Probing orbital symmetry in solution: polarization-dependent resonant inelastic soft x-ray scattering on liquid micro-jet

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Abstract. Polarization-dependent resonant inelastic x-ray scattering is demonstrated here for liquid acetonitrile, acetone and dimethyl sulfoxide, using the liquid micro-jet technique. Selective excitation to an unoccupied orbital with a specific symmetry at the K-edge x-ray absorption of liquid samples determines the polarization-dependent emission of the occupied states. Considering the well-defined unoccupied molecular orbital configuration and utilizing the results of \textit{ab initio} molecular orbital calculations, the polarization-dependent anisotropy in resonant inelastic soft x-ray scattering is discussed in a membrane-free configuration.

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1. Introduction

When molecules are oriented in space, e.g. adsorbed on surfaces [1–3], angular-resolved x-ray emission (XE) spectral measurements allow for the determination of the orientation of the valence (occupied) molecular orbitals (MOs) with respect to the surface plane. If the adsorbed molecular geometry is known, the symmetry of the MOs can be obtained. Such information is the key to understanding functional materials on surfaces, e.g. catalysts [4].

In gas or liquid phase where molecules are randomly oriented, such information cannot be obtained directly. However, by using linearly polarized light and resonant inner-shell excitation to specific unoccupied MOs with a well-defined molecular symmetry [5, 6], it is possible to preferentially excite molecules with a given orientation relative to the incident polarization vector and subsequently detect an angular anisotropy between emission directions in the XE of liquid and gas phase samples as well [7–13].

In this work, we report the first observation of strongly anisotropic XE from liquid phase molecules in a micro-jet. The solvents acetone, acetonitrile and dimethyl sulfoxide (DMSO) were selected as samples due to the different composition of the lowest unoccupied MOs (LUMOs). Furthermore, the symmetry of these molecules is different; whereas DMSO has \( C_s \), acetone has \( C_{2v} \) and acetonitrile has \( C_{3v} \). It has been shown that the angular anisotropy of the emitted x-rays depends on the excitation energy and the symmetry properties of the MOs which are involved in the scattering process [10].

The anisotropy originates from the dipole allowed excitation and relaxation with respect to the polarization vector of the incident light. In acetone and acetonitrile the LUMO consists of one well-localized orbital with known symmetry, \( 3a_1 \) and \( 3e \), respectively. In the case of DMSO, the LUMO and LUMO+1 with comparable absorption intensities are only separated by 0.4 eV, albeit with different symmetries [14–16]; they will be exploited to investigate the different anisotropy as well as to challenge the ability of this method to separate the contributions of these two MOs in liquid phase. It is important to note that the previous studies on the polarization dependence of the resonant inelastic x-ray scattering (RIXS) employed the flow cell technique introducing an additional membrane interface between the sample and the x-ray source [11, 12, 17]. However, in this study, the micro-jet technique is employed for the first time, removing the additional membrane interface which could potentially introduce artifacts such as native oxide emission [12] or membrane-induced orientation of the molecules. Interestingly, a significant angular anisotropy is observed in the micro-jet for the three studied molecules, although it is less pronounced than expected for the free molecule.
2. Experimental

The experiments were carried out at the UE-52 SGM undulator beamline at the BESSY II synchrotron facility of the Helmholtz-Zentrum Berlin. The RIXS spectra were measured under a polarization angle $\Theta$ of the incident light relative to the spectrometer, named vertical for $90^\circ$ and horizontal for $0^\circ$. The degree of polarization of the beamline is 100% in horizontal and drops to 97% in vertical polarization. Our recently developed high-resolution XE spectrometer based on a Rowland circle design, specifically designed for measurements with a liquid micro-jet and previously employed for research from simple ions to biochemical molecules was used for this study [18–22]. Acetone, acetonitrile and DMSO with purity greater than 99.9% were obtained from Sigma-Aldrich and used without further purification. The calibration of the x-ray absorption (XA) spectra was done according to [14, 23–25]. The emission spectra were calibrated using the quasi-elastic scattering peaks in the RIXS spectra. To allow an accurate comparison of intensities, the spectra were area-normalized.

For an understanding of the MO origin of the emission peaks and their symmetry, ab initio quantum chemical calculations for acetone, acetonitrile and DMSO were carried out using the GSCF3 code [26–28]. The calculations for acetone and DMSO have already been published by Atak et al [15]. These calculations are used for a quantitative analysis of the response of the different MOs to the polarized incident light. Using a simple two-step model of the x-ray emission process and assuming a 100% linearly polarized incident beam, the emission intensity can be expressed as [10, 29]

$$I (\Theta) = I_0 \left[ 1 + R \left( \frac{3}{2} \sin^2 \Theta - 1 \right) \right].$$

(1)

$\Theta$ is the angle between the polarization vector of the incident light and the direction of the emitted light. $I_0$ is the total intensity and $R$ is the anisotropy parameter. Here the results of the $ab$ initio calculations for the intensity of the emission lines were used as $I_0$. As shown by Luo et al [10], for low symmetry point groups of non-planar molecules, i.e. for $C_{3v}$ (acetonitrile), $C_{2v}$ (acetone) and $C_{s}$ (DMSO), the anisotropy parameter $R$ is $\frac{3}{5}$ when the emission originates from an orbital with the same symmetry as in the initially excited orbital, indicating that the vertical polarization ($I (90^\circ) = \frac{9}{10} I_0$) is stronger than the horizontal polarization ($I (0^\circ) = \frac{3}{5} I_0$). For an emission originating from an orbital with a different symmetry, $R$ takes the value $-\frac{1}{5}$, indicating that the horizontal polarization ($I (0^\circ) = \frac{9}{10} I_0$) is stronger than the vertical polarization ($I (90^\circ) = \frac{3}{5} I_0$). The two-step model for $R$ can be used, when there is only one localized core–hole involved in the scattering process. The calculated $ab$ initio emission intensities are rescaled based on equation (1) and will be shown in red (horizontal excitation) and blue (vertical excitation) bars under the experimental spectra. The symmetry and the electron distribution of the MOs involved in the absorption and emission processes will be illustrated based on ground state calculations using Gaussian03 software employing the 6-31 G(d) basis set with the B3LYP exchange-correlation functional [30].

3. Results

The polarization-dependent RIXS spectra of acetonitrile excited resonantly on the nitrogen $1a_1$ core orbital to the $3e$ valence state transition are presented in figure 1. The XA spectrum measured in total fluorescence yield (TFY) mode is shown in the inset using the same energy scale as the RIXS. Following the $ab$ initio calculations, relaxations from the valence orbitals,
Figure 1. RIXS spectra of acetonitrile excited at 400.45 eV from the nitrogen 1a_1 core orbital with horizontal (red line) and vertical polarization (blue line) are presented. The difference of the emission intensity under the vertically and horizontally polarized excitations is shown in green. On the upper right corner a TFY XAS spectrum is presented for reference. The calculated intensities are shown as colored bars below the RIXS spectra.

2e, 1e, 7a_1, and 6a_1, to the 1a_1 core–hole are expected to take place. The elastic relaxation to the initial electronic ground state is also visible. This gives rise to a quasi-elastic line, with only vibrational energy losses. These vibrational progressions are seen on the lower energy shoulder of the feature and are responsible for the broadening but could not be resolved in this study due to the resolution limitation [31]. The particular strength of the elastic emission can be attributed to the well localized 3e LUMO and thereby follows the strong resonant transition. This strong anisotropy in the elastic scattering is due to the contribution of the Thomson scattering, which is suppressed under the horizontally polarized excitation [32].

At the emission energy of 390.8 eV, a peak is observed which is attributed to the two relaxations from MOs of 2e symmetry, which are energetically separated by the spectator effect. Both MOs have the same symmetry as the excited 3e LUMO and therefore the emission intensity is stronger under the vertically polarized excitation. The double feature cannot be
clearly resolved due to the resolution limitation. The next most prominent feature is a sharper peak at the emission energy of 389.4 eV. Following the \textit{ab initio} calculations, this feature originates from the $7\alpha_1$ orbital to the $1\alpha_1$ core state transition. As expected, the emission intensity is stronger with horizontally polarized excitation, due to the symmetry difference of the emitting $7\alpha_1$ MO and the excited $3\epsilon$ LUMO. The anisotropy is clearly visible despite the noise level. The reason for the deviation from the experimental observation compared to the theoretical estimation is due to symmetry mixing in liquid phase, e.g. due to nuclear rearrangements or interactions with the surrounding [17]. The surrounding effect is originally related to the liquid phase rather than a possible membrane-induced surrounding effect.

The K-edge oxygen RIXS spectra of acetone, resonantly excited to the $3\beta_1$ LUMO are presented in figure 2 together with the x-ray absorption spectroscopy (XAS) in TFY mode. According to the \textit{ab initio} calculations, relaxations from the valence $5\beta_2$, $4\beta_2$, $3\beta_2$, $2\beta_1$, $1\beta_1$, $8\alpha_1$, $7\alpha_1$ and $6\alpha_1$ orbitals to the $1\alpha_1$ core–hole as well as the elastic relaxation from the $3\beta_1$ orbital are expected to constitute the features. Considering the RIXS spectra besides the elastic peak, four main features are resolved. The most prominent feature centered at the emission energy of 526 eV, originates from the relaxation of the $5\beta_2$ MO. This orbital has a different symmetry from the excited $3\beta_1$ LUMO. Therefore, a more intense signal in the horizontal polarization is expected and is clearly observed in the spectrum. The next most prominent peak observed is considered to originate from the $2\beta_1$ and $8\alpha_1$ MOs. While the symmetry of the $2\beta_1$ is the same as the LUMO, the symmetry of the $8\alpha_1$ is different. Therefore opposing angular anisotropies are expected. Following the \textit{ab initio} calculations and equation (1), the anisotropy in the $2\beta_1$ is expected to be stronger. On the high-energy shoulder of the 522 eV peak, the anisotropy due to the $2\beta_1$, is clearly observable. On the low-energy shoulder, the anisotropy of the $2\beta_1$ relaxation is damped, due to the opposing effect of the $8\alpha_1$ relaxation. Nevertheless, the emission from the $2\beta_1$ orbital is dominating. At the emission energy of 520 eV, an isoemissive point, where the emission under the horizontal and vertical polarizations is identical, is observed, followed by a more intense emission under the horizontal excitation. This can be attributed to the $4\beta_2$ relaxation. Due to the different symmetries, opposite effects of the anisotropy in the emission of the $3\beta_2$, $7\alpha_1$, $1\beta_1$, $6\alpha_1$ relaxations are expected, consequently, in the spectral region at the lower emission energies, the measured anisotropy is too weak to be detected due to the noise level.

The K-edge oxygen RIXS spectra of DMSO are presented in figure 3 together with the XAS in TFY mode. As mentioned above, the LUMO and LUMO+1 of DMSO belong to different symmetric groups, the $15\alpha'$ and $8a'$ MOs, and are only separated by approximately 0.4 eV [14–16]. To monitor the different polarization-dependent behaviors originating from this situation, the excitations were performed on the low- and high-energy shoulder of the XA π feature to address the RIXS spectra which are dominated by either $15\alpha'$ or $8a'$ MO contribution, respectively. The RIXS with an excitation energy of 532.75 eV is considered to be mainly composed of the excitation to the $15\alpha'$ orbital, whereas the RIXS at 533.3 eV is thought to be dominated by the $8a'$ LUMO+1 (see the inset XAS in figure 3). The \textit{ab initio} calculations of transition intensities for excitations of $15\alpha'$ LUMO and $8a'$ LUMO+1 are shown below the RIXS spectra. Following these calculations, relaxations from the valence $14a'$, $7a'$, $13a'$, $12a'$, $6a'$, $5a'$, $4a'$, $11a'$ and $10a'$ orbitals to the $1a'$ core–hole are expected to take place. Depending on the resonantly excited unoccupied orbital, the transitions can be affected differently due to the change in the screening of the core–hole by the spectator electron (compare the $6a'$ and $12a'$ orbitals in the two RIXS spectra). The elastic relaxation is less pronounced and strongly
Figure 2. RIXS spectra of acetone excited at 530.6 eV from the oxygen 1a core orbital with horizontal (red line) and vertical polarization (blue line) are presented. The difference of the emission intensity under the vertically polarized and horizontally polarized excitations is shown in green. On the upper right corner a TFY XAS spectrum is presented for reference. The calculated intensities are shown as colored bars below the RIXS spectra.

broadened by vibrational progressions at the high-energy region of the RIXS spectra. This is due to less localized LUMO orbitals as compared to acetone and acetonitrile [15].

Due to the identical symmetry of the 15a′ LUMO and the 14a′ highest occupied MO (HOMO), relaxation from the HOMO is expected to be more intense for the excitation with vertical polarization. In contrast, for the 7a′ relaxation a stronger emission is expected under the horizontally polarized excitation. This is observable in the RIXS spectrum excited at 532.75 eV. The intensity of the 14a′ relaxation is weaker than the one corresponding to 7a′. Therefore, the angular anisotropy is dominated by the 7a′ contribution. For the higher excitation energies, the 8a′ LUMO + 1 is excited more dominantly, which shifts the polarization dependence. Under an excitation to the 8a′ LUMO + 1, the exact opposite anisotropy effect is expected due to the change in the symmetry of the excited orbital. At the excitation energy of 533.3 eV, the angular anisotropy due to the 8a′ excitation is dominant and the emission of the 14a′ relaxation
**Figure 3.** RIXS spectra of DMSO excited at 532.75 and 533.3 eV from the oxygen 1a′ core orbital with horizontal (red line) and vertical polarization (blue line) are presented. The difference of the emission intensity under the vertically polarized and horizontally polarized excitations is shown in green. On the upper right corner a TFY XAS spectrum is presented for reference. The calculated intensities are shown as colored bars below the RIXS spectra.

At the high-energy shoulder is stronger under the horizontally polarized excitation. The stronger emission of the 7a′ relaxation under the vertical polarization can also be clearly observed.

The next prominent feature in the spectra is the double feature centered at the emission energy of 522 eV. This feature originates from the relaxations of the 13a′, 12a′ and 6a′ to the 1a′ core orbital. In the RIXS spectrum excited at 532.75 eV, the emission due to the 12a′ relaxation is clearly observed around 520 eV in the vertically excited spectrum. This is not the case for the 13a′, where the emission is isoemissive or even slightly more intense under the horizontal excitation. This could be due to the contribution of the slightly excited 8a′ LUMO + 1, where the relaxation of the 13a′ is much stronger and is of opposite anisotropy behavior. With the increasing excitation energy, the emission under the horizontally polarized excitation becomes
dominant for the 13a<sup>′</sup> relaxation. This supports the assumption of a contribution of the 8a<sup>′</sup> LUMO + 1 to the emission spectrum.

Comparing the RIXS spectrum excited at 532.75 eV to the one excited at 533.3 eV, mainly the intensity ratios change but not the qualitative behavior of the peaks. This can be attributed to the energetical shift and the change of the relative transition intensities of the different MOs due to the different spectator shift effects. With an excitation energy of 533.3 eV a slightly more intense emission under the horizontally polarized excitation in the low-energy shoulder of the double feature is visible. This could be due to the contribution of the 6a<sup>′</sup>, 5a<sup>′</sup> and 4a<sup>′</sup> orbitals. The emission due to the 13a<sup>′</sup> and 12a<sup>′</sup> MOs under the vertically polarized excitation is observed in both RIXS, albeit more intense if the excitation is to the LUMO + 1 at 533.3 eV.

4. Conclusion

In conclusion, the polarization-dependent RIXS technique was successfully implemented and applied to liquids using the micro-jet technique in order to investigate the symmetry properties of MOs in soft x-ray regime. This technique depends on the symmetry of the emitting occupied valence orbitals and that of the initially excited unoccupied orbital. The two-step model introduced by Luo et al [10] was employed for the theoretical predictions together with ab initio calculations which were compared to the experimental results. Besides the insights into the MO symmetry details of the investigated molecules in liquid phase, the study challenges the polarization-dependent RIXS on a membrane-free spectrometer in the soft x-ray regime.

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