Core-excitation processes of O(1s) in CO, CO$_2$ and OCS molecules by electron impact

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Abstract. Distorted-wave approximation is applied to study electron-impact excitation of core electrons in CO$_2$, CO and OCS. Differential and integral cross sections for the transitions: $X^1\Sigma^+ \rightarrow 1^3\Pi_u$, $(1\sigma_g \rightarrow 2\pi_u)$ in CO$_2$, $X^1\Sigma^+ \rightarrow 1^3\Pi_u$, $(2\sigma \rightarrow 4\pi)$ in OCS, and $X^1\Sigma^+ \rightarrow 1^3\Pi_u$ $(1\sigma \rightarrow 2\pi)$ in CO are calculated and reported in the (550-1000)-eV incident energy range. Comparison is made among the calculated data for the three targets. The physical origins of the similarity and difference of these data are also discussed. In addition, the generalized oscillator strengths for singlet $1\sigma_g \rightarrow 2\pi_u$ and $1\sigma_u \rightarrow 2\pi_u$ transitions for CO$_2$ are calculated at 1300 eV. The comparison of these results with the available data in the literature is encouraging.

1. Introduction
Investigations on inner-shell excitation or ionization processes in atoms and molecules, involving the promotion of a strongly linked K-shell electron to an unfilled bound or continuum orbital, are both important and interesting [1]. In general, such internal molecular orbitals are highly localized and their participation in the chemical bonding formation is small. Therefore, they are very similar to the corresponding atomic orbitals. Due to this atomic-like character, the shapes and energies for K-shell electronic excitations do not vary significantly in molecules with common atomic constituent, even in different physical states [2]. This property of the inner-shell molecular orbitals can be used in the development of equipments to characterize both gaseous or solid samples [3].

In the last two decades, the inner-shell excitation and ionization processes have received considerable attention. Experimentally, both high-energy photons (vacuum ultraviolet radiation and X-ray) and electrons are used as excitation sources. Such studies include, for instance, photoexcitation [4, 5, 6], photoemission and photoionization [7, 8], electron-impact excitation

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[9, 10, 11, 12, 13] of molecules. On the theoretical side, some solid \textit{ab initio} approaches such as the R-matrix method and the multichannel quantum-defect theory have been applied to study optically stimulated inner-shell excitation of molecules [14, 15, 16]. Although an \textit{ab-initio} multichannel study on electron-impact core-excitation processes is also desirable, computationally couplings between a fast incident electron and a slow outgoing electron is very difficult to deal with. To our knowledge, only studies using the perturbative methods such as the first Born approximation (FBA) [11, 12] and distorted-wave approximation (DWA) [17, 18, 19] can be found in the literature. Despite the simplicity, quite accurate generalized oscillator strengths (GOS) for electron-impact core-excitation of molecules can be provided using these methods. Moreover, the occurrence of shape resonances at incident energies near the excitation thresholds can also be predicted by the DWA.

Recently, Kroin \textit{et al.} [17] reported a theoretical investigation on the excitation of an electron from the carbon 1s orbital, C(1s), to the lowest-lying \pi orbital in a series of triatomic molecules containing only one carbon atom, namely CO$_2$, CS$_2$, and OCS. They observed that in the non-resonant energy region, the theoretical ratios between the integral cross sections (ICS) for transitions leading to the singlet core-excited states and those leading to triplet excited states, referred here as RI(1:3), are nearly the same for the three targets studied therein. This behaviour seems to confirm the atomic-like property of such orbitals.

On the other hand, for molecules containing two or more equivalent atoms of the same chemical element, the molecular-orbital description of the inner-shell wave functions would require a linear combination of the atomic orbitals. Therefore, they are delocalized and no longer atomic. Recently, we have applied the DWA to study the electron-impact core excitation of two isoelectronic molecules: N$_2$ [18] and C$_2$H$_2$ [19]. In these targets, the linear combination of the 1s orbitals of two carbon (nitrogen) atoms has resulted in the delocalized core molecular orbitals 1\sigma_g and 1\sigma_u in C$_2$H$_2$ (N$_2$). The different parity of these molecular orbitals leads to distinct behavior in excitation and ionization processes. For instance, the singlet 1\sigma_u \rightarrow 3\pi_g transition is dipole-allowed whereas the singlet 1\sigma_g \rightarrow 3\pi_g transition is dipole-forbidden. Consequently, the calculated cross sections for the above transitions are expected to be quite different from each other.

In order to better understand the influence of the atomic-like or delocalized character of the K-shell molecular orbitals, in this work we extend the application of the DWA to investigate the electron-impact O(1s) core-excitation processes in the triatomic CO$_2$ and OCS molecules and in the diatomic CO molecule. The differential cross sections (DCS) and ICS for promotion of an electron from the 1\sigma orbital in CO, the 2\sigma orbital in OCS and 1\sigma_g orbital in CO$_2$ to the corresponding lowest unfilled orbital are calculated and compared with each other. The Hartree-Fock (HF) calculations have revealed that the 1\sigma orbital in CO and the 2\sigma orbital in OCS are highly localized whereas the 1\sigma_g orbital in CO$_2$ is delocalized. Therefore, the similarity and difference in the calculated cross sections can provide insight of the dynamics of core-shell excitations by electron impact.

The organization of the present article is as follows: in section 2, an outline of the theory used is presented. Some details of the calculations are also provided. Finally in section 3, we compare the calculated data for the three targets and summarize our conclusions.

### 2. Theory

Details of the basic theory used in this work can be found elsewhere [20, 21, 22, 23]. The electron-impact excitation DCS averaged over molecular orientations is given by:

$$
\frac{d\sigma}{d\Omega} = \frac{1}{8\pi^2} \int d\alpha \sin \beta \, d\beta \, d\gamma \, |f(k'_i, k'_f)|^2,
$$

(1)
Table 1. Vertical excitation energy (\(\Delta E\)) and singlet-triplet energy splitting (\(\delta\)), in eV

| Molecule | \(\Delta E\) for singlet transitions | \(\Delta E\) for triplet transitions | \(\delta\) |
|----------|-------------------------------------|-------------------------------------|---------|
| CO\(_2\) | 554.018, 535.5\(^a\), 535.99\(^b\) | 553.337 | 0.681 |
| OCS      | 550.960, 520.0-560.0\(^c\)        | 549.746 | 1.214 |
| CO       | 550.097                            | 548.486 | 1.611 |

\(^a\) Experimental results of Eustatiu et al. [12];
\(^b\) Experimental results of Miranda et al. [11];
\(^c\) Data from Hitchcock et al. [1].

where \(\hat{k}_f(\hat{k}_i)\) is the linear-momentum direction of the scattered (incident) electron in the Laboratory-Frame (LF), whereas the direction of incident electrons is taken as the LF z-axis. The \((\alpha, \beta, \gamma)\) are the Euler angles which define the direction of the molecular principal axes. The Body-Frame (BF) scattering amplitude \(f(\hat{k}_i, \hat{k}_f)\) is related to the \(T\)-matrix elements by the expression:

\[
f(\hat{k}_i, \hat{k}_f) = -2\pi^2 T_{if}
\]

and is related to the LF scattering amplitude by usual transformations [24].

Using the DWA, the transition \(T\) matrix is given by:

\[
T_{if} = \langle \phi_f \Psi_{k_f}^{(-)} | U_{se} | \phi_i \Psi_{k_i}^{(+)} \rangle
\]

where \(\phi_i\) and \(\phi_f\) are the initial and final target wave functions, respectively. These wave functions are Slater determinants with appropriate symmetries. \(\Psi_{k_i}^{(+)}\) and \(\Psi_{k_f}^{(-)}\) are the initial and final distorted continuum wave functions with the outgoing- (+) and incoming-wave (-) boundary conditions, respectively. \(U_{se}\) is the static-exchange potential operator. The wave functions \(\Psi_{k_i}^{(+)}\) and \(\Psi_{k_f}^{(-)}\) were calculated using the iterative Schwinger variational method [25] in the static-exchange field of the ground state and excited state of the target, respectively. Although the continuum orbitals of the incoming electron are known to be orthogonal to all bound orbitals of the ground-state target, it is not the case for the scattered electron since the continuum wave functions are calculated in the static-exchange field of the open-shell target. For simplicity, these outgoing orbitals were constrained to be orthogonal to all occupied orbitals of the excited target. Further, the transition \(T\) matrix as well as the distorted wave functions are single-center expanded. Such expansions are truncated at the cutoff parameters \(l_c = 90\) and \(m_c = 9\). For the transitions leading to the singlet excited state, the contributions from the higher partial waves were accounted for via the Born-closure procedure [26, 27]. The ground-state configurations of the targets are represented by single-determinant near-HF wave functions. The basis sets used for the HF calculations can be found in [17]. The same basis sets are also used to calculate the wave functions of the lowest unoccupied orbitals (\(2\pi\) in CO, \(2\pi_u\) in CO\(_2\) and \(4\pi\) in OCS) and the vertical excitation energies using an improved virtual orbital approximation [28]. The calculated vertical excitation energies for the singlet and triplet transitions from the O(1s) orbital to the
Figure 1. Present DWA DCS for electron-impact O(1s)$^{-1}$ singlet transitions in CO, CO$_2$, and OCS at (a) 556 eV, (b) 600 eV, (c) 700 eV, and (d) 900 eV. Solid line, results for the $2\sigma \rightarrow 4\pi$ transition in OCS; dashed line, DCS for the $1\sigma_g \rightarrow 2\pi_u$ transition in CO$_2$; dotted line, results for the $1\sigma \rightarrow 2\pi$ transition in CO.

Figure 2. The same as in Fig. 1, but for the triplet transitions.

lowest $\pi$ orbital, as well as the singlet-triplet energy splitting are shown in Table I, in comparison with some available data in the literature. It is seen that the calculated vertical excitation energies for singlet transitions are about 3% higher than the corresponding experimental values for these molecules, except CO, which is quite reasonable.

3. Results and discussion

Fig. 1 compares the calculated DWA DCS for the singlet transitions: $X^1\Sigma^+ \rightarrow ^3\Pi(1\sigma \rightarrow 2\pi)$ in CO, $X^1\Sigma_g^+ \rightarrow ^3\Pi_u(1\sigma_g \rightarrow 2\pi_u)$ in CO$_2$, and $X^1\Sigma^+ \rightarrow ^3\Pi(2\sigma \rightarrow 4\pi)$ in OCS in the (550-900)-eV incident energy range. In Fig. 2, a similar comparison, but for the corresponding triplet transitions, is presented. It is seen in these figures that the DCS calculated for CO are substantially larger than the corresponding results for OCS and CO$_2$ in the covered energy range. In fact, the observed discrepancies are somehow expected. According to Eq. (3), the transition $T$ matrix depends on both the core and excited valence orbitals. The $1\sigma_g$ orbital of CO$_2$ is delocalized and thus is expected to be different from the localized O(1s) orbital of OCS and CO. For the latter two targets, despite their O(1s) orbitals are both strongly localized and atomic-like, the lowest unfilled $\pi$ orbitals of the two targets are certainly very different, since CO is diatomic and OCS triatomic.

For the same reason, the significant differences seen between the DCS calculated for OCS and CO$_2$ at incident energies of 556 and 600 eV can be justified. Nevertheless at higher incident
energies, a fairly good agreement, both qualitative and quantitative, in the DCS calculated for these two targets is seen which is surprising. Maybe, it is because that OCS and CO$_2$ are both triatomic linear molecules, and are also isoelectronic in the valence shell. Thus, there could be some similarities between the $4\pi$ orbital of OCS and the $2\pi_u$ orbital of CO$_2$ that contribute to the good agreement in calculated DCS for these targets at high incident energies. Therefore, our study suggests that the influence of the localized or delocalized character of the core orbitals in the calculated DCS decreases with increasing energies.

In Figs. 3 we show our DWA ICS calculated in the (550-1000)-eV energy range for electron-impact transitions leading to the singlet excited states: $1\sigma_g^{-1}2\pi$ in CO, the $2\sigma^{-1}4\pi$ in OCS, and the $1\sigma_g^{-1}2\pi_u$ in CO$_2$. Calculated ICS for the transitions leading to the corresponding triplet excited states are shown in Fig. 4. As expected, the non-resonant ICS for the excitation of one O(1s) electron in CO are substantially larger than those for OCS and CO$_2$. In addition, for both singlet and triplet transitions, fairly good agreement is seen between the non-resonant ICS calculated for OCS and CO$_2$. Near the excitation thresholds, resonance-like structures are seen in the DWA ICS for the three targets. For singlet transitions, a strong peak located at around 552 eV and two weak peaks around 567 and 588 eV, respectively, are seen in the results of OCS. Similar resonance structures are also seen in the calculated ICS of CO$_2$, except the position of the the strongest peak is located at about 559 eV. On the other hand, only two resonances are seen in the ICS for CO: one sharp feature located at about 553 eV and one shoulder at around 577 eV. For triplet transitions, the resonance structures of the three molecules are quite similar.
to their counterparts in the singlet transitions, except their positions are slightly shifted.

The resemblance between the resonance structures in OCS and CO\textsubscript{2} seems to reinforce the idea that the low-lying unfilled orbitals of the two valence-shell isoelectronic systems are quite similar with each other. In contrast, it is expected that the low-lying excited orbitals of CO are significantly dissimilar to those of OCS and CO\textsubscript{2}. Also, eigenphase analyses (not shown) have revealed that the strongest resonance feature for the singlet transition in CO\textsubscript{2} is due to the occurrence of a $k\pi$ shape resonance. Similar peaks seen in the ICS of CO and OCS are due to a shape resonance in the $k\pi$ scattering channel. For other structures, no eigenphase analyses were performed.

In Fig. 5, we compare our GOS calculated at 1300 eV for the O(1s) core-excitation in CO\textsubscript{2} with the only existing theoretical and experimental data of Eustatiu et al. [12]. Due to the small energy difference between the $1\sigma_g \rightarrow 2\pi_u$ and $1\sigma_u \rightarrow 2\pi_u$ singlet transitions, the experimental GOS are in fact the sum of the contributions of the two transitions. Therefore, specifically for this energy, we have also calculated GOS for the $1\sigma_u \rightarrow 2\pi_u$ singlet transition. The calculated results of GOS for the two transitions are also presented separately in Fig. 5. It is seen that the GOS for the $1\sigma_u \rightarrow 2\pi_u$ singlet transitions grow much faster than those for the $1\sigma_u \rightarrow 2\pi_u$ transition towards the small momentum transfer ($K$) region. This is because the former transition is dipole-allowed and the latter is dipole forbidden. Besides, at large momentum transfers, the GOS of both transitions are very similar. The sum of them agree well with the experimental and theoretical data of Eustatiu et al. [12], which is encouraging.

In summary, the present work reports an application of the DW A to study core-level excitations from the O(1s) orbital to the lowest lying unoccupied valence orbitals in CO, OCS, and CO\textsubscript{2}. The comparison of our DW A GOS for CO\textsubscript{2} with the existing theoretical and experimental data shows good agreement, which confirm the reliability of our method. Moreover, the similarity between the calculated DCS and ICS for OCS and CO\textsubscript{2} at high incident energies as well as the resemblance between the resonance structures in the ICS of these two systems seems to indicate the similarity of the lowest-lying unoccupied orbitals (4\pi in OCS and 2\pi\textsubscript{u} in CO\textsubscript{2}). On the other hand, the discrepancy seen in the low incident energies can partially be attributed to the atomic-like character of the 2\pi orbital in OCS and molecular character of the 1\sigma\textsubscript{g} orbital of CO\textsubscript{2}. 

![Figure 5. GOS for electron-impact core-excitation of CO\textsubscript{2} at 1300 eV. Dotted line, present calculated results for the $1\sigma_u \rightarrow 4\pi_u$ singlet transition; dashed line, DWA GOS for the $1\sigma_g \rightarrow 2\pi_u$ singlet transition; Solid line, present summed GOS; dashed-dotted-dotted line, GOS of Eustatiu et al. [12] using the FBA; full circles, experimental results of GOS of Eustatiu et al. [12].](image-url)
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5. References

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