.55(7b_2^{-1}8b_26b_2^{-1})-0.52(9a_1^{-1}10a_16b_2^{-1})$ $-0.41(9a_1^{-1}8b_28a_1^{-1})$
B_2					25.92	0.08	$0.49(8a_1^{-1}10a_16b_2^{-1})$

[a]Reference 18.
[b]Reference 20.
[c]Reference 21.

traits of the SD–R calculation in the low-energy outer-valence region below 14 eV, while in the intermediate-energy region description and interpretation are radically changed both in energy and intensity of the ionic states. In the energy region of 14.5–20 eV, the intensities of the $(2b_1^{-1})$, $(8a_1^{-1})$, and $(6b_2^{-1})$ states are distributed into many ionized states for which it is meaningless to assign them as "main" and "satellite" states. He I UPS work[18] reported the additional peak at 20.64 eV, though overlapping with the energy region of He I excitation. No prominent peaks were calculated around 20 eV, however, while some continuous ionic states were obtained sparsely with small intensity; all of these states may be attributed to this band. Finally, we notice that the $7a_1$ ionization also undergoes to a breakdown of one-electron

picture, similarly to the previously discussed ionized states and we find its first relatively strong correlation state (0.34) around 25 eV. Figure 1 tells us what happened in the intermediate valence energy region of the PES spectrum of Cl_2O. It also shows us the capability of general-R method to simulate the complexities of the electron processes occurring in the ionizations out of these MOs. On the whole, the agreement both in energy and intensity distribution with the experiment seems quite satisfactory.

B. F_2O

Difluorine monoxide has an iso-valence electronic structure with Cl_2O and belongs to the same point group of C_{2v}. Its He I spectrum[18] consists of vibrationally resolved first
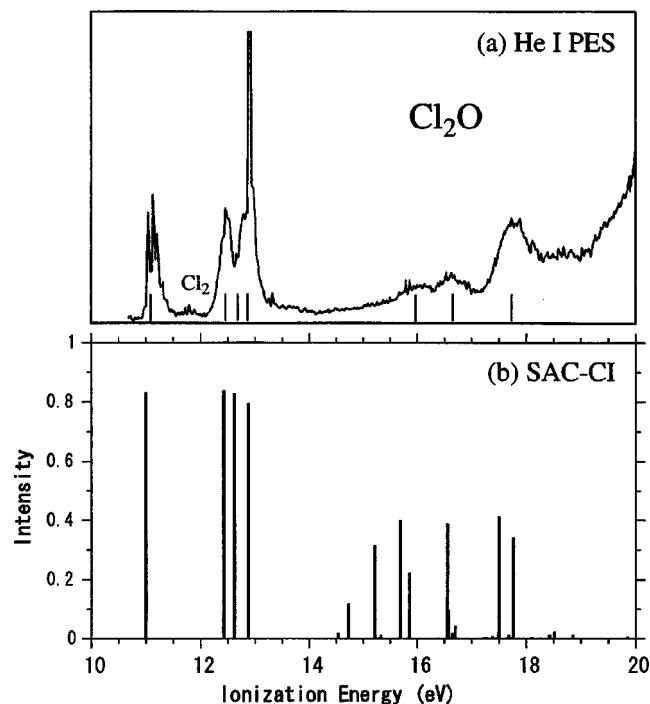
FIG. 1. Valence ionization spectra of Cl₂O by (a) He I UPS (Ref. 18) and (b) SAC–CI general-R method.
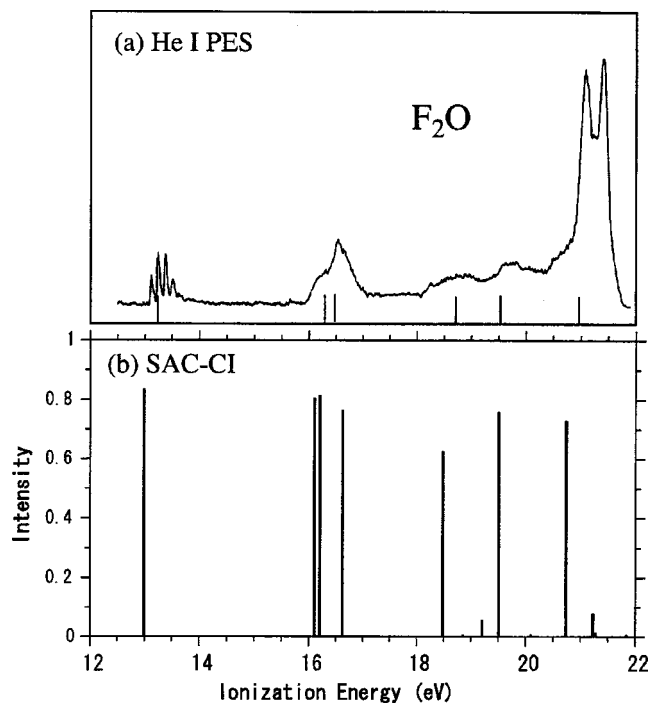

FIG. 2. Valence ionization spectra of F₂O by (a) He I UPS (Ref. 18) and (b) SAC–CI general-R method.

band around 13 eV, then a composite broad band between 16 and 17 eV, to which it follows two features of weak intensity around 19 eV. In particular, an important issue in the F₂O photoelectron spectrum appears in the relatively broad band between 16 and 17 eV. It has remained unresolved until today, whether this band should contain two or three ionized states. On analogy with the band of Cl₂O at around 12.5 eV, it should be compounded of the $(6a_1^{-1})$, $(4b_2^{-1})$, and $(1a_2^{-1})$ ionized states. But, though the PT[24] and the OVGF[22] results seem supportive of this "natural" view, CI calculations[23] and experimental works[18,19] reported only two states contributing to the envelope around 16.5 eV. In order to attempt conclusive assignments for the valence-ionized states of F₂O, the SAC–CI calculations were performed for the energy region up to ~30 eV. The theoretical spectrum was compared with the He I UPS spectrum[18] in Fig. 2. In Table III, we have listed our SAC-CI results together with other theoretical results and experimental data.

The first peak observed at 13.26 eV[18] was unambiguously assigned to the $(2b_1^{-1})$ calculated at 12.99 eV. For the second band, SAC–CI calculations within two different basis sets, apparently eliminated the inconveniences discussed above and gave three ionized states in the expected energy range. It also yielded the correct "natural" ordering; namely $(4b_2^{-1})$, $(6a_1^{-1})$, and $(1a_2^{-1})$, whose IPs were calculated as 16.27, 16.48, and 16.84 eV, in excellent agreement with the experimental values of 16.17 and 16.47 eV. This agreement allows us to propose that inside the second band, beside the $(4b_2^{-1})$ and $(6a_1^{-1})$ ionized states, there must also be the $(1a_2^{-1})$ state. As for the higher energy ionizations lying in the 18–21 eV energy region, the SAC–CI SD–R results would indicate the presence of three main ionized states, the $(1b_1^{-1})$, $(5a_1^{-1})$, and $(3b_2^{-1})$, at 18.84, 19.86, and 21.20 eV,

respectively, in good agreement with the previous theoretical studies and experiments. However, as it was discussed for Cl₂O, this may be only qualitatively correct, since this energy domain of 18–20 eV for F₂O corresponds to the energy region of 16–20 eV for Cl₂O. Therefore, we could well find the analogous strong correlation effects limiting the Koopmans' model. To check for this possibility we have also performed the general-R calculation for F₂O.

Inspecting these latter data, we notice the good agreement between the SD–R and general-R results for the first three states. For the successive three states, though the intensities of general-R calculations were somewhat reduced, severe breakdown of the pole strength of $(1b_1^{-1})$ and $(5a_1^{-1})$ did not occur, as it was the case for the corresponding ionizations of Cl₂O, namely the $(2b_1^{-1})$ and $(8a_1^{-1})$ ionic states. In particular, the intensity of the $1b_1^{-1}$ state was strongly reduced to 0.60, and three secondary states were calculated with the total intensity of 0.16 above 20 eV. The other two ionizations, the $(5a_1^{-1})$ and $(3b_2^{-1})$, though bearing a slightly reduced intensity seem to be better considered as Koopmans-type states. Indeed, they give rise to very weak satellite states but in the energy region between 20 and 30 eV, most thereof were not reported in Table III. At higher energy around 30 eV, an A_1 ionized state was calculated with a pole strength of 0.16 stemming from the inner-valence $4a_1$ ionization which breaks down into many states scattered in this energy region. In conclusion, for the two broad features of medium strength in the PES of F₂O extending from 18 to 20 eV, our general-R results describe them as mostly dominated by one-electron process even though with somewhat reduced intensity. Only two satellite states with weak intensity were calculated in this energy range at 18.86 and 19.21 eV.

TABLE III. Ionization potentials (in eV), monopole intensities, and main configurations of the valence ionized states of F_2O.

State	He I UPS[a] IP	OVGF[b] IP	MRDCI[c] IP	SAC–CI SD–R IP	SAC–CI General-R IP	Intensity	Main configuration ($|C|>0.4$)
B_1	13.26	13.06	13.43	13.22	12.99	0.84	$0.89(2b_1^{-1})$
B_2	16.17	16.46	16.36	16.27	16.11	0.80	$0.86(4b_2^{-1})$
A_1	16.47	16.37	16.17	16.48	16.21	0.81	$0.87(6a_1^{-1})$
A_2		16.95		16.80	16.63	0.76	$0.86(1a_2^{-1})$
B_1	18.68	18.85	17.41	18.84	18.49	0.63	$0.77(1b_1^{-1})-0.45(6a_1^{-1}7a_12b_1^{-1})$
A_2					18.86	0.01	$0.75(4b_2^{-1}7a_12b_1^{-1})+0.71(2b_1^{-1}7a_14b_2^{-1})$
B_1					19.21	0.05	$0.60(4b_2^{-1}5b_22b_1^{-1})+0.52(2b_1^{-1}5b_24b_2^{-1})$ $+0.49(2b_1^{-1}7a_16a_1^{-1})+0.44(6a_1^{-1}7a_12b_1^{-1})$
A_1	19.50	19.49	19.52 19.55	19.86	19.51	0.76	$0.81(5a_1^{-1})$
B_2	20.09	20.57	20.49	21.20	20.74	0.73	$0.82(3b_2^{-1})$
B_1					21.23	0.08	$0.59(2b_1^{-1}5b_24b_2^{-1})+0.55(4b_2^{-1}5b_22b_1^{-1})$ $-0.51(6a_1^{-1}7a_12b_1^{-1})-0.44(2b_1^{-1}7a_16a_1^{-1})$
A_2					21.28	0.01	$0.84(2b_1^{-1}5b_26a_1^{-1})+0.52(6a_1^{-1}5b_22b_1^{-1})-0.44(2b_1^{-1}7a_14b_2^{-1})$
B_2					22.26	0.01	$0.76(2b_1^{-1}7a_11a_2^{-1})+0.60(1a_2^{-1}7a_12b_1^{-1})$
A_2					22.44	0.02	$0.47(3b_2^{-1}7a_12b_1^{-1})+0.43(6a_1^{-1}7a_11a_2^{-1})$
A_1					22.92	0.04	$0.52(6a_1^{-2}7a_1)+0.45(5a_1^{-1}7a_16a_1^{-1})$ $-0.42(3b_2^{-1}7a_14b_2^{-1})-0.41(4b_2^{-2}7a_1)$
B_1					23.15	0.01	$0.66(1a_2^{-1}7a_14b_2^{-1})+0.59(2b_1^{-1}7a_15a_1^{-1})$
B_2					23.72	0.03	$0.68(6a_1^{-1}7a_14b_2^{-1})$
A_1					23.98	0.01	$0.51(2b_1^{-1}7a_11b_1^{-1})$
B_2					24.61	0.04	$0.46(6a_1^{-1}7a_14b_2^{-1})$
A_1					24.96	0.01	$0.71(4b_2^{-1}5b_26a_1^{-1})$
A_1					25.35	0.02	$0.67(6a_1^{-1}5b_24b_2^{-1})$
B_2					25.74	0.02	$0.54(4b_2^{-2}5b_2)$
B_1					26.61	0.01	$0.52(2b_1^{-1}5b_23b_2^{-1})-0.40(1a_2^{-1}7a_13b_2^{-1})$
A_1					27.17	0.02	$0.50(4b_2^{-1}7a_13b_2^{-1})-0.48(5a_1^{-1}7a_16a_1^{-1})$
A_2					28.79	0.03	$0.69(3b_2^{-1}7a_12b_1^{-1})$
A_1					28.98	0.10	$0.49(2b_1^{-1}7a_11b_1^{-1})+0.48(1b_1^{-2}7a_1)+0.41(1b_1^{-1}7a_12b_1^{-1})$
A_1					29.86	0.01	$0.44(5a_1^{-1}5b_23b_2^{-1})$
A_1					30.04	0.20	$0.43(4a_1^{-1})-0.47(3b_2^{-1}5b_26a_1^{-1})$
A_1					31.73	0.02	$0.48(6a_1^{-1}7a_15a_1^{-1})+0.41(5a_1^{-1}5b_24b_2^{-1})$
A_1					31.85	0.04	$0.46(6a_1^{-1}5b_24b_2^{-1})$
A_1					33.02	0.10	$0.53(3b_2^{-1}7a_14b_2^{-1})+0.40(6a_1^{-1}7a_15a_1^{-1})$

[a]Reference 18.
[b]Reference 22.
[c]Reference 23.

C. ClOOCl

Dichlorine peroxide (ClOOCl) is a weakly bound dimer of ClO radical, and therefore its electronic structure is closely related to that of ClO. There being no experimental photoelectron spectra of this molecule, description and understanding of its valence electronic structure has compulsory to be based only on theoretical data, chemical and physical arguments, as well as available information of closely related molecules like ClO radical and Cl_2O. The outer-valence ionization spectrum up to ~19 eV of this peroxide was calculated by the SD–R method only. In Table IV, we summarized the results of IPs, monopole intensity, and ionization character and reported the experimental first IP value.[27]

The first two IPs of ClOOCl are expected to lie very close to each other and almost equal to the first IP of ClO, since the corresponding MOs of this compound are nonbonding orbitals of the weakly interacting $3p$ orbital of terminal chlorines. It was argued in Ref. 27 that there should be a blueshift of ~0.2 eV as results of monomers' interaction, ongoing from the radical IP to that of the peroxide, and therefore the first two IPs of the latter molecule should lie around 11.2 eV. These ionizations were calculated at 11.14 and 11.23 eV as A and B states, respectively, which have to be compared with the experimental value of 11.05 eV;[27] note that the ionization threshold only was reported by the experiment. However, the ordering of these two calculated states appear dependent on the used geometry (experimental and optimized) and basis sets, and therefore it is hardly conclusive here. This problem was also left aside in Ref. 27, wherein OVGF results were quoted, but there which only the first IP was reported and no symmetry was specified for it. Next, two states are also characterized as ionizations mainly from the Cl orbitals. These four states are related to the low-lying ionized states of ClO radical observed at 11.01, 11.87, and 12.47 eV by the He I UPS;[61] they were attributed to the ionizations from 3π orbitals, which have a character of Cl $3p$ orbital.

TABLE IV. Ionization potentials (in eV), monopole intensities and main configurations of the valence ionized states of ClOOCl.

State	Expt.[a]	OVGF[a]	SAC–CI SD–R		
			IP	Intensity	Main configuration
A	11.05	11.39	11.14	0.92	$0.92(13a^{-1})$
B			11.23	0.93	$0.94(12b^{-1})$
A			12.33	0.94	$0.95(12a^{-1})$
B			12.88	0.93	$0.96(11b^{-1})$
A			14.02	0.90	$0.91(11a^{-1})$
B			14.17	0.91	$0.92(10b^{-1})$
A			16.88	0.88	$0.88(10a^{-1})$
B			16.98	0.88	$0.90(9b^{-1})$
A			18.59	0.91	$0.91(9a^{-1})$

[a]Reference 27.

In the ionization spectrum of ClO radical vibrational series were observed in the energy region of 14–15 eV (Ref. 61) and were assigned to six electronic states of the singlet and triplet, which are the ionization from 2π MOs of ClO. In the case of ClOOCl, four ionized states were calculated from 14 to 17 eV, and they were related to ionizations from 2π MOs of ClO, and therefore to ionizations mainly from the $2p$ orbitals of the O atom. These ionized states were calculated as one-electron process by the SD–R method. However, the ionized states calculated at 16.88 and 16.98 eV should interact with the excited configurations for the considerations discussed in Sec. III and thus it is not hard to figure out the appearance of non-Koopmans' states in this energy region, analogously to the dichlorine oxide. Finally, the $(9a^{-1})$ state was calculated at 18.59 eV and this state should be related to the $(7\sigma^{-1})$ state of ClO.

D. Discussion of the correlation lines of Cl$_2$O and F$_2$O in the intermediate-energy valence ionization spectra

One of the main results of the present investigation was the demonstration of the occurrence of many correlation lines at relatively low energy in the ionization spectrum of Cl$_2$O with sizable pole strength; they are derived from the $2b_1$, $8a_1$, and $6b_2$ ionizations. At higher energy region, the breakdown of Koopmans' model is a usual feature of the molecular PES,[47(b),47(c)] and thus it was also observed for the $7a_1$ ionization, though we could not calculate all their features because of the energy cutoff at about 26 eV. However, this characteristic feature of the Cl$_2$O spectrum at low energy did not materialize in that of F$_2$O. Indeed, the corresponding $1b_1$, $5a_1$, and $3b_2$ ionizations resulted to possess yet

enough intensity, 0.64–0.76, as to let us consider them still "main" states. Here, we try to explain the main reason for this different behavior of these correlation effects in the two molecules.

For a satellite state to be observed in the PES, two conditions should be realized. First, the shake-up state, usually described by $2h1p$ (two-hole–one-particle) state, should be energetically close to the $1h$ (one-hole) state. Second, the corresponding coupling amplitude $f(1h,2h1p)$ must be sizable in value, which is even more important. When many of these $2h1p$ configurations strongly interact with a $1h$ state, the pole strength associated with the latter is then distributed over many of the former states according to their squared coupling amplitude. As a result, instead of a single line in the expected energy range, several lines characterize the observed band over a larger energy domain.

First, we discuss the shake-up states in the low-energy region of Cl$_2$O PES. In our previous work on the excitation spectra of these molecules,[17] many low-lying singlet valence-excited states were obtained for Cl$_2$O and four of them appear important in the present analysis; namely, the $1B_1(3b_1\rightarrow10a_1,2.9$ eV), the $1B_2(7b_2\rightarrow10a_1,4.4$ eV), the $1A_2(3b_1\rightarrow15b_2,4.6$ eV), and the $2A_1(9a_1\rightarrow10a_1,4.8$ eV) states. The corresponding triplets were calculated by ~1 eV lower, on the average. Note that the $15b_2$ orbital in Ref. 17 corresponds to the $8b_2$ orbital in the present calculations. Let us first consider the $^2A_1$ states whose intensity is due to the $(8a_1^{-1})$ $1h$ state. From the combination between excitation and ionization, important shake-up states can be described as $(3b_2^{-2}10a_1)$, $(7b_2^{-2}10a_1)$ and $(9a_1^{-2}10a_1)$. Since the calculated IPs of four outer-valence ionized states $(3b_1^{-1})$, $(7b_2^{-1})$, $(9a_1^{-1})$, and $(1a_1^{-1})$ were calculated as 11.0, 12.4, 12.6, and 12.9 eV, respectively, the IPs of these shake-up states were estimated as 13.9, 16.8, and 17.2 eV by the suitable combination of the excitation and ionization. Therefore, the $(7b_2^{-2}10a_1)$ and $(9a_1^{-2}10a_1)$ configurations can effectively interact with the $(8a_1^{-1})$ state, whose IP was calculated as ~16.6 eV. Hamiltonian matrix elements between $(8a_1^{-1})$ and these two configurations are also larger than those between $(8a_1^{-1})$ and $(3b_2^{-2}10a_1)$ as shown in Table V. Actually, the split states calculated at 15.69 and 16.56 eV are described by the linear combination of these configurations. A shake-up state of $(3b_2^{-2}10a_1)$ state was also calculated at 13.83 eV, though the intensity is very small as 4×10^{-4}.

For B_1 states in the energy region of 15–17 eV, the $(3b_1^{-1}10a_19a_1^{-1})$, $(7b_2^{-1}10a_12a_2^{-1})$, and $(3b_1^{-1}8b_27b_2^{-1})$

TABLE V. Hamiltonian matrix elements which are important for the satellite peaks of Cl$_2$O (in a.u.).

	$(3b_1^{-2}10a_1)$	$(7b_2^{-2}10a_1)$	$(9a_1^{-2}10a_1)$
$(8a_1^{-1})$	0.000 56	0.014 86	0.016 14
	$(9a_1^{-1}10a_13b_1^{-1})$	$(7b_2^{-1}10a_12a_2^{-1})$	$(7b_2^{-1}8b_23b_1^{-1})$
$(2b_1^{-1})$	0.041 78	0.018 67	0.018 05
	$(3b_1^{-1}10a_12a_2^{-1})$	$(7b_2^{-1}10a_19a_1^{-1})$	$(3b_1^{-2}8b_2)$
$(6b_2^{-1})$	0.004 34	0.017 60	0.002 85

configurations were possible and their IPs were estimated as 15.5, 17.5, and 17.0 eV, respectively, in the same way. Energetically, the $(3b_1^{-1}10a_19a_1^{-1})$ configurations with some spin functions interact with the $(2b_1^{-1})$ and more shake-up states appear in the energy around ~ 15.5 eV. The Hamilton matrix[18] consists of vibrationally resolved first Hamiltonian matrix element between $(2b_1^{-1})$ and $(3b_1^{-1}10a_19a_1^{-1})$ is also large. The shake-up state $(3b_1^{-1}8b_27b_2^{-1})$ of higher energy also has small intensity at 16.57 eV. Two shake-up states represented by the $(7b_2^{-1}10a_12a_2^{-1})$ and $(3b_1^{-1}8b_27b_2^{-1})$ configurations do not interact with $(2b_1^{-1})$ because they are energetically separated, though the Hamiltonian matrix elements are large as shown in Table V. Finally for the B_2 states in this region, the $(3b_1^{-1}10a_12a_2^{-1})$, $(7b_2^{-1}10a_19a_1^{-1})$, and $(3b_1^{-1}8b_22b_1^{-1})$ configurations are expected to exist at 15.9, 17.0, and 15.6 eV, respectively. Accordingly, the shake-up states, described by linear combinations of the $(3b_1^{-1}10a_12a_2^{-1})$ and $(3b_1^{-1}8b_22b_1^{-1})$, were calculated at 14.98 and 15.31 eV, respectively, but with very small intensities. Only the $(7b_2^{-1}10a_19a_1^{-1})$ energetically close interacts with the $(6b_2^{-1})$ state and gives rise to the split states calculated at 17.50 and 17.77 eV.

On the other hand, the valence excited states of F_2O exist at higher energy in comparison with those of Cl_2O; namely, the $1B_1(2b_1 \rightarrow 12a_1, 5.4$ eV$)$, the $1A_2(2b_1 \rightarrow 10b_2, 6.1$ eV$)$, the $1B_2(4b_2 \rightarrow 12a_1, 8.2$ eV$)$ and the $2A_1(6a_1 \rightarrow 12a_1, 8.5$ eV$)$ states,[17] and consequently only the first two excitations are important for the present analysis. Note that $12a_1$ and $10b_2$ MOS of Ref. 17 correspond to the $7a_1$ and $5b_2$ MOs in the present calculation. For the A_1 symmetry, only the $(2b_1^{-2}7a_1)$ is important and its IP is expected to lie around 18.4 eV. This energy is relatively far from the $(5a_1^{-1})$ whose IP is around 19.5 eV. Actually, this shake-up state is calculated at 17.55 eV with somewhat very small intensity. Other configurations such as $(4b_2^{-2}7a_1)$, $(6a_1^{-2}7a_1)$, and $(1a_2^{-2}7a_1)$ were estimated higher than 24 eV and therefore do not interact with the $(5a_1^{-1})$. For B_1 and B_2 states, the important $(2b_1^{-1}7a_16a_1^{-1})$ and $(2b_1^{-2}5b_2)$ configurations were estimated at 19.6 and 19.1 eV, respectively. These shake-up states were calculated at 19.21 and 18.17 eV; however, the $(1b_1^{-1})$ and $(3b_2^{-1})$ states exist at about 18.5 and 20.7 eV, respectively, hence they do not interact with these shake-up states. Other configurations, i.e., $(2b_1^{-1}5b_24b_2^{-1})$ and $(2b_1^{-1}7a_11a_2^{-1})$, were estimated above 22 eV and have nothing to do with the satellite peaks in this region.

Thus, the difference of the satellite spectra in the intermediate energy region between Cl_2O and F_2O can be interpreted by the consideration of the outer-valence ionized states and the low-lying excited states of these molecules; for Cl_2O, there exist many shake-up states that interact strongly with the one-electron process, whereas such states do not exist for F_2O because of less low-lying excited states.

IV. CONCLUSIVE REMARKS

In this paper we reported the SAC–CI studies on the valence-ionization spectra of dihalogen oxides F and Cl whose importance has recently gained momentum in the photochemistry of the high terrestrial atmosphere but whose understanding of their electronic structure has presented some gaps. Theoretical investigations were performed to cover the entire valence region of the ionization spectra, but practically they were limited up to about 25–30 eV, because experimental spectra have not yet been reported for the inner-valence region. The outer-valence ionizations were first investigated by the SD–R approach which gives quite accurate results for one-electron processes. Then, to check for the validity of this picture and to search for the shake-up and correlation dominated ionic states, possibly populating even the outer-valence region, we adopted the general-R method which can accurately calculate the multielectron processes while preserving a good description of main peaks.

For Cl_2O, we have shown that our data correctly describes the He I PES both in energy and pole-strength distribution and allows us to present firm assignments of the main and secondary features of the experiments up to 20 eV, even though we have calculated the spectrum up to about 25 eV. In particular, our studies pointed out the occurrence of some important satellite lines with non-negligible intensity from ~ 14 eV upward, together with a break-down of the one-particle picture for $(2b_1^{-1})$, $(8a_1^{-1})$, $(6b_2^{-1})$, and $(5b_2^{-1})$ states, all lying in the intermediate outer-valence region.

For F_2O, however, these strong many-body effects observed for Cl_2O appeared less intense and no satellites with interesting intensity were calculated in the corresponding energy region. These were originated mainly by the $1b_1$ ionization, whose relative intensity was strongly reduced and lying at energy greater than 20 eV. Other B_2 satellite states got somewhat less intensity. We have analyzed the origin of this noteworthy difference in the PES of Cl_2O and F_2O with simple terms and explained it qualitatively.

For ClOOCl, we confined our investigation within the SD–R method since there are no experimental data on ionization energies of this molecule. We proposed a qualitative description of the outer-valence ionization spectrum of ClOOCl and discussed its assignments in comparison with the spectrum of ClO.

APPENDIX: EXAMINATION OF THE GEOMETRY AND BASIS SETS

We have examined the effect of the geometry parameters and of the basis set in calculating the ionization spectra of the three above-discussed molecules within the SAC–CI SD–R method; the geometries were shown to be quite important for the excitation energies for Cl_2O and ClOOCl.[17] The experimental and optimized geometries of the molecules adopted in the present work were summarized in Table I of Ref. 17.

For Cl$_2$O, calculations were performed at experimental (r_e = 1.695 87 Å, < ClOCl = 110.86°) and optimized geometry by MP2/6-311G* (r_e = 1.7319 Å, ∠ ClOCl = 111.61°) method. MP2 energy-optimized geometries at 6-311G* or 6-31G* levels, have preferably been used in the theoretical studies[9–12,17] on the VUV electronic spectrum of Cl$_2$O rather than the experimental one. For calculating the ionization spectrum, the differences in the geometrical parameters of Cl$_2$O, which are 1–2 % in the bond distance and less in the bond's angle, did not seem to bring any noticeable effect on the outermost four ionized states. For the states lying in the intermediate outer-valence region, instead the experimental geometry produced higher IPs by 0.2–0.8 eV at both SCF and SAC–CI SD–R levels. The experimental geometry seemed more appropriate to interpret and describe the vertical IPs of Cl$_2$O regardless of the basis sets, while the opposite situation was met in the studies of electronic excitation spectra.[9–12,17]

For Cl$_2$O, we examined three different basis sets. First, we used the 6-311G* basis set for both atoms; i.e., the same as that of MP2 energy optimization. It is the polarized triple-zeta basis sets of Kishnan et al.;[62] $(13s9p1d)/[6s5p1d]$ with ζ_d = 0.75 for Cl and $(11s5p1d)/[4s3p1d]$ with ζ_d = 1.29 for O. Then, we used the cc-pVTZ of Dunning[63] for both atoms; i.e., $(16s10p2d1f)/[5s4p2d1f]$ for Cl and $(10s5p2d)/[4s3p2d]$ for O. Finally, we adopted the triple-zeta basis set of McLean and Chandler,[53] $(13s10p1d)/[6s5p1d]$ with ζ_d = 0.514 for Cl, and that of Huzinaga–Dunning,[55] $(11s6p1d)/[4s3p1d]$ with ζ_d = 0.85 for O. These basis sets generated 70, 98, and 71 AOs, respectively. In the SD–R calculation, the first basis set, i.e., the 6-311G*, and the third one essentially produced the same results for all the valence ionization, whereas the cc-pVTZ basis set gave IPs higher by 0.3–0.5 eV.

For F$_2$O, we also examined three basis sets; the triple-zeta $(10s6p)/[5s3p]$ of Huzinaga–Dunning[55] augmented by one d-type polarization function ζ_d = 0.85 and ζ_d = 0.90 for O and F atoms (57 AOs), the 6-311G* (57 AOs), and the cc-pVTZ (90 AOs). The Dunning's cc-pVTZ basis set gave rather higher IPs within SAC–CI SD–R method similarly to Cl$_2$O. In the case of F$_2$O, there were no remarkable discrepancies between the optimized geometry by MP2/6-311G* and the experimental one. Actually, the geometry dependence was quite small for the IPs and therefore we used the latter geometry in our SAC–CI calculations.

For ClOOCl, the experimental geometry is different from the optimized ones at the MP2 levels using 6-311G* and 6-31G* basis sets, or from that obtained within the CAS–CI, and CASSCF[11,12] methods. The bond distances showed discrepancies by 2%–5%. Its potential surface seemed to have several other local minima and saddle points of different order, especially for the torsional O–O angle, which caused often energy optimization instability. Several problems occurred in both the SCF and SAC–CI calculations using these molecular geometries. We examined at least six different basis sets for the peroxiside; 6-31G*, 6-311G*, pVTZ of Ahlrichs,[64] pVTZ of Sadlej,[65] cc-pVTZ of Dunning, pVTZ of the McLean–Chandler (Cl) and Huzinaga–Dunning (O). Results with the experimental geometry

showed unusual high basis set dependence either at SCF or SAC–CI levels. Discrepancies between the corresponding results ranged around 1–2 eV, making the comparisons troublesome. This situation also seems to replicate, at least in part, even for the optimized geometries. At the moment, we cannot offer any reasonable explanation for this outcome.

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