

# Electronic excitation spectra of Cl<sub>2</sub>O, ClOOCl, and F<sub>2</sub>O: A SAC-CI study

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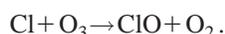
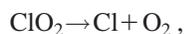
The SAC-CI method was applied to the electronic excitation spectra of Cl<sub>2</sub>O, ClOOCl, and F<sub>2</sub>O. The ensuing theoretical spectra have well reproduced the experimental spectra for Cl<sub>2</sub>O and Cl<sub>2</sub>O<sub>2</sub> and detailed characterizations of the peaks and structures were given by calculating the oscillator strength, second moment, and dipole moment for each state. For the UV region of Cl<sub>2</sub>O, the observed peaks were assigned to the valence excited states in agreement with the previous theoretical studies. For the VUV region, in the present study we have proposed the first theoretical assignments. Both valence and Rydberg excited states were calculated in this energy region, some of which resulted different from the experimental assignments. For Cl<sub>2</sub>O<sub>2</sub>, the broad band of the experimental spectrum was mainly attributed to one intense peak due to the 3B state. The theoretical spectrum above 6 eV was proposed, which so far has not been addressed and clarified before. The excitation spectrum of F<sub>2</sub>O up to about 13.0 eV was calculated and compared with the previous theoretical study. The shape and main features of the calculated spectrum was found to be very similar to that of Cl<sub>2</sub>O, and the valence and Rydberg excited states were clearly discriminated. © 2002 American Institute of Physics. [DOI: 10.1063/1.1433504]

## I. INTRODUCTION

The photoabsorption and dissociation processes of Cl<sub>2</sub>O<sub>2</sub><sup>1-8</sup> and Cl<sub>2</sub>O<sup>8-16</sup> have attracted considerable attention since these processes are involved in the ozone depletion catalytic cycles in the Antarctic stratosphere. It is generally recognized that the most important chain reactions in the ozone depletion cycle start from



The photoabsorption of ClOOCl produces either ClO<sub>2</sub> or ClO, which leads to the destruction of the ozone through the following chain reaction:



Thus, the photoabsorption of ClOOCl playing a key role in the cycle, its UV absorption cross sections, and its photodynamics have been intensively studied both in experimental and theoretical works.<sup>1-8</sup> The absorption spectrum up to only ~6.5 eV has been recorded. The photoabsorption and dissociation processes have also been theoretically investigated and the ClO cleavage was rationalized by some theoretical findings for which the low-lying excited states are characterized as excitations into a localized  $\sigma^*(\text{Cl}-\text{O})$  orbital.<sup>7</sup>

The reactions including Cl<sub>2</sub>O are thought to be less important in the stratospheric chemistry. However, this molecule is the acid anhydride of HOCl, which is one of the

most important chlorine reservoir species in the atmosphere. Therefore, the photochemistry of Cl<sub>2</sub>O has also been studied in recent years. Representative works on the absorption spectrum in the UV region were due to Nee,<sup>12</sup> Lin,<sup>13</sup> Molina *et al.*,<sup>14</sup> Knauth *et al.*,<sup>15</sup> Johnsson *et al.*,<sup>7</sup> and Nickolaisen *et al.*<sup>8</sup> Recently, Motte-Tollet *et al.*<sup>9</sup> observed the VUV absorption spectrum of Cl<sub>2</sub>O. These works have shown several continuous and partially overlapping bands which peak at about 2.3, 2.9, 4.9, and 7.3 eV in the UV region, and at 7.7, 8.7, 9.0, 9.2, and 9.4 eV with well-resolved vibrational structure.

Different theoretical assignments have been proposed for the UV spectrum of Cl<sub>2</sub>O. Del Bene *et al.*<sup>14</sup> have calculated the low-lying singlet excited states of Cl<sub>2</sub>O up to about 5 eV with the EOM-CCSD(T) method and found that three singlet states contributed to the very weak and medium peaks in 2.8–5.0 eV. Recently, Toniolo *et al.*<sup>8</sup> have studied the excitation spectra up to about 7 eV by using the perturbed MRCI method, and have also simulated the spectrum using semi-classical calculations of the integral cross sections. Both studies adopted theoretically optimized geometry in the calculations of the absorption spectrum. On the other hand, Nickolaisen *et al.*<sup>10</sup> performed CASSCF/MRSD-CI calculations with the experimental geometry. Their interpretation of the spectrum was very different from those of Refs. 14 and 8. Consequently, there were some contradictions in the assignments of the excitation spectrum even in the low energy region. It should be also noted that there is no theoretical assignments for the higher energy region, namely, above 8.0 eV.

On the other hand, F<sub>2</sub>O has been much less focused both

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TABLE I. Geometries of Cl<sub>2</sub>O, ClOOCl and F<sub>2</sub>O.

	Expt. <sup>a</sup>	MP2/6-311G*	CAS-MRCI/pVTZ <sup>b</sup>	CCSD(T)/POL1 <sup>c</sup>
Cl <sub>2</sub> O				
<i>R</i> <sub>ClO</sub> (Å)	1.69587	1.7319	1.7139	1.757
<ClOCl	110.886	111.61	113.95	110.7
ClOOCl				
	Expt. <sup>d</sup>	MP2/6-311G*	CAS-CI/VTZ1P <sup>b</sup>	MP2/6-31G* <sup>e</sup>
<i>R</i> <sub>ClO</sub> (Å)	1.704	1.7661	1.7839	1.7442
<i>R</i> <sub>OO</sub> (Å)	1.426	1.3712	1.4544	1.4188
<ClOO	110.1	110.4388	109.7	109.018
<ClOOCl	81.9	84.6346	83.2	85.103
F <sub>2</sub> O				
	Expt. <sup>f</sup>	MP2/6-311G*		
<i>R</i> <sub>FO</sub> (Å)	1.4053	1.409		
<FOF	103.4	103.2		

<sup>a</sup>Reference 44.<sup>b</sup>Reference 8.<sup>c</sup>Reference 16.<sup>d</sup>Reference 45.<sup>e</sup>Reference 7.<sup>f</sup>Reference 46.

theoretically and experimentally, though it is supposed to have similar chemical and spectroscopic properties with Cl<sub>2</sub>O. Little is known on its excited and ionized states. The MRCI method<sup>17</sup> was applied to its vertical excitation spectrum by Valenta *et al.*, but only in the low energy region. Unfortunately, the oscillator strengths were not determined there and the characterization of the excited states seems to be incomplete and questionable.

In this work, we have applied the SAC-CI method to the excitation spectra of Cl<sub>2</sub>O, ClOOCl, and F<sub>2</sub>O. The detailed characterizations of the valence and Rydberg excited states are presented by calculating the oscillator strength, second moment and dipole moment. The SAC<sup>18</sup>/SAC-CI<sup>19–21</sup> method has been successfully applied to various kind of molecular spectroscopies for numerous systems, from simple molecules<sup>22–27</sup> to some biological systems.<sup>28–30</sup> Recently, moreover, very accurate theoretical studies<sup>31–34</sup> on the multi-electron processes were also performed using the SAC-CI general-*R* method.<sup>31,34</sup> In the present study, all the excited states are well-described by one-electron processes; therefore, the SAC-CI SD-*R* method is used.

## II. COMPUTATIONAL DETAILS

Vertical excitation spectra of Cl<sub>2</sub>O, ClOOCl, and F<sub>2</sub>O were investigated by the SAC-CI method. The optimized geometries, by the MP2/6-311G\*<sup>35</sup> method, were used for these molecules because of the reasons described in Sec. III A. Extensive basis sets were adopted for calculating both valence and Rydberg excited states. The valence basis sets were those TZP of Huzinaga–Dunning<sup>36,37</sup> [*5s3p1d*] for O and F, the [*6s5p1d*] of McLean and Chandler<sup>38</sup> for Cl. For Cl<sub>2</sub>O, the Rydberg functions,<sup>39</sup> of double-zeta quality, were added with the exponent of  $\zeta_s = 0.0608, 0.024, \zeta_p = 0.0532, 0.021, \zeta_d = 0.0285, 0.01125$  for O, and  $\zeta_s = 0.0475, 0.01875, \zeta_p = 0.038, 0.015, \zeta_d = 0.0285, 0.01125$  for Cl. For ClOOCl and F<sub>2</sub>O, we added the Rydberg functions of exponent,  $\zeta_s = 0.032, \zeta_p = 0.028, \zeta_d = 0.015$  for O,  $\zeta_s = 0.036, \zeta_p = 0.029, \zeta_d = 0.015$  for F, and  $\zeta_s = 0.025, \zeta_p = 0.02, \zeta_d = 0.015$  for Cl. We have also examined the geometry and

basis set dependence of the excitation energy for the valence excited states using VTZ1P basis sets such as the 6-311G\*<sup>35</sup> and the cc-pVTZ<sup>40</sup> basis sets. This point is discussed in Sec. III A.

The ground and excited states of these molecules were calculated by the SAC/SAC-CI method. The *1s* orbitals of O and F and *1s, 2s,* and *2p* orbitals of Cl were kept frozen as core and all the other MOs were included in the active space. In order to reduce the computational effort, perturbation selection<sup>24</sup> was performed in the state-selection scheme.<sup>41</sup> The threshold of the linked term for the ground state was set to  $\lambda_g = 1 \times 10^{-5}$  and the unlinked terms are adopted as the products of the important linked terms whose SDCI coefficients are larger than 0.005. For the excited states, the threshold of the doubly linked term is set to  $\lambda_e = 1 \times 10^{-6}$ . The thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method are 0.05 and 0.001 for the *R* and *S* operators, respectively.

HF SCF calculations were performed using GAUSSIAN 98<sup>42</sup> and SAC/SAC-CI calculations were done using the SAC96 program system.<sup>43</sup>

## III. RESULTS AND DISCUSSIONS

### A. Ground state geometries for Cl<sub>2</sub>O, ClOOCl, and F<sub>2</sub>O

First we have examined the effect of the geometries and basis sets on calculating the excitation spectra of these molecules. Theoretically determined and experimental geometries for Cl<sub>2</sub>O, ClOOCl, and F<sub>2</sub>O are summarized in Table I.

The experimental geometry of Cl<sub>2</sub>O appears to slightly shrink in comparison with the MP2/6-311G\* one, which is, however, intermediates between those of Refs. 8 and 16. In these theoretical works, optimized geometries were adopted for calculating the vertical excitation spectrum, whereas Nickolaisen *et al.*<sup>10</sup> preferred the experimental one in their CASSCF-MRDCI calculations. Small differences exist in these geometrical parameters, especially in the Cl–O bond

distance. The orbital energies of the four outermost occupied MOs are much less dependent on tiny differences in the geometries; however, those of the anti-bonding MOs change by  $\sim 0.5$  eV. Consequently, the excitation energies were calculated higher by 2–5 tenths of eV with the experimental geometry. We shortly examined the potential energy surfaces (PES) of  $\text{Cl}_2\text{O}$  using the smaller basis sets without Rydberg functions such as 6-311G\* and cc-pVTZ and found that the PES of the ground and excited states had different slope along the Cl–O distance. The excitation energies were calculated rather high with the experimental geometry to interpret the experimental spectrum. Thus, we decided to use the optimized geometry, obtained by the MP2/6-311G\* method, for the final calculations with the extended basis sets of the singlet excited states of  $\text{Cl}_2\text{O}$  up to 10–11 eV.

For  $\text{ClOOCl}$ , the SAC-CI calculations using MP2-optimized geometry also gave better excitation energy than those with the experimental one, regardless of the basis sets, to understand the measured UV electronic spectrum. Our MP2/6-311G\* geometry is quite close to those theoretically determined in Refs. 7 and 8 except for the O–O bond length, which appears somewhat shorter (1.371 Å), but yet close to the CASSCF results. Again, we obtained excitation energies systematically higher by up to 0.5 eV using the experimental geometry. The calculations with optimized geometry further well reproduced the first IP, though little is known on the valence MOs and their IPs: only the first IP was reported in Ref. 47.

For  $\text{F}_2\text{O}$ , there is no large discrepancy between the MP2/6-311G\* geometrical parameters and the experimental ones in the  $C_{2v}$  symmetry. Thus, we simply adopted our MP2/6-311G\* geometry, namely,  $R_{\text{FO}} = 1.409$  Å and  $\angle\text{FOF} = 103.2$  degrees.

## B. $\text{Cl}_2\text{O}$

Dichlorine monoxide is a gaseous molecule belonging to  $C_{2v}$  symmetry with 20 valence electrons. The HF configuration is written as (core) $(6a_1)^2(5b_2)^2(7a_1)^2(2b_1)^2 \times (6b_2)^2(8a_1)^2(2a_2)^2(9a_1)^2(7b_2)^2(3b_1)^2$ . This energy ordering of MOs agrees quite well with the photoelectron spectrum (PES) as far as the outer-valence ionized states are concerned. The UV absorption spectrum of  $\text{Cl}_2\text{O}$  has recently been recorded by Nickolaissen *et al.*<sup>10</sup> from 2 up to 7.5 eV and the VUV spectrum by Motte-Tollet *et al.*,<sup>11</sup> from 6.5 to 9.7 eV. The former spectrum indicates excited states at 2.9 eV (420 nm), 4.1 eV (300 nm), 4.88 eV (254 nm), and 7.24 eV (171 nm) as peaks or shoulders of three congested and partially overlapping bands, whose intensity decreases towards the low energy region through several orders of magnitude. Additionally, a small peak was also found at 2.3 eV (540 nm). Motte-Tollet *et al.* measured some strong absorptions between 6.5–9.7 eV, the structureless band at 7.25 eV proposed as a valence state, and five vibrationally resolved bands peaked at 7.7, 8.7, 9.0, 9.2, and 9.4 eV interpreted as Rydberg excited states. It is important to understand the very nature of these excited states in order to develop the dynamical models for the dissociation patterns of  $\text{Cl}_2\text{O}$ . To this end, detailed theoretical investigations within the

EOM-CCSD(T),<sup>16</sup> CASSCF-MRCI,<sup>10</sup> and CAS/modified MRCI,<sup>8</sup> have been performed. Unfortunately, these studies, though adopting large basis sets, have only searched for low-lying valence excited states and did not cover the higher energy VUV region of the spectrum. Furthermore, the different and to some extent conflicting assignments which have been proposed therein supposedly are originated in the different geometries, as noted in Sec. III A. In this work for dichlorine monoxide, we adopted the energy-optimized structure and calculated 28 singlet excited states up to around its first IP. They are summarized in Table II together with the oscillator strength, dipole moment, and second moment. Therein the results of the aforementioned previous theoretical studies are also given for a comparison.

First, we discuss the spectrum in UV region, 3–7.5 eV, where peaks are attributed to the valence excited states. The SAC-CI stick-spectrum in this region is shown in Fig. 1 together with the UV spectrum. To the weak band around 2.9 eV we assign the first  $B_1$  state calculated at 2.92 eV in agreement with previous studies.<sup>8,16</sup> This is an excited state of HOMO–LUMO transition ( $3b_1 \rightarrow 10a_1$ ) in which the  $2p(\pi)$  charge of O is transferred into the  $3p$  (in plane) of Cl leading to a reduction of the dipole moment. Here this state seems to be differently characterized from the characterization given by Del Bene *et al.*<sup>16</sup> For the shoulder observed at 2.3 eV, no singlet state was calculated, therefore we would assign this to a triplet state. Next, we find a relatively broad band from 3.5 to 6 eV wherein some electronic states possibly contribute to the absorption. We have calculated three states in this energy domain; two almost degenerate states at 4.42 eV ( $1B_2$ ) and 4.57 eV ( $1A_2$ ), and a third state at 4.81 eV ( $2A_1$ ). The oscillator strengths for  $1B_2$  and  $2A_1$  states are consistent with experiment and CI work,<sup>8</sup> though the former one was calculated relatively weak. The  $1B_2$  state is described as  $7b_2 \rightarrow 10a_1$  (LUMO), which corresponds to an  $n - \sigma^*$  transition. Charge flows from Cl into O, and thus resulting in a stronger dipole moment ( $-0.40$  a.u.) for this state. The  $A_2$  state is optically forbidden, but it could acquire intensity by vibronic coupling and therefore contribute to the absorption band.<sup>8</sup> The interpretation up to this band is basically the same as that of Ref. 8.

For the most intense band from 5.8 to 8 eV, peaked at 7.25 and 7.70, only the recent study of Toniolo *et al.* serves to compare with our results. For the first peak, we have calculated three singlet excited states, that is, the  $2B_1$ ,  $3A_1$ , and  $2B_2$  states at 6.97, 7.14, and 7.55 eV, respectively. The  $2B_2$  state, mainly a  $9a_1 \rightarrow 15b_2$  excitation, was calculated to have the largest oscillator strength (0.21) among the valence excited states. Toniolo *et al.* also assigned one or two  $B_2$  states to this peak. However, in the experimental work combined with the MRD-CI calculations of Ref. 19, the  $B_1$  state instead was attributed to this intense peak, even though its oscillator strength was calculated too weak. We further attribute the  $2B_1$  and  $3A_1$  states, characterized as ( $3b_1 \rightarrow 10a_1$ ) and ( $7b_2 \rightarrow 15b_2$ ) excitations, respectively, to the shoulder below this intense band.

Next, we discuss the spectrum of  $\text{Cl}_2\text{O}$  in the energy

TABLE II. Excitation energy (eV), oscillator strength, second moment, dipole moment, and excitation character for the singlet excited states of Cl<sub>2</sub>O.

State	Expt. <sup>a</sup> ΔE	SAC-CI					MR-CI <sup>a</sup> ΔE	MR-CI <sup>a</sup> ΔE	EOM-CCSD(T) <sup>d</sup> ΔE
		ΔE	Osc. str.	$\langle r^2 \rangle$	$\langle r \rangle$	Character <sup>b</sup>			
1A <sub>1</sub>	...	...	...	338	-0.30				
1B <sub>1</sub>	2.90	2.92	0.0001	340	-0.11	3b <sub>1</sub> -10a <sub>1</sub> (V)	2.68	3.42	2.82
1B <sub>2</sub>	4.20	4.42	0.0106	338	-0.40	7b <sub>2</sub> -10a <sub>1</sub> (V)	4.39	4.98	4.23
1A <sub>2</sub>		4.57	-	340	-0.23	3b <sub>1</sub> -15b <sub>2</sub> (V)	4.39	4.97	4.23
2A <sub>1</sub>	4.88	4.81	0.0005	339	-0.45	9a <sub>1</sub> -10a <sub>1</sub> (V)	4.47	5.45	4.66
2A <sub>2</sub>		5.69	...	341	-0.11	2a <sub>2</sub> -10a <sub>1</sub> (V)	4.88	5.88	5.01
2B <sub>1</sub>		6.97	0.0045	341	-0.05	2b <sub>1</sub> -10a <sub>1</sub> (V)	6.41	7.34	
3A <sub>1</sub>		7.14	0.0004	341	-0.23	7b <sub>2</sub> -15b <sub>2</sub> (V)	5.35		
2B <sub>2</sub>	7.25	7.55	0.2066	342	-0.10	9a <sub>1</sub> -15b <sub>2</sub> (V)	6.77	7.98	
3B <sub>1</sub>	7.70	7.85	0.0453	383	0.22	3b <sub>1</sub> -11a <sub>1</sub> (s)	6.58		
4B <sub>1</sub>		8.25	0.0000	343	-0.10	2a <sub>2</sub> -15b <sub>2</sub> (V)			
3A <sub>2</sub>		8.62	...	419	-0.18	3b <sub>1</sub> -8b <sub>2</sub> (p)			
4A <sub>1</sub>	8.68	8.73	0.0103	411	-0.48	3b <sub>1</sub> -4b <sub>1</sub> (p)			
5B <sub>1</sub>		8.74	0.0025	417	-0.29	3b <sub>1</sub> -12a <sub>1</sub> (p)			
5A <sub>1</sub>	9.03	8.98	0.0396	350	0.35	8a <sub>1</sub> -10a <sub>1</sub> (V)			
3B <sub>2</sub>	9.23	9.20	0.0344	384	0.59	7b <sub>2</sub> -11a <sub>1</sub> (s)			
6B <sub>1</sub>		9.34	0.0021	451	0.20	3b <sub>1</sub> -14a <sub>1</sub> (d)			
6A <sub>1</sub>		9.39	0.0173	459	0.25	3b <sub>1</sub> -5b <sub>1</sub> (d)			
4A <sub>2</sub>		9.40	...	471	-0.01	3b <sub>1</sub> -9b <sub>2</sub> (d)			
7A <sub>1</sub>	9.44	9.41	0.0628	393	0.52	9a <sub>1</sub> -11a <sub>1</sub> (s)			
4B <sub>2</sub>	9.44	9.42	0.0257	476	0.30	3b <sub>1</sub> -3a <sub>2</sub> (d)			
7B <sub>1</sub>	9.44	9.43	0.0073	462	-0.55	3b <sub>1</sub> -13a <sub>1</sub> (d)			
5A <sub>2</sub>		9.82	...	457	0.44	2a <sub>2</sub> -11a <sub>1</sub> (s)			
6A <sub>2</sub>		9.98	...	368	0.17	2b <sub>1</sub> -15b <sub>2</sub> (V)			
5B <sub>2</sub>		10.03	0.4409	382	-0.59	6b <sub>2</sub> -10a <sub>1</sub> (V)			
6B <sub>2</sub>		10.17	0.0985	395	0.22	7b <sub>2</sub> -12a <sub>1</sub> (p)			
7A <sub>2</sub>		10.18	...	522	0.48	3b <sub>1</sub> -11b <sub>2</sub> (p)			
8A <sub>1</sub>		10.28	0.0010	432	0.21	7b <sub>2</sub> -8b <sub>2</sub> (p)			
7B <sub>2</sub>		10.31	0.0003	429	-0.35	9a <sub>1</sub> -8b <sub>2</sub> (p)			

<sup>a</sup>Reference 10.<sup>b</sup>V, s, p, and d in the parentheses mean valence, Rydberg s, p, and d excitation, respectively.<sup>c</sup>Reference 8.<sup>d</sup>Reference 16.

region of 7.5–10 eV, whose VUV absorption spectrum was observed and recorded by Motte-Tollet *et al.*<sup>11</sup> In Fig. 2 we compare the SAC-CI stick-spectrum with that experimental in this energy region. At 7.70 eV, a broad band involving well-resolved vibrational structures was observed and interpreted as a Rydberg <sup>1</sup>B<sub>1</sub> (4s) state. We support this assignment: We have indeed calculated the 3B<sub>1</sub> state, (3b<sub>1</sub> → 11a<sub>1</sub>, 4s), at 7.85 eV with an oscillator strength of 0.045. For the peaks extending in the 8.5–9.1 eV region, optically allowed A<sub>1</sub> and B<sub>1</sub> 4p-Rydberg excited states were assigned and the band's profile was fitted to four vibrational progressions related to these two states.<sup>11</sup> Accordingly, we have got two 4p-Rydberg states, 4A<sub>1</sub>(3b<sub>1</sub> → 4b<sub>1</sub>, 4p) and 5B<sub>1</sub>(3b<sub>1</sub> → 12a<sub>1</sub>, 4p) states at 8.73 and 8.74 eV, respectively, the first transition having a dominant oscillator strength. Dipole forbidden transition into 4p-Rydberg state is also calculated as the 3A<sub>2</sub> state at 8.62 eV. For the peak observed at 9.03 eV, we assign though the valence excited state 5A<sub>1</sub>(8a<sub>1</sub> → 10a<sub>1</sub>, V) calculated at 8.98 eV. This peak was reported to exhibit a vibrational envelope different from those of b<sub>1</sub> → 4s and b<sub>1</sub> → 4p transitions and was assigned to b<sub>2</sub> → 4s Rydberg transition in the experimental work.<sup>11</sup>

In the energy region of 9.1–9.7 eV, two series of peaks were observed; namely, relatively low intensity peaks appearing at 9.1–9.35 eV and high-intensity peaks extending

from 9.35 to 9.7 eV. Both peaks were assigned dominantly to be b<sub>1</sub> → 4d transition and some contribution from a<sub>1</sub> → 4s was also suggested.<sup>11</sup> In this energy region, we have calculated many congested Rydberg states. For dipole allowed transitions to 4s-Rydberg states, the 3B<sub>2</sub>(7b<sub>2</sub> → 11a<sub>1</sub>) and 7A<sub>1</sub>(9a<sub>1</sub> → 11a<sub>1</sub>) excited states were calculated with considerable oscillator strengths at 9.20 and 9.41 eV, respectively. The 3d-Rydberg transitions were also calculated as 6B<sub>1</sub>(3b<sub>1</sub> → 14a<sub>1</sub>), 6A<sub>1</sub>(3b<sub>1</sub> → 5b<sub>1</sub>), 4B<sub>2</sub>(3b<sub>1</sub> → 3a<sub>2</sub>), and 7B<sub>1</sub>(3b<sub>1</sub> → 13a<sub>1</sub>). Around 10 eV below the first IP, we have moreover calculated many electronic states, one of which, the 5B<sub>2</sub> state is assigned to be a valence excited state (6b<sub>2</sub> → 10a<sub>1</sub>) bearing a very large oscillator strength of 0.44. Unfortunately, no experimental data are available in this energy region.

The experimental oscillator strengths were reported for the VUV absorption spectrum in 6.5–9.7 eV.<sup>11</sup> For the valence and Rydberg transitions, at 7.25 and 7.70 eV, respectively, our calculation estimated 0.207 and 0.045, respectively, in comparison with the experimental values of 0.076 and 0.085. For the peaks between 8.1–9.2 eV, the sum of the calculated oscillator strengths for the 4A<sub>1</sub>, 5A<sub>1</sub>, and 3B<sub>2</sub> states amounted to 0.087, which appears relatively small in comparison with experiment (0.188). The calculated oscillator strengths for the energy region of 9.2–9.7 eV summed up

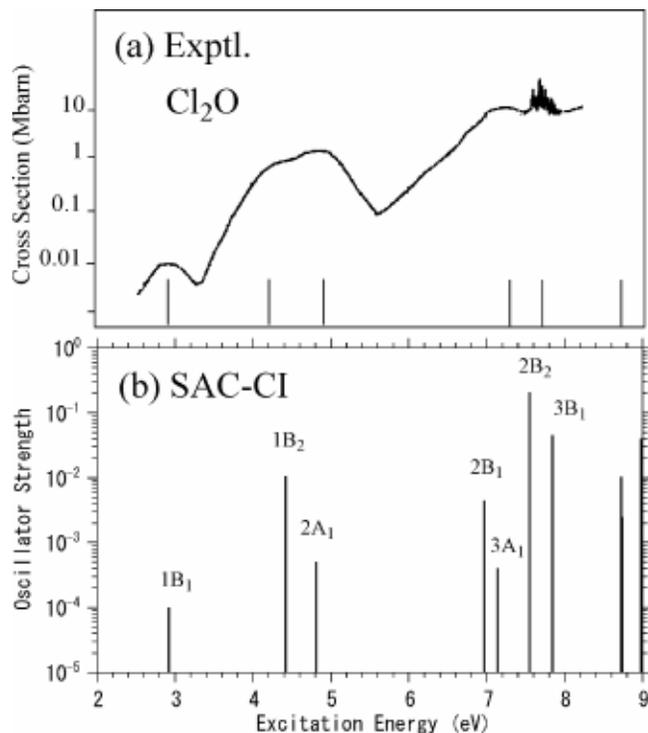


FIG. 1. (a) Experimental (Refs. 15 and 11) and (b) SAC-CI excitation spectra of  $\text{Cl}_2\text{O}$  in the UV region.

to 0.115, whereas in Ref. 11 a value of 0.156 was reported for this region.

### C. CIOOCI

Dichlorine peroxide is regarded as the most stable dimer of the ClO radical.<sup>47,48</sup> Its geometry has been determined in the recent experimental work of Birk *et al.*<sup>45</sup> and belongs to the  $C_2$  point group. The HF configuration of  $\text{Cl}_2\text{O}_2$  reads as (core)  $\dots (11a)^2(10b)^2(11b)^2(12a)^2(13a)^2(12b)^2$ . The UV spectrum of  $\text{Cl}_2\text{O}_2$  was recorded by Cox *et al.*,<sup>1</sup> Burkholder *et al.*,<sup>3</sup> and More *et al.*<sup>2,4,5</sup> Experimentally a broadband was observed extending from about 3.4 to about 6 eV with its maximum at 5.06 eV, and other absorption seemed to be observed at around 6.5 eV and beyond. The electronic excited states of  $\text{Cl}_2\text{O}_2$  have been theoretically investigated by Jensen *et al.*,<sup>6</sup> Stanton *et al.*,<sup>7</sup> and more recently also by Toniolo *et al.*,<sup>8</sup> using the RPA, EOM-CCSD, and CAS-MRCI methods, respectively. In these studies, it was noted that the singlet excited state calculated near 5.1 eV, the  $3B_1$ , has a relatively strong oscillator strength and could well be responsible for the photodissociation into  $\text{ClO}_2 + \text{Cl}$  or ClO radicals. However, there are some differences in these studies. The excitation energies of the CAS-MRCI calculations were calculated to be smaller by 0.4–1.1 eV than those of the EOM-CCSD calculations. Differences were found in the calculated oscillator strengths too; Stanton *et al.* calculated three intense transitions to the  $4A$ ,  $2B$ , and  $3B$  states, while Toniolo *et al.* showed that only the  $3B$  state is responsible for intense absorption. Note that Toniolo *et al.* used the experimental geometry, while Stanton *et al.* adopted a MP2/6-31G\* geometry. Unfortunately, both calculations do

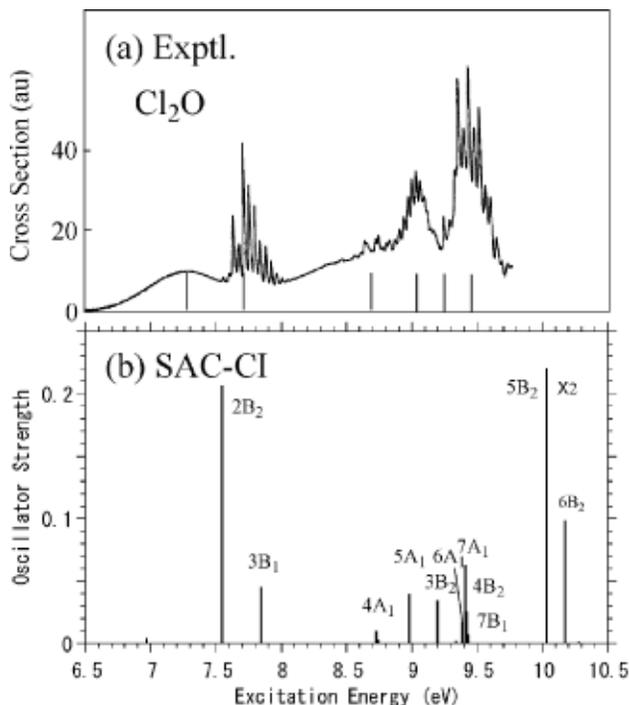


FIG. 2. (a) Experimental (Ref. 11) and (b) SAC-CI excitation spectra of  $\text{Cl}_2\text{O}$  in the VUV region.

not cover the energy region of the shorter wavelength where the experimental intensity remains high around 6.5 eV.

In Table III, we present our SAC-CI results for the  $\text{Cl}_2\text{O}_2$  singlet excited states together with the previous theoretical results. We also compared the SAC-CI excitation spectrum with the experimental spectrum in Fig. 3. Since we were further interested in predicting the VUV spectrum and searching for the Rydberg excited states in this unexplored energy region, we calculated seven lowest states for each symmetry. As discussed in Sec. III A, we adopted the MP2/6-311G\* optimized structure for the final results.

First, for the prominent peak of the experimental spectrum, the  $1A \rightarrow 3B$  transition was calculated at 5.57 eV with a somewhat large oscillator strength of 0.19. This transition should represent the broad absorption band with the band maximum at 5.03 eV. This state is characterized as the  $12b \rightarrow 19a$ , and  $14a$  excitation, which corresponds to  $n \rightarrow \sigma^*$  and for which some charge reorganization was also found, as it is seen in the dipole moment's value. In the lower energy region of the band maximum, two pairs of  $A$  and  $B$  degenerate states were calculated at around 3.8 and 5.2 eV. These states should contribute to the absorption observed in the long-wave tail of the experimental spectrum and were also found in other theoretical works.<sup>7,8</sup> It is very natural that our results in the lower energy region look very similar to those of EOM-CCSD, since the latter method is just identical to the SAC-CI one: differences in the results are essentially due to the different geometries and basis sets employed. As to the difference between our results and those of Toniolo *et al.*, it is that the  $4A$  state is, in our study, calculated higher than the  $3B$  state, which is opposite in the CAS-MRCI work. In our results the  $A$  states are always calculated higher than the  $B$  states, among the pairs. Our study shows that the  $3B$  state is

TABLE III. Excitation energy (eV), oscillator strength, second moment, dipole moment, and excitation character for the singlet excited states of ClOOCI.

State	SAC-CI					MR-CI <sup>b</sup>	EOM-CCSD <sup>c</sup>
	$\Delta E$	Osc. str.	$\langle r^2 \rangle$	$\langle r \rangle$	Character <sup>a</sup>	$\Delta E$	$\Delta E$
1A	...	...	521	-0.33	...	...	...
1B	3.77	0.0007	523	-0.16	13a-17b,13b (V)	3.48	3.88
2A	3.85	0.0003	523	-0.22	12b-17b,13b (V)	3.52	3.91
2B	5.22	0.0012	522	-0.66	12a-17b,13b (V)	4.36	5.03
3A	5.28	0.0004	522	-0.64	12a-19a,11b-17b (V)	4.38	5.03
3B	5.57	0.1885	525	0.00	12b-19a,14a (V)	4.93	5.42
4A	5.69	0.0044	525	-0.03	12b-17b,13b (V)	4.50	5.41
4B	6.56	0.0110	525	-0.09	11a-17b,13b (V)	5.39	6.54
5A	6.72	0.0039	525	-0.07	10b-17b,13b (V)	5.42	6.55
6A	7.49	0.0023	524	-0.47	11b-17b,13b (V)	...	...
5B	7.64	0.0319	524	-0.45	11b-19a,14a (V)	...	...
6B	8.32	0.2075	533	-0.45	13a-31b,32b (V, R)	...	...
7A	8.43	0.0080	562	0.49	13a-15a,14a (R)	...	...
8A	8.53	0.0302	534	0.09	13a-14a,12b-32b (V, R)	...	...
7B	8.54	0.0242	566	1.34	12b-14a,15a (R)	...	...

<sup>a</sup>V and R in the parentheses mean valence and Rydberg excitation, respectively.

<sup>b</sup>Reference 8.

<sup>c</sup>Reference 7.

largely responsible for the main absorption around 5 eV, in agreement with the CAS-MRCI work,<sup>8</sup> for other states calculated at 3.8 and 5.2 eV bear negligible or very weak intensity.

Next, we address the energy region higher than 5 eV, where the intensity remains strong until around 6.5 eV and possibly beyond. It seems to be difficult to interpret or predict the spectrum in this energy region by the previous studies of Refs. 7 and 8, since the oscillator strengths therein were calculated negligibly small. In our calculations instead, we have got two states at around 6.5 eV, the 5A and 4B

states, whose summed up oscillator strength ( $\sim 0.02$ ) is fully compatible with the experiment. We have further calculated two more states at  $\sim 7.5$  eV and four more states at  $\sim 8.5$  eV. Up to the 6A and 5B states, i.e., up to  $\sim 7.5$  eV, all the calculated excited states have almost the same second moments  $\langle r^2 \rangle$  less than 525; namely all of these states have dominantly valence character. However, four states calculated at around 8.5 eV could well be assigned to the Rydberg excitation.

#### D. F<sub>2</sub>O

There are no experimental data of the UV or VUV electronic spectrum for fluorine monoxide and very few theoretical investigations have been reported. Valenta *et al.*<sup>17</sup> studied the vertical excitation and ionization spectra of F<sub>2</sub>O by the MR-SDCI method with the DZP basis sets augmented with Rydberg-type functions. They calculated only the lowest two singlet and triplet excited states for each symmetry of the C<sub>2v</sub> point group. In the present work, we have calculated 4 or 5 singlet excited states for each symmetry lying below the first IP (13.75 eV). The SAC-CI results were summarized in Table IV, where additionally, for comparison, those of Valenta *et al.*<sup>17</sup> were listed. The SAC-CI stick-spectrum is depicted in Fig. 4.

Comparing the calculated SAC-CI spectrum of F<sub>2</sub>O with that of Cl<sub>2</sub>O, each state is blue-shifted by ca. 2–4 eV. The transition characters of the F<sub>2</sub>O excited states appear very similar to those of Cl<sub>2</sub>O. Valence excited states exist lower in energy than the Rydberg states and these latter were predicted only above 10 eV. We have also calculated the second moment for each state and found that two low-lying excited states in each symmetry were valence excited states; namely, all they have  $\langle r^2 \rangle = 126$ –128, that is almost the same as the ground state value.

There should then be three or four bands in the far UV/VUV spectrum as in the case of Cl<sub>2</sub>O. We calculated the lowest dipole-allowed transition at 5.36 eV for the first B<sub>1</sub>

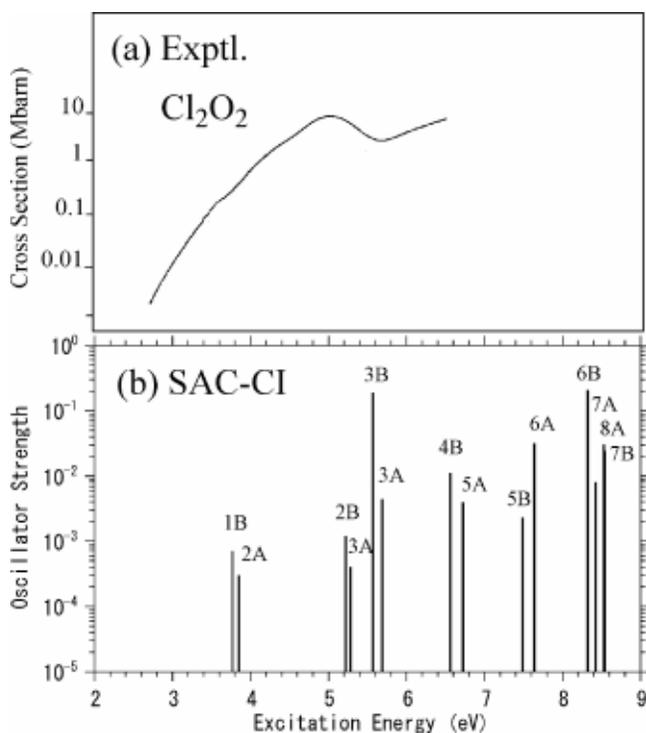


FIG. 3. (a) Experimental (Ref. 5) and (b) SAC-CI excitation spectra of Cl<sub>2</sub>O<sub>2</sub>.

TABLE IV. Excitation energy (eV), oscillator strength, second moment, dipole moment, and excitation character for the singlet excited states of F<sub>2</sub>O.

State	SAC-CI					CI <sup>b</sup>	
	$\Delta E$	Osc. str.	$\langle r^2 \rangle$	$\langle r \rangle$	Character <sup>a</sup>	$\Delta E$	Character
1A <sub>1</sub>	...	...	126	0.13			
1B <sub>1</sub>	5.36	0.0001	127	0.29	2b <sub>1</sub> -12a <sub>1</sub> (V)	5.58	V <sub>R</sub>
1A <sub>2</sub>	6.05	...	127	0.16	2b <sub>1</sub> -10b <sub>2</sub> (V)	5.62	R
1B <sub>2</sub>	8.17	0.0031	126	-0.24	4b <sub>2</sub> -12a <sub>1</sub> (V)	8.24	V <sub>R</sub>
2A <sub>1</sub>	8.52	0.0077	126	-0.26	6a <sub>1</sub> -12a <sub>1</sub> (V)	8.29	V <sub>R</sub>
2A <sub>2</sub>	9.08	-	127	-0.21	1a <sub>2</sub> -12a <sub>1</sub> (V)	8.41	V <sub>R</sub>
2B <sub>1</sub>	9.86	0.0008	127	-0.20	1a <sub>2</sub> -10b <sub>2</sub> (V)	10.81	V <sub>R</sub>
3A <sub>1</sub>	10.33	0.0184	127	-0.26	4b <sub>2</sub> -10b <sub>2</sub> (V)		
3B <sub>1</sub>	10.33	0.0000	158	-0.04	2b <sub>1</sub> -7a <sub>1</sub> (s)		
4A <sub>1</sub>	11.32	0.0069	168	-0.15	2b <sub>1</sub> -4b <sub>1</sub> (p)		
3A <sub>2</sub>	11.39	...	180	-0.31	2b <sub>1</sub> -6b <sub>2</sub> (p)		
2B <sub>2</sub>	11.43	0.1606	128	-0.10	6a <sub>1</sub> -10b <sub>2</sub> (V)	11.46	R <sub>V</sub>
4B <sub>1</sub>	11.52	0.0068	173	0.25	2b <sub>1</sub> -10a <sub>1</sub> (p)		
4A <sub>2</sub>	12.24	...	235	0.98	2b <sub>1</sub> -5b <sub>2</sub> (d)		
3B <sub>2</sub>	12.24	0.0008	239	0.32	2b <sub>1</sub> -2a <sub>2</sub> (d)		
5A <sub>1</sub>	12.29	0.0000	235	1.42	2b <sub>1</sub> -3b <sub>1</sub> (d)		
5B <sub>1</sub>	12.40	0.0016	226	0.25	2b <sub>1</sub> -9a <sub>1</sub> (d)		
5A <sub>2</sub>	13.06	...	283	1.89	2b <sub>1</sub> -7b <sub>2</sub> (p)		
4B <sub>2</sub>	13.28	0.0258	158	0.60	4b <sub>2</sub> -7a <sub>1</sub> (s)		

<sup>a</sup>V, s, p, and d in the parentheses mean valence, Rydberg, s, p, and d excitation, respectively.

<sup>b</sup>Reference 17.

state. For the second band, around 8–8.5 eV, the 1B<sub>2</sub> and 1A<sub>1</sub> excited states should make a contribution, both of which are characterized as transition into the anti-bonding 12a<sub>1</sub> MO. Transitions to another anti-bonding MO, the 10b<sub>2</sub>, were calculated at around 10 eV, namely the 2B<sub>1</sub> and 3A<sub>1</sub> states, which somehow would correspond to some lower energy shoulder of the strongest peak. That is, the 2B<sub>2</sub> state, whose transition was calculated with quite large oscillator strength at 11.43 eV. Around this energy region, two Rydberg excited states, the 4A<sub>1</sub> and 4B<sub>1</sub> states, were additionally calculated.

The correspondence of our results to those of Valenta *et al.* was shown in Table IV. Though the excitation energies calculated by the SAC-CI method look quite similar to those of the MRCI method, their interpretation resulted somewhat different. We did not find genuine Rydberg excited states, or valence-Rydberg mixed-nature states, up to about 11.3 eV. Only the 3B<sub>1</sub> state at 10.3 eV has Rydberg character, whereas all the other states characterized in Ref. 17 as Ryd-

berg appear here to be valence excited states. In this latter work, the nature of excited states was based, and proposed by their authors, on grounds of the final-orbital picture, the second moment for each excited state having not been examined. They also did not calculate the oscillator strengths, and therefore it was hard to figure out the main features of the expected F<sub>2</sub>O spectrum.

#### IV. CONCLUSION

The electronic excitation spectra of Cl<sub>2</sub>O, ClOCl, and F<sub>2</sub>O have here been investigated by the SAC-CI method. The singlet excited states manifolds below the first IP were calculated and the theoretical spectra for Cl<sub>2</sub>O and Cl<sub>2</sub>O<sub>2</sub> confronted and discussed with respect to previous theoretical studies and experiments. Agreement with the latter seems on the whole satisfactory. The oscillator strength, second moment, and dipole moment for each state were calculated and detailed characterizations of peaks and structures recorded experimentally were given, helping thus to a more precise understanding and description of the electronic excitation processes occurring on these molecules.

For the UV absorption spectra of Cl<sub>2</sub>O, our results supported the previous theoretical assignments. For the VUV region, the present calculations gave the first theoretical assignments of the 8.0–11.0 eV energy window. Both valence and Rydberg excited states were calculated therein, some of which are different from the experimental assignments.<sup>11</sup>

The SAC-CI spectrum of Cl<sub>2</sub>O<sub>2</sub> was calculated in the 2–9 eV region. The theoretical spectrum above 6 eV was calculated and predictions of the yet unknown experimental spectrum proposed which have not been addressed in the previous theoretical studies. The excited states below 7.5 eV were assigned as valence excitation, while Rydberg excited states were found around 8.5 eV.

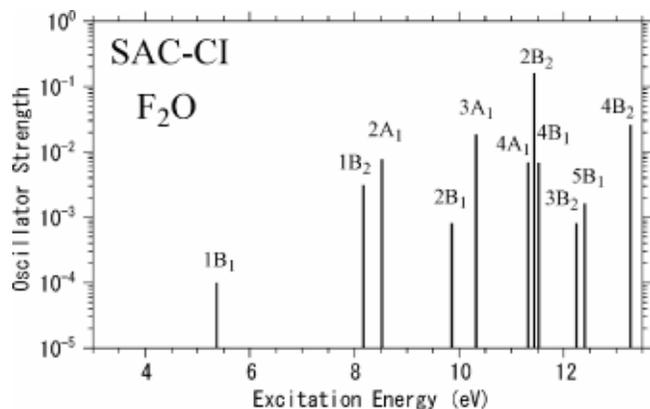


FIG. 4. SAC-CI excitation spectra of F<sub>2</sub>O.

For F<sub>2</sub>O, many valence and some Rydberg excited states up to about 13.0 eV were calculated. The gross shape of the calculated spectrum was found to be very similar to that of Cl<sub>2</sub>O, each state being blue-shifted by 2–3 eV. We discriminate the valence and Rydberg excited states by calculating the second moments. The excited states calculated by Valenta *et al.*<sup>17</sup> were found to be basically valence excited states, some of which are different from their assignments.

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