

Orientation effects in elastic scattering of polarized X-rays by linear molecules

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Strong orientation effect is discovered theoretically upon the change of the scheme of suggested experiment on anomalous elastic x-ray scattering of linearly polarized x-ray radiation by linear diatomics near the ionization thresholds of inner molecular orbitals. Studied are the effects on the shape of theoretical scattering spectra of additional excitations/ionizations of outer-shell electrons. Within the one-centre approximation for the molecular orbitals wavefunctions the analytical structure of the linear molecule's formfactor is obtained. The dipole transition matrix elements and photoabsorption cross sections are calculated by the methods of the theory of non-orthogonal orbitals.

Keywords: elastic scattering, polarization, cross section

1. Introduction

Recently, the interest to the studies of the fundamental process of elastic scattering of x-ray radiation by atoms (Pratt *et al.*, 1994, Hopersky *et al.*, 1997) and molecules (Gel'mukhanov *et al.*, 1997) near the inner shell ionization thresholds has significantly grown. Of particular interest are the regions of the scattering spectra in the immediate vicinity of ionization thresholds. Those are the regions of anomalous dispersion. After scattering a photon, an atom or a molecule remains in its initial state. Nevertheless, during its virtual existence in the excited state it can demonstrate its real many-electron nature. Studies on such peculiarities can give a unique information on the structure and properties of scatterers, specifically, on many-electron effects and their quantum interference.

2. Theory

Consider the case of the scattering of the x-ray photon with energy ω , wavevector \mathbf{k} , and polarization vector \mathbf{e} . Let us define the scattering plane as the one containing the wavevectors of incident \mathbf{k}_1 and scattered \mathbf{k}_2 photons. Consider the case when the polarization vectors of incident \mathbf{e}_1 and scattered \mathbf{e}_2 photons are perpendicular to the scattering plane: $(\mathbf{e}_1 \cdot \mathbf{e}_2)^2 = 1$. In non-relativistic approximation, let us define the wavefunction of the $\varphi_{n\gamma}$ -electron with principal quantum number n and the spin part χ , which transforms according to irreducible representation γ with the string μ , in the form of one-centre expansion over the functions $|n\gamma\mu\rangle$ with fixed values of angular momentum l :

$$|\varphi_{n\gamma}\rangle = |n\gamma\mu\chi\rangle = |n\gamma\mu\rangle |\chi\rangle, \quad |n\gamma\mu\rangle = \sum_l a_l^{n\gamma} |n\gamma\mu\rangle = \sum_l a_l^{n\gamma} R_l^{n\gamma}(r) Y_l^\mu(\vartheta, \varphi),$$

where radial and angular parts of the wavefunction $|n\gamma\mu\rangle$ are $R_l^{n\gamma}(r)$ and $Y_l^\mu(\vartheta, \varphi)$, and r, ϑ, φ are spherical coordinates.

Method of calculation of the single and multiple excitation/ionization wavefunctions, as well as the approximations employed are described in detail by Yavna *et al.* (1994, 1998).

Then the expression for the differential cross section of the anomalous elastic scattering of polarized photon by linear molecule into the solid angle $d\Omega$ in atomic units has the form:

$$d\sigma_{\perp} / d\Omega = r_0^2 \left| F + \sum_{q, n\gamma \leq f} Q_{n\gamma}^q(\omega) \right|^2,$$

where r_0 is electron classical radius, f is the Fermi level, q is the rank of the irreducible tensor operator of transition. For the formfactor of linear molecule, considering expansion of the exponent over the spherical functions $C_q^{(t)}$ of the rank $t \geq 0$, ($q = 0, \dots, \pm t$), one obtains:

$$\left\{ \begin{aligned} F &= \langle \phi | \sum_{j=1}^m e^{i(\mathbf{k} \cdot \mathbf{r}_j)} | \phi \rangle = \sum_{\mu_1, \mu_2, n\gamma, l_1, l_2, t} i^t (2t+1) \langle n\gamma l_1 | j_t(kr) | n\gamma l_2 \rangle^* \\ &* C_{l_1 l_2}^{\mu_1 \mu_2} P_t(\cos \Theta_k), \\ k &= |\mathbf{k}| = |\mathbf{k}_1 - \mathbf{k}_2| = (2\omega/c) \cdot \sin\left(\frac{\theta}{2}\right) \\ \langle n\gamma l_1 | j_t(kr) | n\gamma l_2 \rangle &= \int_0^{\infty} R_{l_1}^{n\gamma}(r) \cdot R_{l_2}^{n\gamma}(r) \cdot j_t(kr) \cdot r^2 dr, \\ |\phi\rangle &= \det \|\varphi_{n\gamma}\| \end{aligned} \right.$$

where $|\phi\rangle$ is the molecule ground state wavefunction, m is the number of electrons in molecule; \mathbf{r}_j is the j -th electron's radius-vector; θ is the angle between the vectors \mathbf{k}_1 and \mathbf{k}_2 (the scattering angle); Θ_k is the angle between the scattering vector \mathbf{k} and molecular axis OZ; ω is the energy of the scattered photon; c is the speed of light; j_t is the spherical Bessel function of the first kind and of the order t ; P_t is the Legendre polynomial of the first kind and of the power t ; $C_{l_1 l_2}^{\mu_1 \mu_2}$ are the angular coefficients with the structure:

$$C_{l_1 l_2}^{\mu_1 \mu_2} = (-1)^{l_1 - \mu_1} (l_1 \| C^{(t)} \| l_2) \begin{pmatrix} l_1 & t & l_2 \\ -\mu_1 & q & \mu_2 \end{pmatrix}.$$

Within the dipole approximation, the anomalous dispersion Kramers-Heisenberg terms of the amplitude of the elastic scattering of photon by molecule have the form:

$$\left\{ \begin{aligned} Q_{n\gamma}^q(\omega) &= \alpha \sum_{\varepsilon > f} \frac{\overline{\omega}_{\varepsilon} \cdot \omega_{\varepsilon}^2}{\omega^2 - \overline{\omega}_{\varepsilon}^2} \left| \langle \phi_{n\gamma, \varepsilon} | \hat{D}_q | \phi \rangle \right|^2, \\ \overline{\omega}_{\varepsilon} &= \omega_{\varepsilon} - i \cdot \Gamma_{n\gamma} / 2, \end{aligned} \right.$$

where $\alpha = 2/3$ at $q = 0$ and $\alpha = 1/3$ at $q = \pm 1$; ε is the set of the quantum numbers of the virtual electron; ω_{ε} is the energy of the transition from the ground state $|\phi\rangle$ to the excited state $|\phi_{n\gamma, \varepsilon}\rangle$ with the vacancy in the $n\gamma$ -shell; $\Gamma_{n\gamma}$ is the total decay width for the vacancy in the excited state; the symbol $\sum_{\varepsilon > f}$ implies summation/integration over the states of the discrete/continuous spectra; \hat{D}_q is the electric dipole transition operator.

3. Results of the calculations

In this work we calculate the differential cross sections of anomalous elastic scattering of photon by molecule originally oriented with respect to the scattering plane and the polarization vectors of incident and scattered photons. Considered are two proposed experimental schemes displayed in Figure 1. In the scheme (a) the molecular axis is perpendicular to the polarization vectors of incident and scattered photons, and it lies in the plane of scattering being parallel to the wavevector of incident photon. In this case the sum over the rank q in the expression for $Q_{n\gamma}^q(\omega)$ contains two terms ($q = \pm 1$). In the scheme (b) the molecular axis is parallel to the polarization vectors of incident and scattered photons and perpendicular to the scattering plane. In this case the sum over the rank q has only one term ($q = 0$).

Note that in the case of the molecules CO and N₂ the shape and the absolute values of the differential cross sections of elastic scattering hardly depend on the scattering angle θ . It is known (Gel'mukhanov *et al.*, 1997) that the criterion of such independence is $R < \lambda \cdot (4\pi \cdot |\sin(\theta/2)|)^{-1}$, where R is internuclear distance, λ is the incident photon wavelength. In the near edge regions this inequality is fulfilled for the CO and N₂ molecules ($R_{CO} = 1,128 \text{ \AA}$; $R_{N_2} = 1,098 \text{ \AA}$; $\lambda_{CO} = 17,85 \text{ \AA}$; $\lambda_{N_2} = 30,41 \text{ \AA}$). For this reason we display the calculations results for the angle 0° .

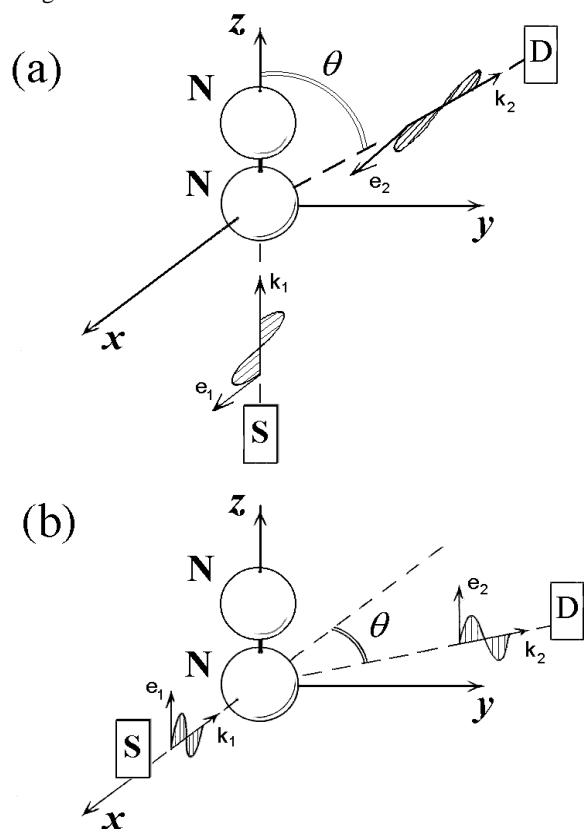


Figure 1
The orientation of the N₂ molecule with respect to the polarization vectors of incident and scattered photons in the schemes of the proposed anomalous elastic scattering experiment. S is a photon source, D is a detector of the scattered photons.

In studies of the effect of the processes of multiple excitation/ionization on the anomalous elastic scattering spectrum the following virtual states are included: $1\pi^{-1}2\pi^{1(1,3}\Sigma^+, 1,3\Sigma^-, 1,3\Delta)m\sigma^{-1}\epsilon\gamma$, $m\sigma^{-1}n\sigma^{-1}(^3\Sigma)2\pi^{1,2}\Pi\epsilon\sigma$ ($n = 4, 5$) and $m\sigma^{-1}5\sigma^{-1(1,3}\Sigma)n\sigma\epsilon\gamma$ ($n = 6, 7$); $m=2$ – CO and $m=1$ – N₂. In this work in calculation of wavefunctions and matrix elements we employed the one-centre method by Yavna *et al.*, 1998, 2000

The differential cross sections of anomalous elastic scattering of photon by the N₂ and CO molecules for the scattering angle of 0° calculated with inclusion of the processes of single and multiple excitation/ionization are shown in Figure 2 and Figure 3 respectively.

As it follows from the data in Figures 2,3, the swap from scheme (b) (series of the excited states $m\sigma^{-1}n\pi$; $n>f$) to scheme (a)

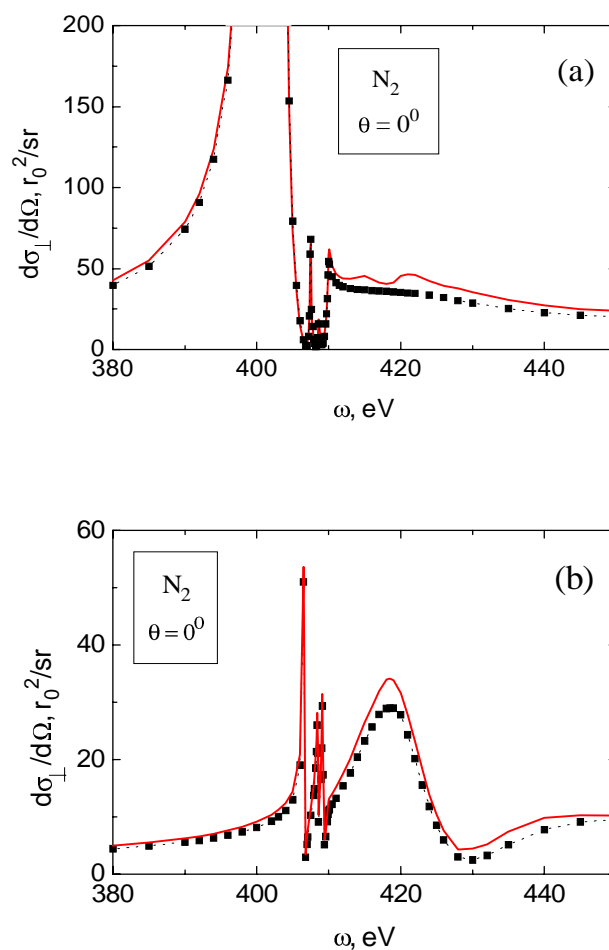


Figure 2
Differential cross section of anomalous elastic scattering of linearly polarized x-ray radiation by the N₂ molecule. Squares represent the results of calculation with inclusion of only the channels of single excitation/ionization, solid line – with additional inclusion of virtual states of one photon double excitation/ionization.

(series of the excited states $m\sigma^{-1}n\pi$; $n>f$) leads to a strong orientation effect – the appearance in the long-wave spectral region of an additional giant elastic scattering resonance

connected with the virtual excitation $m\sigma-2\pi$ with the width of 0,20 eV (Tronc *et al.*, 1980), the oscillator strength of 0,232 and the energy of 402,1 eV (this work) for the N_2 , and with the width of 0,16 eV (Domke *et al.*, 1990), the oscillator strength of 0,118 and the energy of 296,1 eV (this work) for the CO molecule.

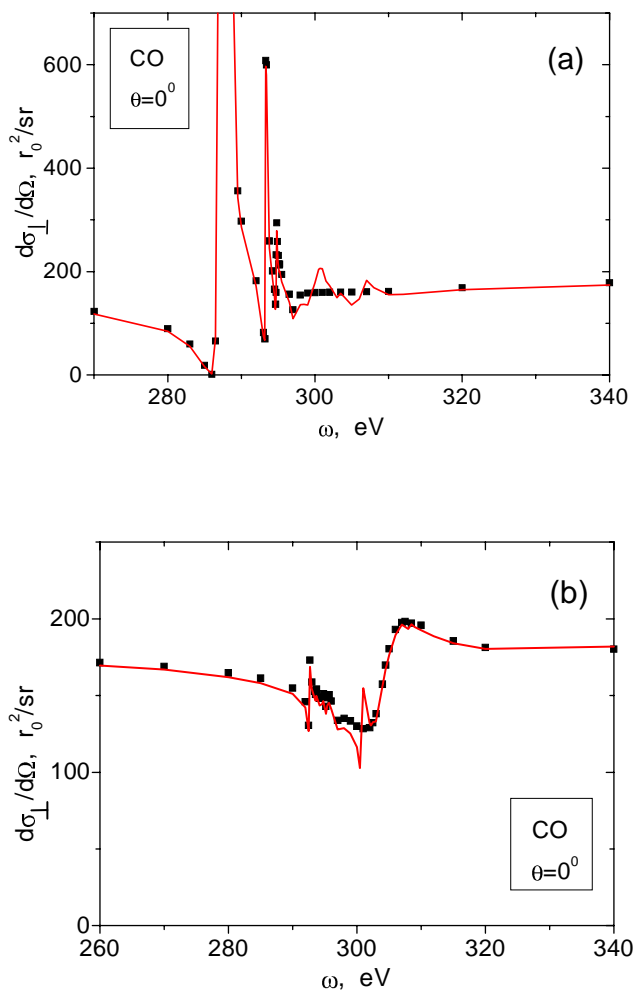


Figure 3
Differential cross section of anomalous elastic scattering of linearly polarized x-ray radiation by the CO molecule. Squares represent the results of calculation with inclusion of only the channels of single excitation/ionization, solid line – with additional inclusion of virtual states of one photon double excitation/ionization.

4. Conclusion

The results obtained support the general conclusion of molecular spectra theory on orientation effect and concretize it as applied to the problem of theoretical description of the process of anomalous elastic scattering of polarized x-ray radiation by a free molecule oriented in space.

With the CO and N_2 molecules as an example it is shown that the inclusion of the processes of multiple excitation/ionization significantly refines the results of calculations as compared with those where only the channels of single excitation/ionization are included.

The results of the calculations performed in this work are predictions.

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