

Multiple ionization upon K-shell photoabsorption of the CO and N₂ molecules

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The spectra of multiple ionization of CO and N₂ in the gas phase in the region of the K-shell ionization thresholds of C and N are studied theoretically. The processes of additional excitation/ionization from 1π and 5σ-shells are included. The effects of many-electron correlations on the extension of multiplet structure for some configurations of multiple excitations is studied. Absolute values of photoabsorption cross sections are calculated in some of the channels of multiple ionization.

Keywords: photoabsorption, cross-section, multiple ionization

1. Introduction

The studies on the excitation/ionization spectra of the CO and N₂ molecules carried out with the use of various experimental methods by Kay *et al.* (1977), Hitchcock *et al.* (1980), Schmidbauer *et al.* (1992), Shigemasa *et al.* (1993), Köppe *et al.* (1995), Kempgens *et al.* (1996) allowed to discover a complex fine structure of X-ray absorption in the region of carbon and nitrogen K-shell ionization thresholds.

The calculation by Padiál *et al.* (1978) allowed assignment of the main feature in the experimental spectrum to one-electron σ-resonance. Hitchcock *et al.* (1980), basing on comparison of the electron energy loss spectrum and X-ray photoelectron spectrum, supposed that some features in the spectrum may be connected with the states of multiple ionization. Kay *et al.* (1977) were the first to measure the absolute values of the carbon X-ray K-absorption intensity in CO. The absolute values of the carbon and nitrogen photoabsorption cross sections in CO and N₂ were measured recently by Köppe *et al.* (1995) and by Kempgens *et al.* (1996). The calculation of the intensity of processes of single and of several types of multiple excitation/ionization with taking monopole rearrangement of electron shells into account is performed by Bandarage *et al.* (1993), Schirmer *et al.* (1990), Yavna *et al.* (1994), Schirmer *et al.* (1991). Comparison of the results of theoretical and experimental studies allows one to conclude that a good agreement of the 1π⁻¹2π¹(^{1,3}Σ⁺)mσ⁻¹εγ-ionization spectra in CO (m=2) is obtained. The mechanism of formation of 1π⁻¹2π¹(^{1,3}Σ⁻,^{1,3}Δ)mσ⁻¹εγ and mσ⁻¹5σ⁻¹2π⁰εσ – spectra of multiple excitation/ionization of CO had been investigated theoretically by Yavna *et al.* (1998). The aim of this study is to calculate the spectra of the N₂ molecule. We also show the CO spectra to for comparison.

2. Theory

In the calculation of |nγμχ>-photoelectron wavefunctions, a one-centre expansion over the functions |nγlμχ> with fixed values of orbital quantum number l is used, where n is a principal quantum number, γ and μ stand for the irreducible

representation and its string by which the wavefunction is transformed and χ is the spin part of the wavefunction:

$$|\varphi_{n\gamma}\rangle = |n\gamma\mu\chi\rangle = |n\gamma l\mu\rangle |\chi\rangle,$$

$$|n\gamma l\mu\rangle = \sum_i \alpha_i^{n\gamma} |n\gamma l\mu\rangle = \sum_i \alpha_i^{n\gamma} R_i^{n\gamma}(r) \cdot Y_l^{\mu}(\vartheta, \varphi).$$

The main disadvantage of one-centre method is slow convergence of the series when calculating the wavefunctions in molecules with ligands heavier than hydrogen. In this work in calculation of the photoelectron wavefunction we employed the approximate method by Yavna *et al.* (1994) to calculate the series of functions |nγlμ> with large values of orbital quantum numbers. Within this method the terms |nγlμ>, starting from some large enough l₀, are substituted by respective terms of the wavefunctions of occupied states which were determined beforehand by numerical solution of a multi-centre problem (here and below, they are numbered with a subscript i). As a result, the photoelectron wavefunction assumes the form:

$$|n\gamma l\mu\rangle = \sum_{i \leq l_0} \alpha_i^{n\gamma} |n\gamma l\mu\rangle + \sum_i \alpha_i^{n\gamma} \sum_{l > l_0} \alpha_i^{l\gamma} |i\gamma l\mu\rangle.$$

The functions |nγlμ> with l ≤ l₀ are determined as expansions over basis set:

$$\alpha_i^{n\gamma} |n\gamma l\mu\rangle = \sum_k \alpha_{ki}^{n\gamma} |k\gamma l\mu\rangle + \sum_i \alpha_{ki}^{n\gamma} \alpha_i^{l\gamma} |i\gamma l\mu\rangle.$$

The basic functions of discrete and continuous energy spectra |klγlμ> with fixed values of orbital quantum numbers are obtained by numerical solution of one-electron Hartree-Fock equation:

(ĥ - ε_{kγlμ}) |klγlμ> = 0, where ĥ is a system's Fockian. The system of algebraic equations of the type:

$$\left\{ \begin{array}{l} \sum_k \sum_{i \leq l_0} \alpha_{ki}^{n\gamma} [k\gamma l'\mu | \hat{h} | kl\gamma l\mu - \varepsilon_{n\gamma} \delta_{kk'} \delta_{ll'}] + \\ \sum_i \alpha_i^n \sum_i \alpha_i^{i\gamma} \langle k\gamma l'\mu | i\gamma l\mu \rangle [\varepsilon_i - \varepsilon_{n\gamma}] = 0; \\ \sum_k \sum_{i \leq l_0} \alpha_{ki}^{n\gamma} \alpha_i^{i\gamma} \langle i\gamma l'\mu | kl\gamma l\mu \rangle [\varepsilon_{i'} - \varepsilon_{n\gamma}] \delta_{i'l'} + \\ \sum_i \alpha_i^n \left[\sum_{i'} \alpha_{i'i}^{n\gamma} \alpha_i^{i\gamma} \langle i\gamma l'\mu | \hat{h} | i\gamma l\mu \rangle - \varepsilon_{n\gamma} \delta_{i'i'} \right] = 0; \end{array} \right.$$

determines the coefficients α_{ki}ⁿ, α_{ki}^{nγ} and α_i^{nγ}.

To calculate the extent of the multiplet structure of mσ⁻¹nγ¹n₁γ₁-configuration in the Hartree-Fock approximation with respect to its centre of gravity, a secular equation is constructed employing the methods reported by Condon & Shortley (1949). The basis is formed of one-determinant wavefunctions with uncoupled one-electron momenta |mσ⁻¹nγ¹n₁γ₁(α_iM_ΓM_S)> where M_Γ and M_S stand for the line of irreducible representation and the projection of total spin momentum, i numbers the sets of quantum numbers for electron configurations (α). After solving the secular equation by the method of Yavna *et al.* (1998), the wavefunctions of terms are determined in the form:

$$|\Gamma S M_{\Gamma} M_S, k\rangle = \sum_i \alpha_{ki}(\Gamma S) \cdot |m\sigma^{-1} n\gamma^{-1} n_1 \gamma_1 (\alpha_i M_{\Gamma} M_S)\rangle,$$

where the subscript k numbers the terms of the configurations, α_{ki} are the configuration mixing coefficients, Γ and S are the irreducible representation and spin of the term, respectively.

Final state of the phototransition, which was obtained by combining the photoelectron function |εγμχ> and the function |ΓSM_ΓM_S, k>, has the form:

$$|\Phi_k(\Gamma_0 S_0 = 0)\rangle = \frac{1}{\sqrt{2}} \left(|\Gamma S M_{\Gamma} M_S = \frac{1}{2}, k\rangle |\varepsilon\gamma\mu\chi = -\frac{1}{2}\rangle - |\Gamma S M_{\Gamma} M_S = -\frac{1}{2}, k\rangle |\varepsilon\gamma\mu\chi = \frac{1}{2}\rangle \right)$$

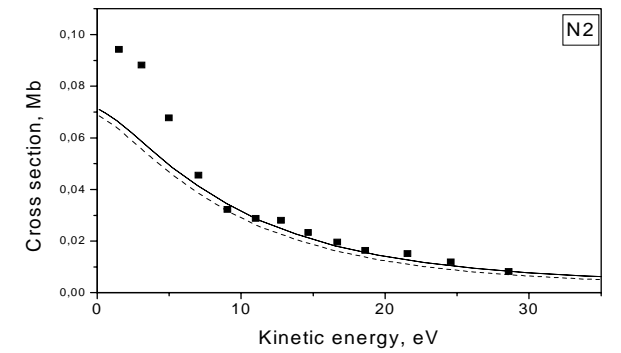
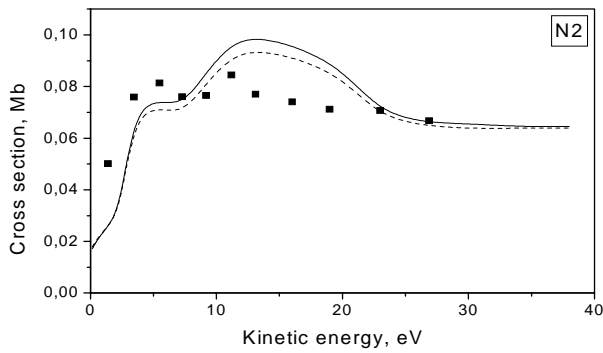
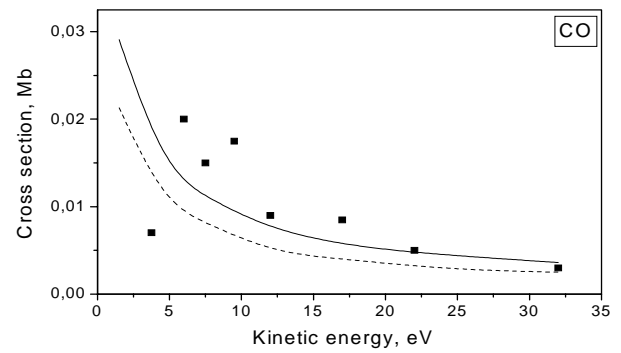
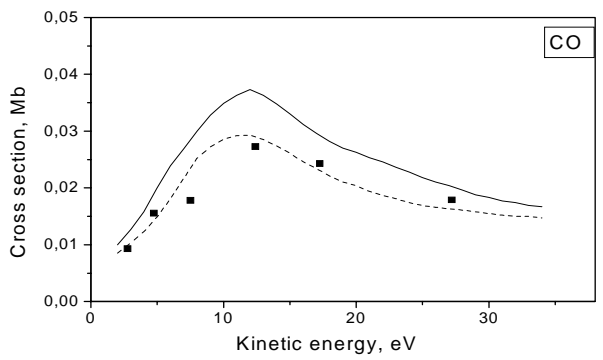


Figure 1
Cross sections of $1\pi^{-1}2\pi^{1}({}^3\Sigma^{+})m\sigma^{-1}\varepsilon\gamma$ ionization of CO (m=2) and N₂ (m=1). The experiment is shown with squares.

Figure 3
Cross sections of $1\pi^{-1}2\pi^{1}({}^1\Sigma^{-}, {}^3\Sigma^{-}, {}^1\Delta, {}^3\Delta)m\sigma^{-1}\varepsilon\gamma$ – ionization of CO (m=2) and N₂ (m=1). The experiment is shown with squares.

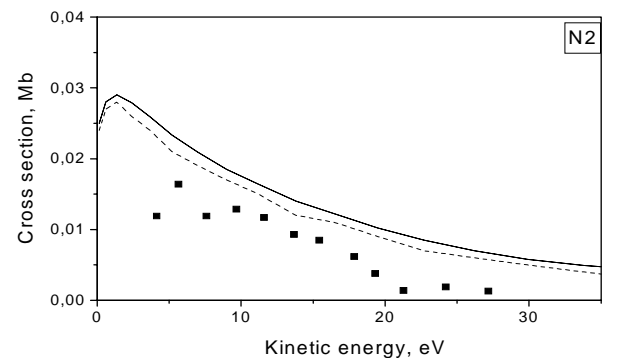
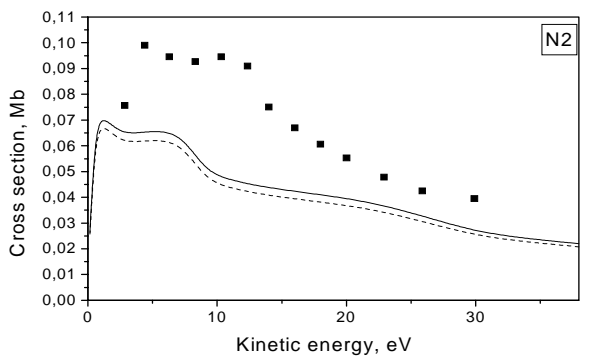
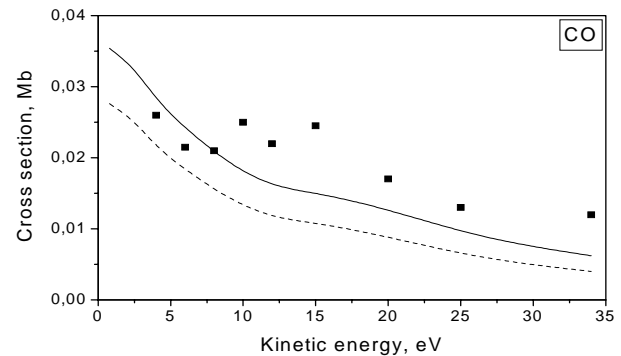
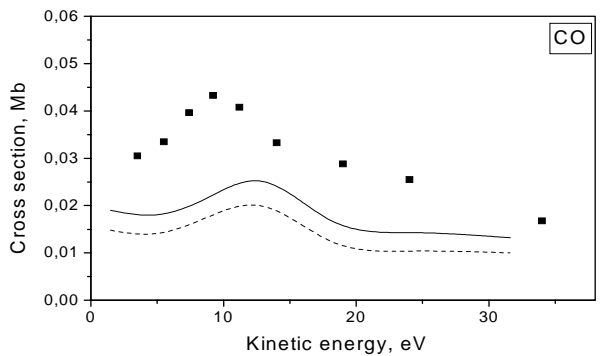


Figure 2
Cross sections of $1\pi^{-1}2\pi^{1}({}^1\Sigma^{+})m\sigma^{-1}\varepsilon\gamma$ ionization of the CO (m=2) and N₂ (m=1). The experiment is shown with squares.

Figure 4
Cross sections of $m\sigma^{-1}5\sigma^{-1}({}^3\Sigma)2\pi^{1}{}^2\Pi\varepsilon\sigma$ – ionization of CO (m=2) and N₂ (m=1). The experiment is shown with squares.

where Γ_0 and S_0 are irreducible representation and spin of the final configuration term.

In this case the matrix element of the dipole transition operator is:

$$\begin{aligned} \langle \Phi_k(\Gamma_0 S_0 = 0) | \hat{D}_q | \Phi \rangle &= \sum_{i,q} [a_{ki}(\alpha_i A_q + \beta_i B_q)]; \\ A_q &= N \left[\langle n_i \gamma_i \mu_i | \hat{d}_q | 2\sigma \rangle - \sum_{k_3 \gamma_3 \mu_3 \leq f} \frac{\langle n_i \gamma_i \mu_i | k_3 \gamma_3 \mu_3 \rangle \langle k_3 \gamma_3 \mu_3 | \hat{d}_q | 2\sigma \rangle}{\langle k_3 \gamma_3 \mu_3 | k_3 \gamma_3 \mu_3 \rangle} \right] \frac{\langle \epsilon \gamma \mu | r | n \eta \rangle}{\langle r | n | r | n \rangle}; \\ B_q &= N \left[\langle \epsilon \gamma \mu | \hat{d}_q | 2\sigma \rangle - \sum_{k_3 \gamma_3 \mu_3 \leq f} \frac{\langle \epsilon \gamma \mu | k_3 \gamma_3 \mu_3 \rangle \langle k_3 \gamma_3 \mu_3 | \hat{d}_q | 2\sigma \rangle}{\langle k_3 \gamma_3 \mu_3 | k_3 \gamma_3 \mu_3 \rangle} \right] \frac{\langle n_i \gamma_i \mu_i | r | n \eta \rangle}{\langle r | n | r | n \rangle}, \end{aligned}$$

where $|\phi\rangle$ is the ground state of the molecule, f is the Fermi level, α_i and β_i is the angular coefficients and N is the product of the overlap integrals of the wave functions of those electrons that do not take part in the transition.

3. Satellites of $2\sigma 1\pi 2\pi\epsilon\gamma$ Excitation/Ionization

The appearance of σ -photoelectron is connected with the formation of $1\pi^{-1}2\pi^1(^1\Sigma^+)m\sigma^{-1}2\Sigma\epsilon\sigma$ - and $1\pi^{-1}2\pi^1(^3\Sigma^+)m\sigma^{-1}2\Sigma\epsilon\sigma$ -terms. In the latter case the photoabsorption probability is close to zero. The possibility for final states connected with $1\pi^{-1}2\pi^1(^3\Sigma^+)m\sigma^{-1}2\Sigma\epsilon\sigma$ configuration is determined by the interaction of $1\pi^{-1}2\pi^1(^3\Sigma^+)m\sigma^{-1}2\Sigma$ - and $m\sigma^{-1}2\Sigma$ -configurations. The values of radial part of the matrix element for the interaction are equal to 0.016 a.u. (CO) and 0.020 a.u. (N₂). The contributions of $m\sigma^{-1}2\Sigma$ to the total vector of final state are 0.125 (CO) and 0.130 (N₂). Calculated electron spectra caused by the transitions into the states of CO and N₂ molecular residue terms $1\sigma^{-1}1\pi^{-1}2\pi^1(^1\Sigma^+)$ and $1\sigma^{-1}1\pi^{-1}2\pi^1(^3\Sigma^+)$ are compared with the experiment by Köppe *et al.* (1995), Kempgens *et al.* (1996) in Figure 1 and Figure 2, respectively. The electron spectra connected with formation of terms $1\pi^{-1}2\pi^1(^1\Sigma^-, ^3\Sigma^-, ^1\Delta, ^3\Delta)m\sigma^{-1}\epsilon\gamma$ were summed up because of the proximity of respective ionization thresholds. They are compared with the experiment by Köppe *et al.* (1995), Kempgens *et al.* (1996) in Figure 3. One should note that the contribution to the resulting theoretical curve from the process with the formation of the $^1\Sigma$ -term is about by one order of magnitude less than that from other terms.

4. Satellites of $m\sigma 5\sigma 2\pi\epsilon\sigma$ Excitation/Ionization

One-electron $m\sigma 2\pi$ transition can be accompanied by ejection of σ -symmetry core electrons without change of symmetry. In this work we study the processes of photoabsorption with the additional excitation of electrons from 5σ -shells. According to dipole selection rules, allowed is the transition into the states with $m\sigma^{-1}5\sigma^{-1}(^3\Sigma)2\pi^1 2\Pi$ - terms of molecular residue. The results of calculation of respective electron spectra are compared with the experiment by Köppe *et al.* (1995), Kempgens *et al.* (1996) in Figure 4.

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