

Photoelectron-Auger electron angular correlations in photoionization of fixed-in-space molecules

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Abstract. The K-shell Auger decay studies of fixed-in-space diatomic molecules are reviewed. The Auger-electron-photoelectron angular correlations after ejection of the C 1s electron of CO in the laboratory frame are not sensitive to the details of the Auger-electron wave function, as are the Auger-electron angular distributions in the molecular frame. Different arguments in favour of creation of delocalized gerade (g) or ungerade (u), or localized right or left core hole in photoionization process are analyzed. In several high resolution photo- and Auger-electron studies of N₂ molecule the g and u states have been resolved, and their results demonstrated delocalized character of the core holes. The recent coincident study of the Auger- and photoelectrons in the molecular frame showed that they form a quantum entangled Bell state, and whether the core hole is better thought of as being localized or delocalized depends on the directions in which the photoelectron and the Auger-electron are emitted. This phenomenon exists owing to overlap of g and u lines and interference of the corresponding decay channels.

1. Introduction

The last decade was marked by a broad application of different coincidence techniques which allow selecting the processes with a well defined direction of molecular axis in space from the photoionization of an ensemble of randomly oriented molecules in a gas phase (see Ref. [1-8] and references therein). We consider here the photoionization of core levels of diatomic molecules. This photoionization process is followed usually by an Auger decay producing a doubly charged molecular ion. As the next step this ion dissociates producing different atomic ions. If these three processes are fast compared to the period of molecular rotation, the direction of motion of the fragment ion(s) gives the direction of the molecular axis at the moment of photoionization [9-10]. In the processes considered below this condition is implied to be fulfilled. With the contemporary coincidence techniques it is possible to detect simultaneously the photoelectron, the Auger electron and the atomic ion(s). The new information to be extracted from these most sophisticated studies is discussed in this talk with emphasize on the theoretical consideration.

The first measurements of angle-resolved Auger emission from fixed-in-space molecules for the C K-shell of CO molecule led to controversial results [11,12]. As for the theoretical description, there were several studies of the general properties of the angular distribution of Auger electrons [13-17], but the numerical calculations are scarce [18-20]. More detailed studies performed recently in [21,22] are discussed below. In atoms Auger electron-photoelectron coincidence experiments have proved to

be a very suitable tool to provide an unambiguous spectroscopic characterization of the emitted electron spectra [23,24], and even have been proposed as “complete experiment” [25] from which the transition amplitudes and phases either of photoionization or of Auger decay can be obtained experimentally. So far the applications of coincidence techniques to molecules did not allow performing the complete experiment, though many important problems have been elucidated.

2. Theoretical calculations

We assume that the two-step model holds which implies that the photon absorption is much faster than the Auger decay [26]. Under this condition the amplitude of the process is expressed through the product of a dipole d and a Coulomb V matrix elements

$$\left\langle \Psi_{\Lambda_f}^{N-2} \psi_{p_A}^-(\mathbf{r}_A) \psi_p^-(\mathbf{r}_p) | S | \Psi_0 \right\rangle = \left\langle \Psi_{\Lambda_f}^{N-2} \psi_{p_A}^-(\mathbf{r}_A) | V | \Psi_{\Lambda^+}^{N-1} \right\rangle \left\langle \Psi_{\Lambda^+}^{N-1} \psi_p^-(\mathbf{r}_p) | d_{\lambda} | \Psi_0 \right\rangle. \quad (1)$$

Here $|\Psi_0\rangle$ is the ground state wave function of a molecule containing N electrons, λ is projection of the photon angular momentum in a photon frame with the z axis directed along the photon beam, $\Psi_{\Lambda^+}^{N-1}$ and $\Psi_{\Lambda_f}^{N-2}$ are a singly and a doubly charged molecular ion wave functions of the intermediate and final states, respectively, $\psi_p^-(\mathbf{r}_p)$ and $\psi_{p_A}^-(\mathbf{r}_A)$ are the photoelectron and the Auger electron wave functions defined in the molecular frame, and p and p_A are the momentum of the photoelectron and of Auger electron respectively. In the two-step model there must be only one intermediate $\Psi_{\Lambda^+}^{N-1}$ state.

Inserting into equation (1) all necessary wave functions one can show that the double differential cross section for the photoionization+Auger decay of fixed-in-space molecules is factorized into a product of a part describing the photoionization process, and a part describing the Auger decay [15], which are connected with each other only through the conservation law of the projection of the orbital angular momentum Λ^+ of the intermediate singly charged ion state (equal to zero for the K-shell hole, the spin does not influence the process). It means that the Auger electron angular distribution does not depend on the photon energy and its polarization.

Our numerical calculations of the Auger decay presented below are based on the codes developed earlier for the study of photoionization process [27,28]. At first the single electron wave functions of the ground state of the neutral molecule are calculated in the HF approximation. The photoelectron wave function is found in the relaxed core HF (RCHF) approximation as a solution of the HF equation with the potential formed by the self-consistent HF wave functions of a singly charged ion. It is orthogonalized to the ground state wave functions. With these wave functions the dipole matrix elements are calculated. When necessary, many electron correlations are taken into account in the random phase approximation (RPA).

The initial state for the Auger decay is described by the self-consistent HF wave function of the singly charged molecular ion. The Auger electron wave function is calculated in the frozen HF field of the doubly charged ion. Since the Auger electron energy in the particular cases considered here is large, about 250 eV or higher, the contribution of many-electron correlations is expected to be negligibly small. Therefore the majority of calculations have been performed within the HF and RCHF approximations. In calculations of the Auger decay amplitudes $A_{l,m} \equiv \langle \Lambda_f \varepsilon_A l m | V | \Lambda^+ \rangle$ we followed the procedure described in [29].

3. Angular distribution of Auger electrons from C 1s shell of CO molecule

The Auger decay of the C 1s hole state leads predominantly to three lowest doubly ionized states, $X^1\Sigma(5\sigma^{-2})$, $A^1\Pi(5\sigma^{-1}1\pi^{-1})$, and $B^1\Sigma(5\sigma^{-1}4\sigma^{-1})$. Since X and A states are not well separated in the Auger electron spectrum [12], it is preferable to discuss the B state. In the experiments shown below with fixed-in-space molecules the photon beam is directed perpendicular to the molecular axis, and the Auger electron (and photoelectron) is detected in the plane perpendicular to the photon beam. In the first study of Guillemin et al [11] it was found that the molecular frame Auger electron angular

distributions strongly depend on the photon energy and the direction of polarization in contradiction with the two step model. In a subsequent study of Weber et al [12] for the B state the dependence on the light polarization has not been observed, but the angular distributions were found to be only weakly structured. The authors argued that this is a consequence of failure of the axial recoil approximation as was mentioned earlier by Weber et al [30]. In the most recent measurements of Avaldi et al [31] for the B state it was found again that the Auger electron angular distributions depend on the photon energy and polarization though not so dramatically, and that they are strongly structured which supports the applicability of the axial recoil approximation. Our theoretical calculations within the two step model for the B state are shown in Figure 1 together with the available experimental data. The results of the study of the Auger electron – photoelectron angular correlations for the B and X states averaged over the molecular orientations are published in [21,22]. Theoretical calculations in the HF approximation based on the two-step model agree quite well with the measurements. However both experiment and theory are not sufficiently sensitive to the details of the Auger electron wave function. At the same time, the calculations demonstrate that the Auger electron angular distribution measured in the molecular frame without coincidence with photoelectrons is sensitive to the individual contributions of different partial waves of the Auger electron (see Figure 1d) and therefore can give more detailed information on the Auger decay process. Evidently, further experimental studies are necessary to answer all questions.

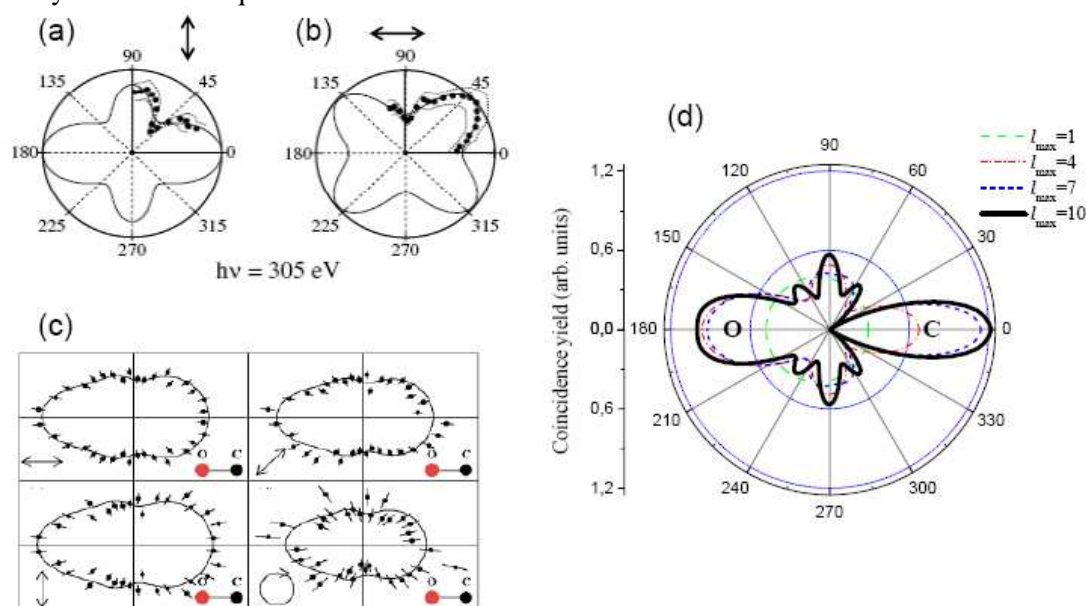


Figure 1. Auger electron angular distributions in the molecular frame for the B line of CO molecule after ionization of the C K-shell, photon energy is 305 eV, molecular axis is horizontal. (a),(b) Experimental results from [11], light polarization is mentioned by arrows, C and O ions are not distinguished. (c) Experimental results from [12], kind of light polarization is mentioned in the low left corners. (d) Results of calculation in the RCHF approximation from [21]; different curves show the angular distributions obtained with different numbers of partial waves in the Auger electron wave function.

4. On the possibility of localization of the core hole state: theory

The question of whether the K-shell vacancy in a homonuclear diatomic molecule is localized on one atom or delocalized over both is discussed for a long time. This question was risen in [32] in connection with calculations of ionization potentials of homonuclear diatomic molecules in the HF approximation that were substantially higher than the experimental values. Bagus and Schaefer [33] demonstrated that allowing for a localization of the 1s hole state in the HF-type calculation lowers the

total energy of the $O_2^+(1s^{-1})$ ion yielding a good agreement with experiment. On the other hand, the HF approximation must not reproduce the experimental energies with a high precision, and it was shown soon afterwards by Cederbaum and Domcke [34] that going beyond the HF approximation by taking into account the correlational energy already in the second order of perturbation theory in the Coulomb interaction leads to a good agreement with experiment with delocalized (symmetry adopted) gerade (g) and ungerade (u) states. A large contribution of the relaxation energy found in the HF approximation with the localized hole states in [33] is equal to the sum of relaxation energy and the change of correlational energy in the Green's function approach with delocalized hole states. Therefore from the HF calculation alone one could not come to conclusion that the K-shell hole states in O_2 or N_2 are localized. Recent state-of-the-art *ab initio* calculations of Thiel et al [35] and Ehara et al [36] with symmetry adopted g and u wave functions and with many-electron correlations taken into account gave a perfect agreement with the experimental ionization potentials for the $1\sigma_g$ and $1\sigma_u$ hole states as well as for their energy splitting.

4.1. Symmetry constraints on the wave functions

Consider now the symmetry constraints on the wave functions in the photoionization and the subsequent Auger decay processes within the two-step model on the example of the N_2 molecule. The initial state $|\Psi_0\rangle$ of N_2 has a definite parity (gerade). Photon is a particle with ungerade parity. Therefore the final state of the system ion+photoelectron must possess ungerade parity. What are the constraints imposed by this condition on the ion and the photoelectron wave functions separately? Let us restrict for simplicity the consideration by a single particle approximation in which the ground state of N_2 molecule is described by a single-configuration Slater determinant. Then the core-hole photoabsorption and the Auger decay amplitudes are

$$d_i(\vec{k}_p) = \langle \psi_{\vec{k}_p}^- | d | \varphi_i \rangle, \quad V_i(\vec{k}_A) = \langle \psi_{\vec{k}_A}^- \varphi_i | V | \varphi_j, \varphi_j \rangle \quad (2)$$

It is assumed here that the electrons of only one valence orbital φ_j are involved in filling the core-hole i . Doubly differential cross section for the process of core ionization of N_2 molecule with a subsequent Auger decay in which both photo- and Auger-electrons are ejected at some fixed angles is given within the two-step model by the equation

$$\frac{d\sigma_i}{d\Omega_{\vec{k}_A} d\Omega_{\vec{k}_p}} \propto |f_i(\vec{k}_A, \vec{k}_p)|^2 = |V_i(\vec{k}_A) d_i(\vec{k}_p)|^2, \quad i = 1\sigma_g \text{ or } 1\sigma_u. \quad (3)$$

In a general case a two-particle wave function (or a particle-hole wave function) is presented as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_h(\mathbf{r}_1)\psi_p(\mathbf{r}_2) - \psi_h(\mathbf{r}_2)\psi_p(\mathbf{r}_1)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_h(\mathbf{r}_1) & \psi_h(\mathbf{r}_2) \\ \psi_p(\mathbf{r}_1) & \psi_p(\mathbf{r}_2) \end{vmatrix}. \quad (4)$$

Suppose that each one particle wave function here does not possess a definite parity. Then it can be presented as a linear combination of g and u components with some coefficients a, b, c, d

$$\psi_p(\mathbf{r}_i) = a\psi_p^g(\mathbf{r}_i) + b\psi_p^u(\mathbf{r}_i), \quad \psi_h(\mathbf{r}_i) = c\psi_h^g(\mathbf{r}_i) + d\psi_h^u(\mathbf{r}_i), \quad i = 1, 2. \quad (5)$$

Inserting that into eq. (4) gives

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left\{ ac [\psi_p^g(\mathbf{r}_1)\psi_h^g(\mathbf{r}_2) - \psi_p^g(\mathbf{r}_2)\psi_h^g(\mathbf{r}_1)] + bd [\psi_p^u(\mathbf{r}_1)\psi_h^u(\mathbf{r}_2) - \psi_p^u(\mathbf{r}_2)\psi_h^u(\mathbf{r}_1)] \right. \\ \left. + ad [\psi_p^g(\mathbf{r}_1)\psi_h^u(\mathbf{r}_2) - \psi_p^g(\mathbf{r}_2)\psi_h^u(\mathbf{r}_1)] + bc [\psi_p^u(\mathbf{r}_1)\psi_h^g(\mathbf{r}_2) - \psi_p^u(\mathbf{r}_2)\psi_h^g(\mathbf{r}_1)] \right\} \quad (6)$$

The expressions in the first two square brackets here are gerade, while in the third and the fourth square brackets they are ungerade. Since the total wave function must be ungerade, the following conditions have to be fulfilled: $a = d = 0$, or $b = c = 0$, that is either

$$\psi_p(\mathbf{r}_1) = b\psi_p^u(\mathbf{r}_1), \quad \psi_h(\mathbf{r}_1) = c\psi_h^g(\mathbf{r}_1), \quad \text{or} \quad \psi_p(\mathbf{r}_1) = a\psi_p^g(\mathbf{r}_1), \quad \psi_h(\mathbf{r}_1) = d\psi_h^u(\mathbf{r}_1). \quad (7)$$

So, from the condition for the two-particle wave function to have a definite parity follows that if the hole is created in the gerade state, the photoelectron must be in ungerade state, and vice versa. From this consideration follows that *for the hole state to be localized one must imply that already in the initial state $|\Psi_0\rangle$ the wave functions are localized.*

After the Auger decay the total system (N_2^{2+} + photoelectron + Auger electron) must retain u parity. Since in the experiment discussed below only the contribution of g states $^1\Sigma_g^+(1\pi_u^{-2}), ^1\Delta_g(1\pi_u^{-2})$, and $^3\Pi_g(1\pi_u^{-1}, 2\sigma_u^{-1})$ of the N_2^{2+} ion have been selected, the two-electron subsystem (photoelectron + Auger electron) must have ungerade parity. Then from the consideration given above it follows that the photoelectron and the Auger electron must always possess an opposite parity. If from some measurement one determines that the Auger electron is in the g state, then according to (7) the photoelectron must be in the u state, and vice versa. In other words, this two-electron system constitutes an entangled Bell state.

4.2. The role of overlap of the g and u lines

Before doing the next step, we must take into account the relation between the widths of the g and u photo- or Auger-electron lines and the energy splitting between them. Three cases are possible.

1) The g/u energy splitting is much larger than the widths of these lines, like in the case of the $2\sigma_g$ and $2\sigma_u$ states of N_2 (the energy splitting is 19 eV). Then the g and u lines are well separated in energy, and the corresponding hole states are delocalized.

2) The g/u energy splitting is much smaller than the widths of these lines, like in the case of the $1\sigma_g$ and $1\sigma_u$ states of Ne_2 dimer [37]. Then the $1\sigma_g$ and $1\sigma_u$ lines can never be separated, and the consideration in both delocalized and localized bases are equivalent.

3) The g/u energy splitting is of the same order of magnitude as the widths of these lines, as is the case for the $1\sigma_g$ and $1\sigma_u$ hole states of N_2 molecule. We consider this case in more detail below.

The Lorentzian widths of the $1\sigma_g$ and $1\sigma_u$ lines in N_2 (about 0.12 eV) are approximately equal to their energy splitting (about 0.1 eV), and in the photoelectron-Auger electron coincidence experiment the photoelectrons from these shells could not be resolved [38]. Therefore below we treat the case of N_2 as if the g and u states were degenerate. Then instead of (3) we get

$$\frac{d\sigma_K}{d\Omega_{\vec{k}_A} d\Omega_{\vec{k}_p}} \propto \left| V_{1\sigma_g}(\vec{k}_A) d_{1\sigma_g}(\vec{k}_p) + V_{1\sigma_u}(\vec{k}_A) d_{1\sigma_u}(\vec{k}_p) \right|^2. \quad (8)$$

Now we have a square modulus of the sum of two amplitudes which includes also the interference term, so that this equation actually describes a deviation from the two-step model.

Since the photoelectrons from both g and u shells are supposed to have equal energies, one can introduce another set of wave functions localized on one of two nitrogen atoms, right (R) or left (L)

$$\varphi_R = \frac{1}{\sqrt{2}}(\varphi_{1\sigma_g} + \varphi_{1\sigma_u}), \quad \varphi_L = \frac{1}{\sqrt{2}}(\varphi_{1\sigma_g} - \varphi_{1\sigma_u}), \quad d_{R,L}(\vec{k}_p) = \frac{1}{\sqrt{2}} \left[d_{1\sigma_g}(\vec{k}_p) \pm d_{1\sigma_u}(\vec{k}_p) \right] \quad (9)$$

and similarly for the Coulomb amplitudes (2). The two sets of wave functions, $\varphi_{1\sigma_g}$ and $\varphi_{1\sigma_u}$, or

φ_R and φ_L , are equivalent. Inserting the amplitudes (9) into equation (8) we obtain

$$\frac{d\sigma_K}{d\Omega_{\vec{k}_A} d\Omega_{\vec{k}_p}} \propto \left| V_R(\vec{k}_A) d_R(\vec{k}_p) + V_L(\vec{k}_A) d_L(\vec{k}_p) \right|^2 = \left| V_{1\sigma_g}(\vec{k}_A) d_{1\sigma_g}(\vec{k}_p) + V_{1\sigma_u}(\vec{k}_A) d_{1\sigma_u}(\vec{k}_p) \right|^2. \quad (10)$$

and the process can be considered in both basis sets.

The photoelectron and the Auger electron wave functions can be expanded in spherical functions

$$\psi_{\vec{k}_p}^-(\mathbf{r}) = \sum_{l,m} Y_{lm}^*(\vec{k}_p) f_{\epsilon lm}(\vec{r}). \quad (11)$$

The orbital angular momentum l in this expansion takes only even values for the g states and only odd values for the u states.

If either photoelectron or Auger electron is not detected, one must integrate over all directions of \vec{k}_p or \vec{k}_A . This integration of the interference term gives zero since the g and u Legendre polynomials are mutually orthogonal, and we are coming to the result

$$\frac{d\sigma_K}{d\Omega_{\vec{k}_p}} \propto |d_{1\sigma_g}(\vec{k}_p)|^2 + |d_{1\sigma_u}(\vec{k}_p)|^2, \quad (12)$$

that is the angular distribution of photoelectrons is given by *incoherent* sum of the g and u hole states. In the R/L basis we analogously obtain

$$\frac{d\sigma_K}{d\Omega_{\vec{k}_p}} \propto |d_R(\vec{k}_p)|^2 + |d_L(\vec{k}_p)|^2. \quad (13)$$

So, the interference term contributes only provided both photo- and Auger-electrons are detected in coincidence, and the two-dimensional angular distribution of one of them for a fixed direction of the other do not possess the inversion symmetry (see fig. 5). If we integrate over the ejection angles of either photo- or Auger-electron the interference term disappears, and the result is given by the incoherent sum of two contributions, g and u, or L and R.

5. Experimental evidences of the symmetry of the N₂ core hole states

The main difference between the equations (12) and (13) lies in the fact that the g and u states are energetically splitted, while the R and L states must have equal energies. If in experiment the contributions of the g and u states can be resolved, then one can conclude that the hole state is delocalized and must be characterized by its parity.

There are several high resolution experiments for N₂ molecules where the g/u splitting was resolved. In these experiments only photoelectrons or only Auger electrons were detected. In addition to the g/u splitting of about 0.1 eV also the vibrational splitting of 0.3 eV was resolved. Though the $1\sigma_g$ and $1\sigma_u$ lines with the same vibrational quantum numbers are strongly overlapping, the absence of the interference terms between them allows unambiguous separation of their contributions.

For the first time the contributions of the $1\sigma_g$ and $1\sigma_u$ shells of N₂ have been resolved by Hergenbahn et al [39] who measured the corresponding partial cross sections. This study proved the theoretical prediction made in [40] that due to continuum-continuum channel interaction the σ^* shape resonance feature appears not only in the $1\sigma_g$ but also in the $1\sigma_u$ cross section. Later, more detailed experimental and theoretical study on the vibrationally resolved $1\sigma_g$ and $1\sigma_u$ lines [41] allowed determining in addition to the corresponding partial cross sections also the symmetry and vibrationally resolved angular asymmetry parameter β . It was shown that the energy dependencies of the parameters β for these two shells are substantially different, and even the vibrational motion gives an important contribution in a good agreement with the theory.

High resolution photoelectron spectra of N₂ molecule measured in the extended photon energy region up to 1 keV have been used to discover the modulation with energy of the $1\sigma_g$ and $1\sigma_u$ cross sections [42,43]. According to the prediction of Cohen and Fano [44] the photoelectron waves ejected from two atomic centers interfere producing modulation of the cross sections analogous to the modulation observed in the classical Young's double slit experiment. These modulations are better seen in the ratio of the g and u cross sections since the waves emitted from the two atomic centres

have either equal phases (for the g state) or differ by π (for the u state). The corresponding results are shown in Figure 2. The effect could not exist for the localized R and L hole states.

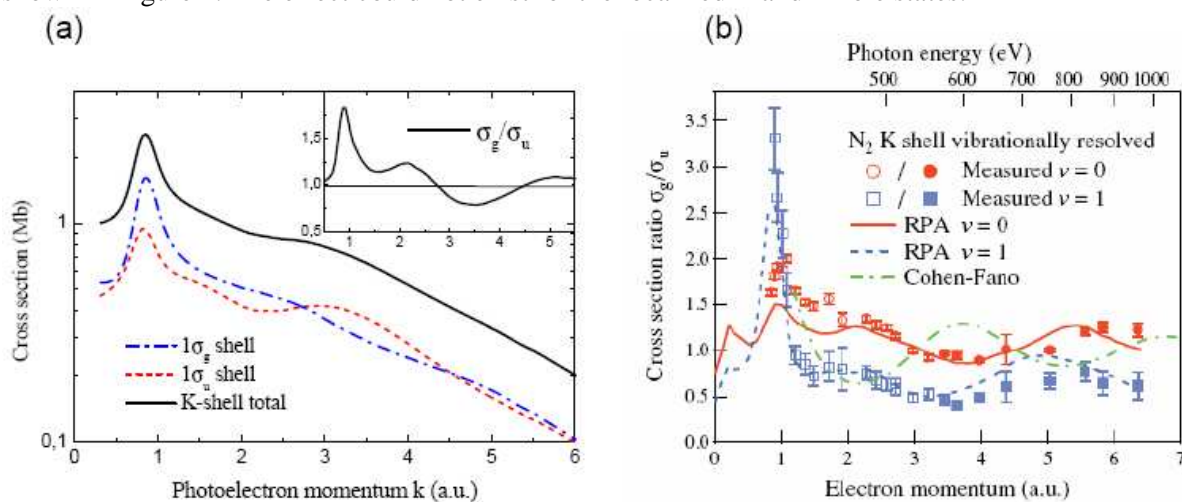


Figure 2. (a) The theoretical (RCHF+RPA) partial photoionization cross sections [42,43] for the $1\sigma_g$ and $1\sigma_u$ shells of N_2 (without vibrational resolution) and their sum as a function of photoelectron momentum. In the inset the ratio of the g and u cross sections is shown. (b) Comparison of vibrationally resolved experimental cross section ratios with theoretical calculations (from [43]). The result of direct application of the Cohen-Fano equation [44] is also shown.

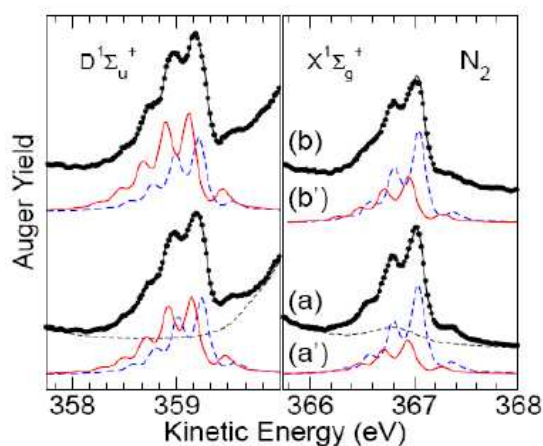


Figure 3. The $N\ 1s^{-1}$ Auger transitions to the final states $X\ ^1\Sigma_g^+$ and $D\ ^1\Sigma_u^+$ recorded with excitation energy (a) 500 eV and (b) 600 eV. The solid lines through the data points represent the fit results and the short-dashed lines the background. The vibrational progressions for the g hole state are indicated by dashed blue lines and for the u hole states by solid red lines (from [46]).

At last, in the most recent experiments [45,46] the g/u and the vibrational splitting of the Auger lines produced by the Auger decay of the $1\sigma_g$ and $1\sigma_u$ hole states of N_2 into the quasi-stable $X\ ^1\Sigma_g^+$ and $D\ ^1\Sigma_u^+$ final states have been observed for the first time (see Figure 3). Since the Auger decay time is of the order of 7 fs, while the hopping time for the hole between the two centres is about 40 fs, the existence of this splitting clearly demonstrates that the hole states produced by photoionization are the symmetry adopted g and u states.

6. Photo- and Auger-electron coincidence angular distributions in the molecular frame

In the recent experiment [38,47] it was shown that detecting in coincidence photo- and Auger-electrons in the molecular frame gives the possibility to distinguish between the local and non-local character of the hole state. Following this idea, let us consider the photoelectron angular distributions

for several fixed Auger electron ejection angles calculated in RCHF approximation as described in section 4. Figure 4 shows the non coincident Auger electron angular distributions for the $1\sigma_g$ and $1\sigma_u$

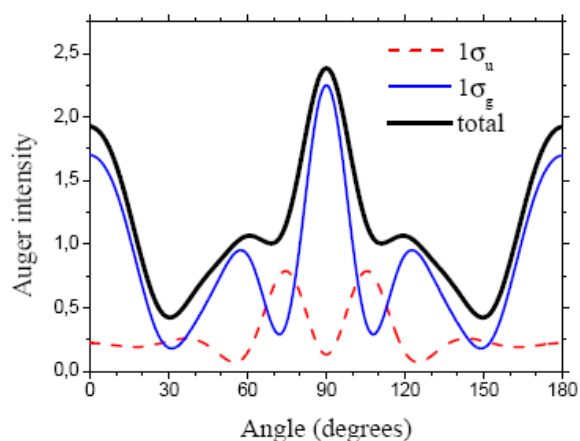


Figure 4. Auger electron angular distributions in the molecular frame. Molecular axis is oriented along 0° - 180° .

hole states of N_2 calculated in the HF approximation. If the hole state were localized, from (9) follows that the g and u shells must give equal contributions. According to Figure 4 these contributions are equal at the Auger electron emission angles of about 30° , 65° , and 80° . Figure 5 shows the photoelectron angular distributions provided the Auger electron is emitted at these angles. Shown are also the contributions of the R and L hole states separately. All three angular distributions do not possess the inversion symmetry due to asymmetry in the experimental geometry (the inversion symmetry is fulfilled only at the Auger electron emission angle 90°). At 65° and 80° the contributions of the R and L states are of the same order of magnitude, and the total result strongly differs from the sum of the R and L states due to a strong contribution of the interference term. It means that the hole state in these cases could not be thought of as being localized. Contrary to that for the 30° Auger ejection angle the photoelectron angular distribution is rather close to the individual contribution of the R hole state (except for the lobe at 300° - 360°). Therefore one can say that in this case the hole state can be thought of as being localized. Evidently, at 150° Auger ejection angle the angular distribution will be the inversion image of that at 15° with the main contribution given by the L hole state. More results are given in [38,47].

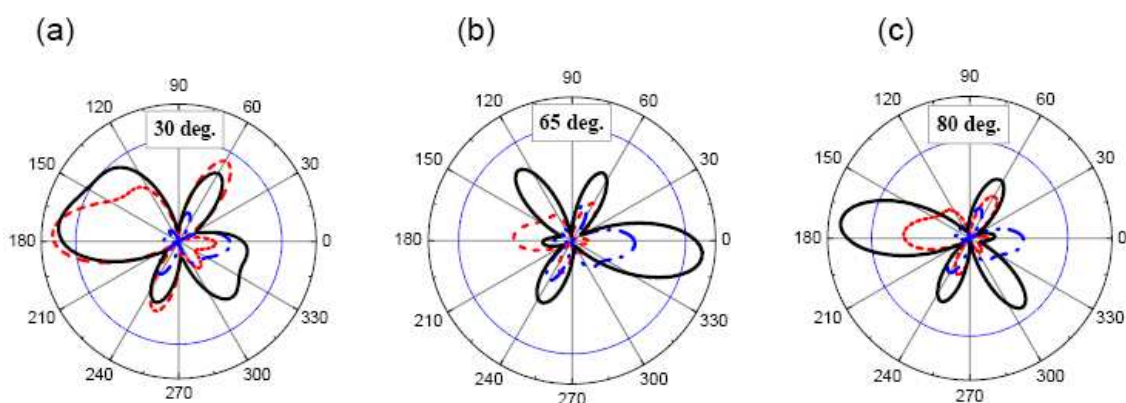


Figure 5. Photoelectron angular distributions from the K-shell of N_2 molecule corresponding to the Auger electron ejection angles equal to 30° (a), 65° (b), and 80° (c). Molecular axis is oriented along 0° - 180° . Circularly polarized light is moving perpendicular to the planes of figures.

In the van der Waals Ne_2 dimer the bonding energy is only 3 meV, and the g/u energy splitting is negligibly small. Therefore to a good approximation one can imply that the two atoms in the initial

state are not interacting, and the hole state is produced in an individual atom, i.e. is localized. In Figure 6 we show the photoelectron angular distributions for ionization of the Ne K-shell calculated in the g/u and R/L bases for photoelectron energy 11 eV. The angular distributions for the g and u , and for R and L states are strongly different. The problem is how they can be separated. One way has been realized in the recent experiment of Dörner group [37] where the photoelectron angular distribution has been measured for the asymmetric dissociation of Ne_2 dimers into the Ne^{2+} and Ne^+ ions. The angular distributions shown in Figures 6c,d were found to be asymmetric as follows from the calculations in the R/L basis. This is a clear evidence that the $1s$ hole state in this dimer is localized.

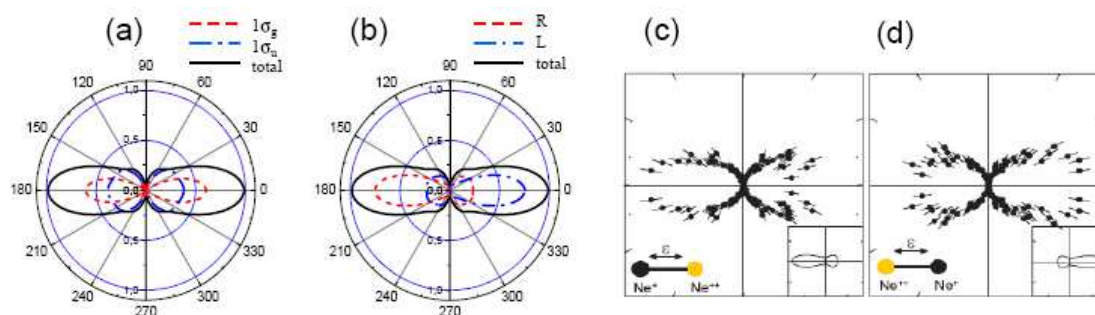


Figure 6. (a),(b). Angular distributions of the 11 eV photoelectrons from Ne_2 K-shell calculated in the HF approximation. Molecular axis is oriented horizontally, light polarization is parallel to the molecular axis. Shown are also the angular distributions for the g and u states (a), and for the R and L states (b). (c),(d). Experimental angular distributions from [37] for the same conditions when the dimer dissociates into a singly and a doubly charged ions as shown in the left corners of the figures. In the right corners the theoretical angular distributions from (b) are reproduced.

7. Conclusions

The study of Auger-electrons in coincidence with photoelectrons in the molecular frame gives the possibility to shed a new light on the fundamental problems of molecular physics, such as the applicability of the two-step model, and localization of the core hole states. While the applicability of the two-step model needs further investigations, the problem of localization of the core hole states has been substantially clarified by the recent measurements and calculations [36-39, 45-48]. From the very high resolution measurements of either photoelectron or Auger electron spectra in N_2 molecule it evidently follows that the hole state is delocalized. And only from the angular resolved coincidence measurements of the photo- and Auger-electrons in the molecular frame one can conclude that at some particular angles of the Auger electron emission the photoelectron angular distributions look as if the hole state were localized. But even in these cases the results of experiment are adequately described by calculations in the symmetry adopted g/u basis. Another situation is taking place in Ne_2 dimer. Here due to a very weak interatomic interaction the hole state to a good approximation is localized indeed, and that has been proved experimentally in [37] on the example of asymmetric dissociation. Another kind of asymmetric dissociation has been studied in [49] in the case of C_2H_2 molecules. Since this is a polyatomic molecule, the vibrational degrees of freedom can influence the dissociation process [50], and only with taking them into account the interpretation of that data can be complete.

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