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Original Investigations

An *ab initio* Investigation of the Inner Shell Excited States of the Molecule Cl_2

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Restricted Hartree–Fock calculations of the Cl_2 molecule have been carried out to investigate the X-ray excited states below Cl $2p$-electron ionization potential. Some inner shell excited states are shown to have a valence or a valence-Rydberg nature that results in a considerable intensity of the appropriate transitions in the X-ray absorption spectrum. A significant interaction among some electron configurations with a $2p$ vacancy is predicted.

Key words: X-ray states of Cl_2 – Absorption spectrum of Cl_2 – Cl_2

1. Introduction

The X-ray ultraviolet states of Cl_2 were studied by using the synchrotron radiation and a grazing-incidence spectrometer [1]. The $L_{2,3}$-absorption spectrum with high resolution (~0.05 Å) was interpreted as follows. Maxima of the experimental spectrum (Fig. 1) are brought into correlation with the transitions of the $2p$ electron terminating on the valence or Rydberg vacant orbitals. The spin-orbital interaction is taken into account by splitting all the theoretical levels into two components corresponding to a total moment of five $2p$ electrons of a Cl atom $J = 3/2$ and $J = 1/2$. The broad bands A and B are assigned to the transitions terminating on the valence orbital σ_u^* (antibonding molecular orbital $5\sigma_u$). The sharp maxima C---O are interpreted as the transitions terminating on Rydberg orbitals; therefore they are assigned to the s-, p- and d-levels by fitting the maximum energies with the help of Rydberg's formula with a definite orbital quantum number ($\hbar = m = e = 1$):

$$E - E_\infty = -\frac{1}{2(n - \delta_l)^2}. \tag{1}$$

The following values of quantum defects and vertical ionization potentials were

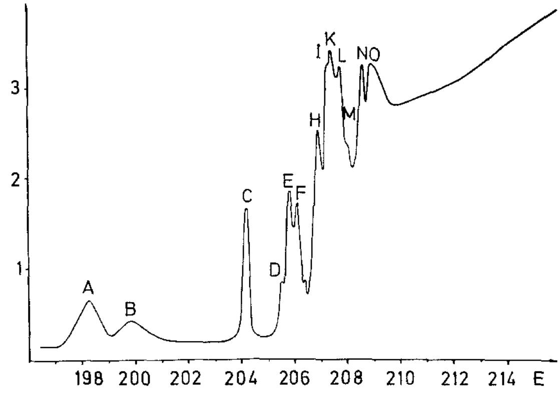

Fig. 1. The $L_{2,3}$-absorption spectrum of the molecule Cl_2 [1] (intensities in relative units)

obtained: $\delta_s = 2.13$, $\delta_p = 1.53$, $\delta_d = 0.2$, $E_\infty(2p_{3/2}) = (208.0 \pm 0.3)$ eV, $E_\infty(2p_{1/2}) = (209.6 \pm 0.3)$ eV. Both theoretical and experimental results on the $L_{2,3}$-absorption of Cl_2 are given for comparison in Table 1 where the energy value 208.0 eV is taken to be zero.

2. One-electron Ionic Model

In the present paper the restricted Hartree–Fock (RHF) calculations of the Cl_2 molecule have been carried out by the use of the IBMOL-5 program [2] to investigate the X-ray states below the 2*p*-level ionization potential of this molecule. A direct investigation of some close excited states using the self-consistent RHF method is impossible because of bad convergence of the iterative process. In order

Table 1. Theoretical and experimental data for X-ray ultraviolet states of the molecule Cl_2, eV

Experiment Maximum	T_v[a]	Calculation Transition	$\bar{\varepsilon}$	State $3\sigma_g^{-1}$ f^*10^4[b]
A	−9.73	$3 \rightarrow 5\sigma_u^*$	−9.47	51.3
B	−8.13	$1 \rightarrow 5\sigma_u^*$	−7.87	25.7
C	−3.82	$3 \rightarrow 6\sigma_g$	−3.14	29.0
D	−2.35	$3 \rightarrow 3\pi_u$	−2.20	0.8
		$3 \rightarrow 6\sigma_u$	−2.14	4.9
E	−2.19	$1 \rightarrow 6\sigma_g$	−1.54	14.5
F	−1.90	$3 \rightarrow 7\sigma_g$	−1.51	1.5
G	−1.57	$3 \rightarrow 3\pi_g$	−1.41	0.8
		$3 \rightarrow 1\delta_g$	−1.39	0.9
		$3 \rightarrow 8\sigma_g$	−1.36	8.8
H	−1.09	$3 \rightarrow 4\pi_u$	−1.09	0.4
		$3 \rightarrow 7\sigma_g$	−1.07	2.7

[a] From the edge $\omega_\infty(3/2) = 208.0$ eV.

[b] Taking into account statistical weights 2:1 of transitions, for example, $77.0 = 2^*25.7 + 1^*25.7$ for the transition on the orbital $5\sigma_u^*$.

to overcome this difficulty within the framework of the RHF method the following so-called one-electron ionic model [3, 4] is used to compute the high excited states. An occupied orbital i of the ground state of the molecule is the initial one, and the vacant ν level of RHF state i^{-1} is the final one under electron transition $i \rightarrow \nu$. The total energy $E_{\nu i}$ of the state νi is calculated by using the following equation:

$$E_{\nu i} = E_i + \tilde{\varepsilon}_\nu, \tag{2}$$

and the energy of transition $i \rightarrow \nu$ is

$$\omega_{\nu i} = E_{\nu i} - E_0 = E_i - E_0 + \tilde{\varepsilon}_\nu. \tag{3}$$

The symbol νi means the final state with one vacancy on orbital i and excited electron on orbital ν, which is vacant in the ground state of the molecule; i^{-1} means a singly ionized configuration with a vacancy on inner orbital i; E_0 and E_i are the total energies of the ground and i^{-1} states respectively, $\tilde{\varepsilon}_\nu$ is the energy of the orbital ν of the state i^{-1}. Thus, in this method all highly excited states νi can be obtained from only one calculation of the state i^{-1}. A confirmation of this approach can be carried out with the help of Roothaan's theory of the open shells [5].

For convenience let us consider a triplet state νi $(S = 1)$. It allows us to use exchange coupling operators M_i instead of indefinite Lagrangian multipliers.[1] The RHF operator for the vacant orbital ν of the ion i^{-1} has the form:

$$F_c = h + 2\sum_{r\in\mathcal{F}} J_r - \sum_{r\in\mathcal{F}} K_r + J_i - 1/2K_i + M_i, \tag{4}$$

and the operator for the same orbital ν of the electron configuration νi is

$$F_{0\nu} = h + 2\sum_{r\in\mathcal{F}} J_r - \sum_{r\in\mathcal{F}} K_r + J_i - K_i + 2\sum_{r\in\mathcal{F}} M_r. \tag{5}$$

In Eqs. (4) and (5) the designations of the paper [5] are used. $\mathcal{F}$ is the set of closed shells of the respective configurations. From a comparison of these two operators F_c and $F_{0\nu}$ we may conclude that they are equal within the values of the operators K_i, M_i and M_r. In the case of Rydberg transition $i \rightarrow \nu$ the orbital ν overlaps with the occupied MO only slightly, and, since the operators K_i, M_i and M_r have an exchange nature this fact allows us to neglect these operators:

$$F_{0\nu} \simeq F_c \simeq h + 2\sum_{r\in\mathcal{F}} J_r - \sum_{r\in\mathcal{F}} K_r + J_i, \tag{6}$$

$$F_c|\tilde{\nu}\rangle = \tilde{\varepsilon}_\nu|\tilde{\nu}\rangle, \tag{7}$$

where $\tilde{\nu}$ is the orbital ν from the state i^{-1}.

Let us determine the energies of the states νi and i^{-1} as follows:

$$E_{\nu i} = \langle \tilde{\nu} i|\mathcal{H}|\tilde{\nu} i\rangle, \tag{8}$$

$$E_i = \langle \tilde{i}|\mathcal{H}|\tilde{i}\rangle, \tag{9}$$

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[1] The direct calculations of the CO molecule [3] showed that the orbital energies of X-ray Rydberg triplet and singlet states are in agreement to within 0.02 eV.

where $|\tilde{v}i\rangle$ and $|\tilde{i}\rangle$ are the total wave functions of the states vi and i^{-1} built by using orbitals of the state i^{-1}, $\mathscr{H}$ is the Hamiltonian of the molecule. By calculating the matrix elements in Eqs. (8) and (9) the validity of Eq. (2) can be shown easily. The physical sense of Eqs. (2) and (7) is clear: $|\tilde{v}\rangle$ and $\tilde{\varepsilon}_v$ are, respectively, the eigenstate and the eigenvalue of the excited electron in the field of the positive ion with the i vacancy.

It should be pointed out that in the case of electron configurations with open shells the orbital energies $\tilde{\varepsilon}$ do not have so simple a physical interpretation as, for instance, for the closed shells configurations (Koopmans' theorem). But because of the negligible values of exchange integrals between the inner shell vacancy and the photoelectron on a diffuse level in the X-ray excited states we can obtain an expression analogous to Koopmans' theorem and assign to the orbital energies a definite physical sense

$$T_{vi} \equiv \Delta E_{vi} = E_{vi} - E_i = \tilde{\varepsilon}_v. \tag{10}$$

For the inner level i Coulomb operator J_i can be reduced to the operator of the interaction of the point charges [6, 7]:

$$J_i = 1/r_{\text{A}}, \tag{11}$$

where A is an atom to which the level i belongs. It leads to the following equation of the well known $Z + 1$ model [6–10]

$$F_c = F_{Z+1}, \tag{12}$$

where F_{Z+1} is RHF operator for the N-electron ion $Z + 1$ with closed shells; for the vacant orbitals of the F_{Z+1} operator Koopmans' theorem holds:

$$T_v = \varepsilon_v, \tag{13}$$

which is in agreement with Eq. (10).

As shown for the molecule CO [3] the term values T_{vi}[2] of the lowest Rydberg states calculated in the way discussed here, with the help of ionic model $Z + 1$ for vacant orbitals, and performing the self-consistent calculation of X-ray excited states agree with an accuracy of about 10^{-2} eV. It is to the point to note that the model $Z + 1$ is of the same accuracy as the one-electron ionic model presented here since it neglects all exchange corrections.

3. Calculation and Discussion

The intermediate Gaussian basis set ($10s6p$) has been taken from Roos and Siegbahn [11] with the following contraction: $s(4, 2, 4{*}1)$ and $(p(4, 2{*}1)$, to which were added two Gaussians with small orbital exponents for each type of s, p, d functions placed in the middle of the Cl—Cl bond (the fictitious atom I). It was done in order to describe a very diffuse character of states of at least the lowest members of the Rydberg series. The $L_{2,3}$-spectra of the isoelectronic hydrides HCl,

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[2] Term value T_{vi} = distance from an ionization limit [9, 10].

H_2S, PH_3 and SiH_4 have recently been discussed and assigned on the basis of *ab initio* (Hartree–Fock level) calculations of the X-ray ultraviolet states within the ionic model for vacant orbitals $Z + 1$ in the same basis set [9, 10].

The calculated energies of vacant orbitals are found to be very nearly independent of the type of the $2p$ shell originating orbitals, and so the results of calculations of the energies of the terminating orbitals $\tilde{\varepsilon}_v$ and of the transition oscillator strengths f_{vi} are listed for the state $3\sigma_g^{-1}$ only (Table 1). The present theoretical investigation confirms the validity of dividing the highly excited states in the $L_{2,3}$-absorption spectrum into two groups: valence (or molecular) states and Rydberg ones. Thus, the maxima *A* and *B*, for example, are caused by the transitions terminating on the antibonding molecular orbital $5\sigma_u$. The electron density of this orbital is localized near the molecule which provides a significant overlap between the originating ($2p$) and terminating ($5\sigma_u$) orbitals, hence the great f-value for this transition as compared with those on the other orbitals. The latter, in contrast to the molecular orbital $5\sigma_u$, consist of the added diffuse functions and their electron densities are localized behind the molecule and their energies may often fit the Rydberg series (1). But there are several valence-Rydberg orbitals among the calculated ones in which there occurs a significant mixing of Rydberg-valence. This can be readily seen from the following calculated compositions of the orbitals $6\sigma_g$, $7\sigma_g$, and $8\sigma_g$ (only the basis functions with the largest coefficients c_i are given):

$$\tilde{\varphi}_{6\sigma_g} = -0.45s(\mathrm{Cl}_1) - 0.45s(\mathrm{Cl}_2) + 0.98s_1(\mathrm{I}) + 0.20s_2(\mathrm{I}),$$

$$\tilde{\varphi}_{7\sigma_g} = -0.17s(\mathrm{Cl}_1) - 0.17s(\mathrm{Cl}_2) + 0.85s_1(\mathrm{I}) - 0.98s_2(\mathrm{I}) - 0.64d_1(\mathrm{I}) - 0.15d_2(\mathrm{I}),$$

$$\tilde{\varphi}_{8\sigma_g} = -0.27s(\mathrm{Cl}_1) - 0.27s(\mathrm{Cl}_2) + 0.98s_1(\mathrm{I}) - 1.03s_2(\mathrm{I}) + 0.51d_1(\mathrm{I}) + 0.30d_2(\mathrm{I}).$$

Moreover, from the adduced composition of the orbitals $7\sigma_g$ and $8\sigma_g$ one can see that there is a significant *s–d* Rydberg mixing in these orbitals, i.e. these states are not simply assigned to Rydberg states with a definite value of $1 - s, p,$ or d types. All these features cause the calculated quantum defects of these orbitals to have different values. The existence of such orbitals shows the significant difference of the potential acting on an excited electron from an atom-like one in the molecule Cl_2.

The maximum *F* is of special interest to us because it has anomalous experimental quantum defects: $\delta_{5s} = 2.32$ or $\delta_{3d} = 0.32$. Moreover, the calculated energy and the f-value for the orbital $7\sigma_g$ do not agree with the experimental data for this maximum. These distinguishing peculiarities can be explained by the following. The structure F---G corresponds to electron configurations with an unpaired electron on the molecular orbitals $3\sigma_u$ or $1\pi_u$ and an excited electron on the orbitals $7\sigma_g$, $3\pi_g$, $1\delta_g$ or $8\sigma_g$. The RHF energies of these configurations differ from each other by $\simeq 0.1 \div 0.2$ eV. It is natural to assume a significant interaction between these configurations which may lead to energy deviations of the states from the values predicted by using the Rydberg formula (1).

4. Transition Oscillator Strengths

One-electron transition oscillator strengths are calculated by the conventional equation:

$$f_{vi} = 2/3\omega_{vi} \sum_{mm'} |\langle \tilde{v}m'|\mathbf{r}|im\rangle|^2, \tag{14}$$

which includes the summing over all degenerate states m' and m of the orbitals $|\tilde{v}\rangle$ and $|i\rangle$, respectively. The transition oscillator strengths are known to be more susceptible to the accuracy of the used wave functions than to the energies of the states. In the case of X-ray transitions the wave functions of the inner shell and the vacant orbitals included in the transition matrix element $\langle \tilde{v}m'|\mathbf{r}|im\rangle$ are localized in essentially different regions of space, therefore the vacant wave functions should be made more precise in the inner region. Naturally, it is of particular importance for the diffuse Rydberg orbitals. A comparison of the theoretical transition f-values (Table 1) and the relative heights of maxima in the experimental $L_{2,3}$-spectrum of Cl_2 (Fig. 1) shows them to be in semiquantitative agreement excluding the maximum F. Evidently, large widths of the maxima A and B are caused by the transitions on vibrational and LS sublevels of the final inner excited state, which leads to a decrease in the relative heights of these maxima.

5. Additional Comments

The results of calculations show that there are no quasistationary states above the K- and $L_{2,3}$-ionization limit (in the interval 0–20 eV). This makes it possible to predict an unresonant character of X-ray absorption in this region of both the K- and $L_{2,3}$-absorption of the Cl_2 molecule in accordance with the theory of quasistationary states developed in [4, 12, 13]. The K- absorption spectrum of Cl_2 molecule [14] confirms our suggestion. Unfortunately, there are no experimental data available on $L_{2,3}$-absorption above the ionization limit.

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