

On the high-resolution HeI photoelectron spectrum of Cl₂O

F. Motte-Tollet ^{a,1}, J. Delwiche ^b, J. Heinesch ^a, M.-J. Hubin-Franskin ^{a,2},
J.M. Gingell ^c, N.C. Jones ^c, N.J. Mason ^c, G. Marston ^d

^a *Laboratoire de Spectroscopie d'Electrons diffusés, Université de Liège, Institut de Chimie-Bât. B6c, B-4000 Liège, Belgium*

^b *Thermodynamique and Spectroscopie, Université de Liège, Institut de Chimie-Bât. B6c, B-4000 Liège, Belgium*

^c *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*

^d *Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 6AD, UK*

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Abstract

The high-resolution HeI (58.4 nm) photoelectron spectrum of dichlorine monoxide, Cl₂O, has been recorded in the region of the four lowest-energy ionic electronic states. Formation of the ion in its ground and excited electronic states is accompanied in each case by vibrational excitation. In particular, the vibrational structure of the first and second excited states of Cl₂O⁺ is resolved. Analysis of the vibrational progressions associated with formation of the various ionic states has been completed, allowing confirmation of the symmetry and bonding characteristics of the four highest-energy occupied molecular orbitals of Cl₂O. © 1998 Elsevier Science B.V.

1. Introduction

The spectroscopy and photochemistry of chlorine oxides have received considerable attention in recent years due to the involvement of these molecules in the chemical transformations that lead to depletion of ozone in the Earth's stratosphere. Dichlorine monoxide, Cl₂O, is currently thought to play, at most, a minor role in the chemistry of the polluted stratosphere but is related structurally to the oxides of chlorine that play a significant role. In addition, it is the anhydride of HOCl, a reservoir for active chlorine in the stratosphere, and is also widely used as a laboratory source of ClO, a radical that is central to

the catalytic loss of stratospheric ozone. In this Letter, we report recent high-resolution HeI (58.4 nm) photoelectron spectra of Cl₂O and new ionization energy values for the four lowest-energy electronic excited states of the molecular ion.

There is only one reported measurement of the Cl₂O photoelectron spectrum which was performed by Cornford et al. [1] at an energy resolution of about 40 meV. Eight valence ionization energies were determined, the first being localised at an adiabatic energy value of 10.94 eV. Within the experimental resolution, only the lowest-ionization energy band of the spectrum exhibited vibrational structure, assigned by the authors to the excitation of two progressions involving the symmetric stretch vibrational mode ν_1 and the bend vibrational mode ν_2 . The associated frequencies were slightly greater in

¹ Collaborateur scientifique FNRS.

² Directeur de recherche FNRS.

the ionic ground electronic state than in that of the neutral, suggesting a slightly antibonding character to the outermost occupied molecular orbital. The photoelectron spectrum also showed a sharp peak at 12.79 eV assigned to ionization of a chlorine 3p nonbonding electron. Recently, a discharge flow-photoionization mass spectrometer apparatus coupled to a synchrotron radiation source allowed the determination of the adiabatic ionization energy of Cl₂O equal to 10.909 ± 0.016 eV [2].

The HeI photoelectron spectrum of Cl₂O was recorded between the 10.5 and 13.5 eV ionization energies, spanning the four lowest-energy electronic excited states of the molecular ion. The 20 meV energy resolution of our spectrometer allowed us to resolve the vibrational structure of each electronic band. The present work follows our recent study on the VUV photoabsorption spectroscopy of Cl₂O [3].

2. Experiment

The spectrum was recorded using a photoelectron spectrometer equipped with a 180° hemispherical electrostatic analyser working in the constant pass energy mode and detailed elsewhere [4]. The spectrum was scanned by sweeping a retarding voltage between the chamber and the entrance slit of the analyser. Accuracy of the voltage ramp was recently improved by the use of a 18 bit D/A converter covering a 0–9.9999 V range. The photons were produced through a dc discharge in He in a two-stage differentially pumped lamp. The whole spectrometer is under the control of a Macintosh computer which also allows treatment and analysis of the data.

The energy resolution of the spectrometer was set to about 20 meV and the calibration of the ionization energy scale was carried out by observing the $v' = 0$ levels of the X²Σ_g⁺ N₂⁺ and X²Π_g Cl₂⁺ electronic states which are located at 15.579 [5] and 11.480 eV [6], respectively. The accuracy of the scale was estimated to be ± 0.006 eV. The spectrum was corrected for the transmission of the analysing system.

Deconvolution of the spectrum allowed a number of features appearing as shoulders in the raw spectrum to be clearly resolved and hence to provide more precise energy values. The procedure employed was the ratio method of Van Cittert [7] with Allen

and Grimm's algorithm [8]. The Ar⁺ 2P_{3/2} peak was used as the instrumental profile.

Gaseous Cl₂O was prepared by slowly passing a stream of chlorine through a reaction column packed with dried mercuric oxide [9]. The spectrum of the effluent gas showed the presence of only Cl₂ impurity. The best Cl₂O/Cl₂ ratio was obtained by carrying out the reaction at room temperature and purifying Cl₂O through multiple distillation in vacuo at -80°C .

3. Cl₂O molecule

Microwave spectroscopy [10,11] and electron diffraction experiments [12,13] have shown that Cl₂O is bent in its electronic ground state and belongs to the C_{2v} symmetry group. The equilibrium parameters are $r_e(\text{Cl-O}) = 0.169587$ nm and $\angle_e(\text{Cl-O-Cl}) = 110.886^{\circ}$. The three normal vibrational modes have A₁ (ν_1 and ν_2) and B₁ (ν_3) symmetries, respectively. Their corresponding wavenumbers (and energies) derived from infrared and Raman spectroscopies are 642 cm⁻¹ (0.0796 eV) for ν_1 , 296 cm⁻¹ (0.0367 eV) for ν_2 and 686 cm⁻¹ (0.0851 eV) for ν_3 [14,15].

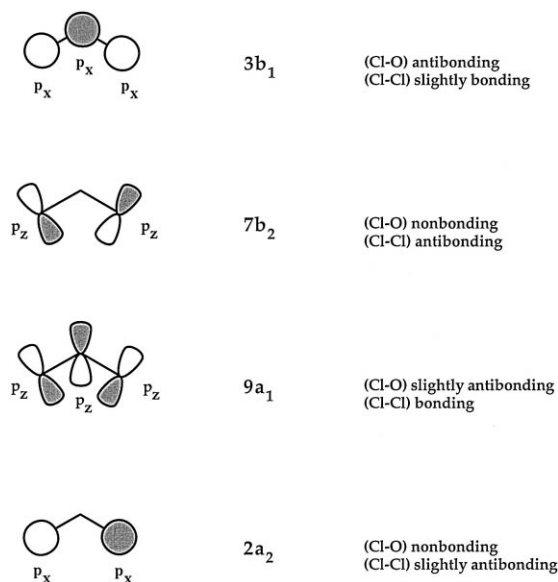


Fig. 1. The four highest-energy occupied orbitals of the Cl₂O molecule illustrated in terms of their constituent atomic orbitals.

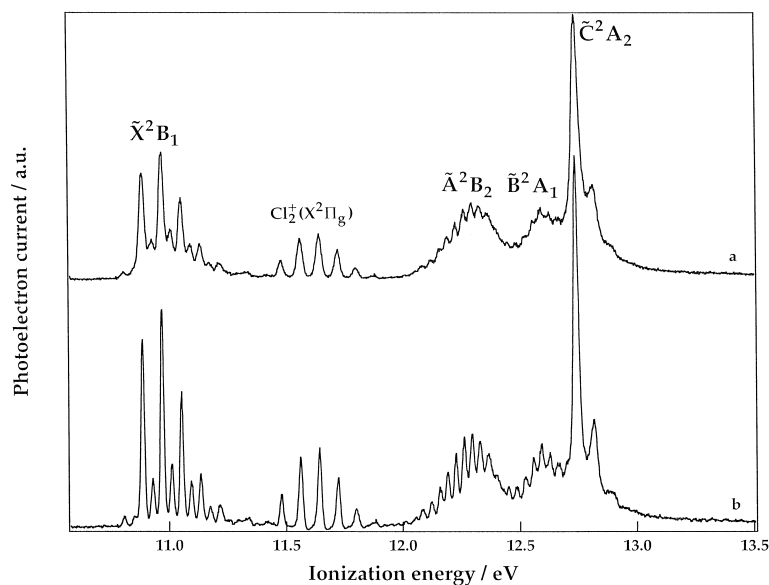


Fig. 2. HeI (58.4 nm) photoelectron spectrum of Cl_2O in the region of the four lowest-energy electronic states of the molecular ion. (a) Raw spectrum; (b) deconvoluted spectrum.

Cl_2O is a 20-valence electron molecule. The energetic ordering of its outermost valence molecular orbitals has been probed by earlier photoelectron spectroscopy [1] and a recent Hartree–Fock theoretical calculation [16]. The ground state of the molecule

is \tilde{X}^1A_1 and its electronic configuration is expected to be:

$$(\text{core}) \dots (2a_2)^2 (9a_1)^2 (7b_2)^2 (3b_1)^2$$

Table 1

Energy peak values (eV)^a and analysis of the vibrational structure associated with the ionic ground electronic state

n	$n\nu_1$	$\Delta E(\nu_1)$	$n\nu_1 + \nu_2$	$\Delta E(\nu_1)$	$\Delta E(\nu_2)$	$n\nu_2$	$\Delta E(\nu_2)$
0	10.887	—	10.930	—	0.043	10.887	—
1	10.971	0.084	11.012	0.082		10.930	0.043
2	11.054	0.083	11.096	0.084		10.971	0.041
3	11.137	0.083	11.178	0.082		11.012	0.041
4	11.218	0.081	11.258	0.080		11.054	0.042
5	11.296	0.078	11.335	0.077		11.096	0.042
6	11.375	0.079	(11.419) ^b	(0.084)		11.137	0.041
7						11.178	0.041
8						11.218	0.040
9						11.258	0.040
10						11.296	0.038
11						11.335	0.039
12						11.375	0.040
13						(11.419) ^b	(0.044)
hot bands	10.807	0.080					
	10.851				0.036		

^a Estimated uncertainty: ± 0.006 eV.

^b The energy of this vibrational peak coincides with that of the $v'' = 1(X^1\Sigma_g) \rightarrow v' = 0(X^2\Pi_g)$ electronic transition in chlorine.

Each of these four molecular orbitals has been predicted by Nelson et al. [17] to contain significant Cl p character. Alternatively, information on the nature of the molecular orbitals can be obtained using Walsh's treatment of a 20-valence electron non-hydride AB_2 molecule [18]. Pictorial representations of the four outermost occupied molecular orbitals are illustrated in Fig. 1 with descriptions of the expected approximate bonding or antibonding character along the (Cl–O) and (Cl–Cl) coordinates. The molecular orbitals $3b_1$ and $9a_1$ are built respectively from p_x and p_z orbitals centred on each atom and overlapping out-of-phase. They correlate with the molecular orbital π_u^* in the symmetry group $D_{\infty h}$ of the linear molecule. Molecular orbitals $7b_2$ and $2a_2$ are linked to the molecular orbital π_g in the linear configuration. They are formed from p_x and p_z orbitals centred on each chlorine atom, respectively and can be viewed in a first approximation as non-bonding (Cl–O) 3p chlorine orbitals.

4. Results and discussion

The raw photoelectron spectrum of Cl_2O between 10.5 and 13.5 eV ionization energies is displayed in Fig. 2a, while Fig. 2b shows the spectrum obtained after deconvolution, in which the vibrational features are better resolved. In the following results, the energy positions of the peaks as well as the figures [3–5] will relate to the deconvoluted spectrum.

The electronic band extending from an ionization energy of 11.4–11.8 eV is attributed to the chlorine impurity and linked to the formation of the Cl_2^+ ion in its ground electronic state $X^2\Pi_g$ (Fig. 2). This impurity does not interfere with the Cl_2O photoelectron spectrum since there are no Cl_2O^+ ionic electronic states in the energy region of the $X^2\Pi_g$ state [1]. Higher-energy Cl_2^+ states are expected to appear above 13.5 eV [6,19,20] and so are not observed in the present spectrum.

Analysis of the vibrational envelope of the bands provides information about the bonding characteristics and hence the symmetry of the four outermost occupied molecular orbitals of the neutral molecule in its electronic ground state. Analyses of the four observed transitions are presented in the following sections.

4.1. First band

The 10.7–11.4 eV ionization energy range of the photoelectron spectrum is enlarged in Fig. 3. It is composed of a broad electronic band involving well-resolved vibrational structure, clearly visible in the deconvoluted spectrum. The band relates to the loss of an electron from the highest-occupied molecular orbital (HOMO) and hence to the formation of the molecular ion in its ground electronic level.

Energies of the vibrational peaks are tabulated in Table 1 and are compared to the adiabatic and vertical ionization energy values previously reported in the photoelectron [1] and photoionization efficiency spectra [2] in Table 2. Our adiabatic and vertical ionization energies are both lower than the earlier values. In particular, the energy differences

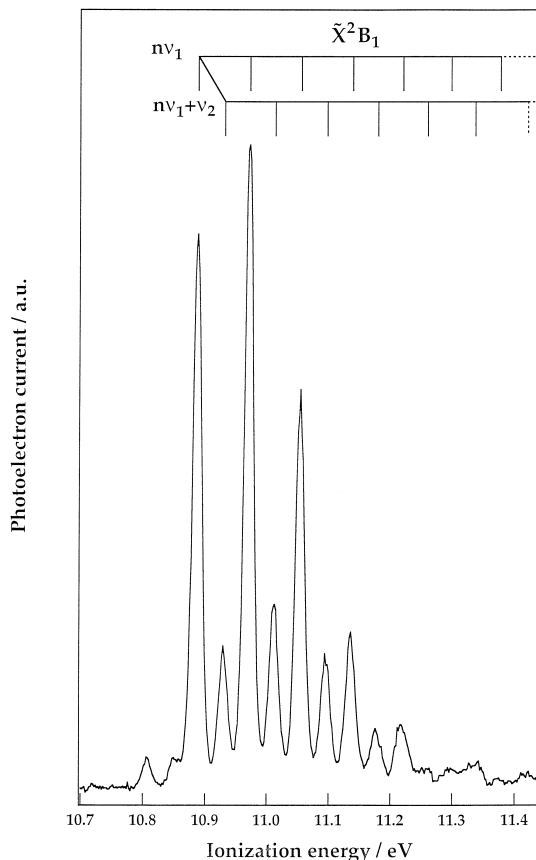


Fig. 3. HeI (58.4 nm) photoelectron spectrum of Cl_2O in the region of the ionic ground electronic state \tilde{X}^2B_1 .

Table 2
Assignment of the four lowest-energy electronic states of Cl_2O^+

Ionic State	AIE	VIE	Cornford et al.		Thorn et al. (AIE)
			(AIE)	(VIE)	
\tilde{X}^2B_1	10.887	10.971	10.94	11.02	10.909 ± 0.016 eV
\tilde{A}^2B_2	12.016	12.297	–	12.37	–
\tilde{B}^2A_1	≤ 12.453	12.593	–	12.65	–
\tilde{C}^2A_2	12.742	12.742	–	12.79	–

The adiabatic and vertical ionization energies, AIE and VIE, respectively, are also tabulated and compared to the literature data of Cornford et al. [1] and Thorn et al. [2]. Energies are in eV (estimated uncertainty: ± 0.006 eV).

with the previous work of Cornford et al. [1] are significant ($\Delta = 0.053$ and 0.049 eV for the adiabatic and vertical energies, respectively). However, our 10.887 ± 0.006 eV adiabatic energy value agrees well, within the errors bars, with the recent 10.909 ± 0.016 eV value of Thorn et al. [2]. The intensity alternation of the vibrational peaks leads us to interpret the band envelope in terms of two progressions involving the ν_1 and ν_2 vibrational modes, i.e. either $n\nu_1$ and $n\nu_1 + \nu_2$, as previously proposed by Cornford et al. [1], or $n\nu_1$ and $n\nu_2$, as detailed in Table 1. However, if the $n\nu_2$ progression is excited, it would be quite long, in contradiction with the

(Cl–Cl) slightly bonding predicted character of the outermost molecular orbital (Fig. 1) [18]. The ν_1 frequency is higher in the molecular ion (~ 0.083 eV) than in the neutral molecule (0.0796 eV) indicating (Cl–O) antibonding character, consistent with the predicted shape of the $3b_1$ molecular orbital (Fig. 1) and confirming the ionic electronic ground state as \tilde{X}^2B_1 (Table 2 and Fig. 2).

4.2. Second and third bands

The second and third electronic bands of the Cl_2O photoelectron spectrum extend from 12.0 to 12.7 eV ionization energies, as displayed in Fig. 4. Both bands exhibit vibrational structure not previously resolved. The features correspond to the formation of the molecular ion in its first and second excited electronic states. The vibrational pattern of the second band, less well resolved than in the first band, suggests that the corresponding ionic electronic state has a shorter lifetime than the ground ionic electronic state, with predissociation being a likely cause. Both vibrational envelopes have been analysed in terms of a long progression involving excitation of the ν_2 bending mode (Fig. 4 and Table 3). Excitation of this mode demonstrates a change in the

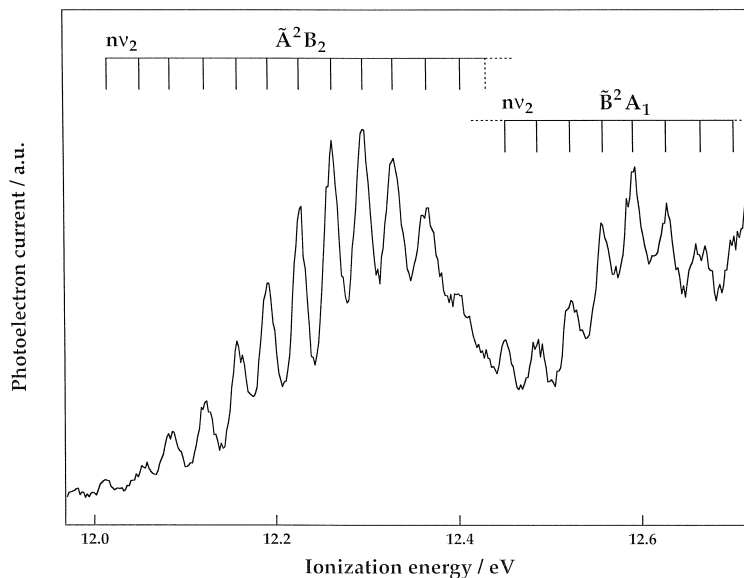


Fig. 4. HeI (58.4 nm) photoelectron spectrum of Cl_2O in the region of the ionic first and second excited electronic states \tilde{A}^2B_2 and \tilde{B}^2A_1 .

Table 3

Energy peak values (eV)^a and analysis of the vibrational peaks associated with the first and second excited electronic states of the molecular ion \tilde{A}^2B_2 and \tilde{B}^2A_1 , respectively

n	$n\nu_2$	ΔE
\tilde{A}^2B_2		
0	12.016	–
1	12.052	0.036
2	12.085	0.033
3	12.123	0.038
4	12.159	0.036
5	12.193	0.034
6	12.227	0.034
7	12.263	0.036
8	12.297	0.034
9	12.330	0.033
10	12.367	0.037
11	12.404	0.037
12	(12.432) ^b	(0.028)
\tilde{B}^2A_1		
n	12.453	–
$n+1$	12.488	0.035
$n+2$	12.524	0.036
$n+3$	12.560	0.036
$n+4$	12.593	0.033
$n+5$	12.629	0.036
$n+6$	12.667	0.038
$n+7$	(12.703) ^b	(0.036)

^aEstimated uncertainty: ± 0.006 eV.

^bPeak structure appearing as a shoulder.

(Cl–O–Cl) angle, and therefore along the (Cl–Cl) coordinate, between the neutral ground and the ionic excited electronic states. Of the outermost molecular orbitals, $7b_2$ and $9a_1$ are both candidates for the originating orbital, $7b_2$ being (Cl–Cl) antibonding and $9a_1$ bonding along the (Cl–Cl) coordinate. However, as the ν_2 vibration frequency is about the same in the neutral and ionic states, we cannot use this to distinguish between the two possible orbitals.

The same arguments apply to the third electronic band around 12.6 eV. However, this band closely resembles the first ionization band in the photoelectron spectrum of sulphur dioxide [21] which has been assigned to the ionization of an electron from the $6a_1$ (O–O) bonding HOMO orbital. Since the sulphur dioxide and dichlorine monoxide molecules have, to a first approximation, the same valence molecular orbitals [18], we relate the 12.6 eV electronic band to the loss of an electron from the $9a_1$ (Cl–Cl) bonding molecular orbital. The second ex-

cited state of the Cl_2O^+ molecular ion would then be the \tilde{B}^2 state (Fig. 2 and Table 2). Its first observable vibrational peak is at 12.453 eV (Fig. 4 and Table 3). The corresponding adiabatic $v' = 0$ level may be hidden in the high-energy side of the second photoelectron band (Fig. 4). This \tilde{B}^2A_1 assignment then leaves the second (12–12.4 eV) band as arising from ionization of an electron from the $7b_2$ (Cl–Cl) antibonding molecular orbital and to the formation of the \tilde{A}^2B_2 ionic state (Fig. 2 and Table 2). Therefore, we assign the low-intensity peak at 12.016 eV to the $v = 0$ term (Tables 2 and 3).

4.3. Fourth band

The energy region relating to the loss of an electron from the (HOMO-3) molecular orbital is enlarged in Fig. 5. It comprises a sharp intense peak

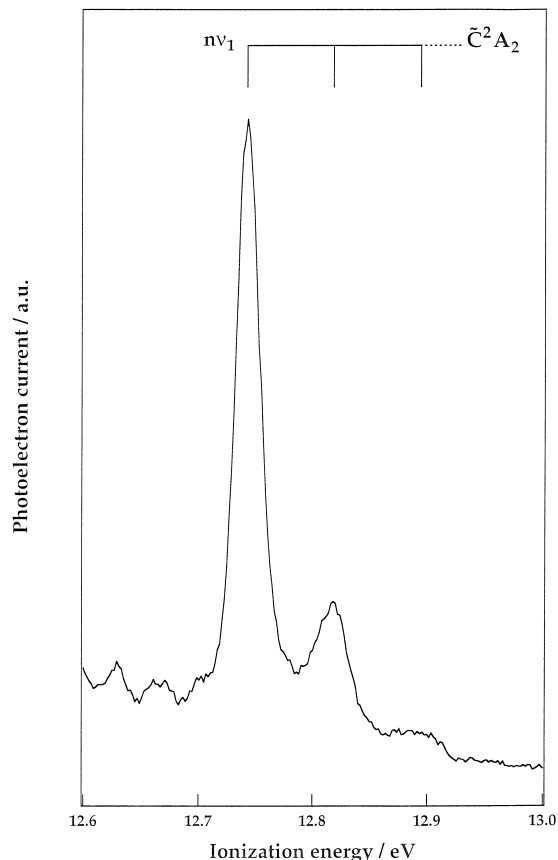


Fig. 5. HeI (58.4 nm) photoelectron spectrum of Cl_2O in the region of the ionic third excited electronic state \tilde{C}^2A_2 .

Table 4

Energy peak values (eV)^a and analysis of the vibrational structure associated with the ionic third excited electronic state \tilde{C}^2A_2

n	$n\nu_1$	ΔE	ν_2	ΔE
0	12.742	—	—	—
1	12.818	0.076	(12.78) ^b	(0.038)
2	12.894	0.076		

^aEstimated uncertainty: ± 0.006 eV.

^bPeak structure appearing as a shoulder.

located at 12.742 eV with, at its high-energy side, only a few peaks of much lower intensity involving excitation of a small vibrational progression in the ν_1 symmetric stretching vibrational mode (Table 4). Excitation of one quantum of ν_2 might be visible as a shoulder at 12.78 eV. This band shape is characteristic of the ionization of an electron nonbonding along both (Cl–O) and (Cl–Cl) coordinates. It is therefore attributed to the loss of an electron from the $2a_2$ molecular orbital, built mainly from the chlorine 3p nonbonding orbitals. The corresponding ionic electronic state would then be the \tilde{C}^2A_2 state, with an adiabatic energy of 12.742 eV (Fig. 2 and Table 2).

5. Conclusion

The photoelectron spectrum of Cl_2O has been recorded in the region of the ionic ground electronic state and of its three lowest-energy excited electronic states. The high-energy resolution of the spectrometer allowed us to observe the vibrational envelope of each ionic state. Analysis of the vibrational progressions has given information on the nature of the ionized orbitals and confirms the ground state electron configuration of the molecule to be $\dots(2a_2)^2(9a_1)^2(7b_2)^2(3b_1)^2$.

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