Anisotropy of Polarized X-ray Emission from Molecules

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Anisotropy of Polarized X-Ray Emission from Molecules


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Strongly anisotropic, polarized Cl K-V x-ray emission from gas-phase CF3Cl has been observed following resonant excitation with a linearly polarized x-ray beam. Distinctively different angular distributions are observed for x-ray emission involving molecular orbitals of different symmetries. A classical model of the x-ray absorption-emission process accurately describes the observed radiation patterns.

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X-ray fluorescence spectrometry is widely used for quantitative chemical analysis in research and industry, and it is generally assumed that x-ray emission is isotropic [1]. The observation of anisotropic x-ray emission from molecular crystals and solids has been attributed to the inherent ordering of those samples [2], and it has been expected that randomly oriented samples, such as gas-phase molecules, will display isotropic x-ray emission. However, excitation by a photon or particle beam will generally leave an atomic or molecular target in an anisotropic state, and this anisotropy is manifested in the polarization and angular distribution of emitted photons [3,4]. We report the first observation of strongly anisotropic, polarized x-ray emission from gas-phase molecules. Specifically, the Cl 1s orbital of CF3Cl was resonantly excited to an occupied valence molecular orbital (MO) using a narrow-bandwidth, linearly polarized x-ray beam, and a polarization-selective x-ray emission spectrometer was used to measure the angular dependence of the intensity of Cl K-V x-ray emission, in which a valence MO fills the Cl 1s hole. Distinctively different angular distributions are observed for Cl K-V emission involving valence MOs of different symmetries. A simple classical model accurately describes the observed anisotropies for the different MOs. This study demonstrates that the technique of polarized, angle-dependent x-ray-emission spectroscopy, following resonant photoexcitation of randomly oriented targets, produces an ensemble of core-excited states having cylindrical symmetry with respect to that axis [3,4]. In addition, the photoexcited system is symmetric with respect to reversal of that axis. These symmetry properties are retained in the emitted x-radiation patterns.

In order to measure angular distributions, the target chamber and emission spectrometer were mounted on a rotation platform to record x-ray spectra at different emission angles θ with respect to the polarization vector of the incident x-ray beam. The plane normal to the propagation direction of the incident x-ray beam serves as

Figure 1: Schematic diagram of the instrumentation used for the measurement of the angular distribution of polarized x-ray emission from gas-phase targets.
a reference plane for defining the observed polarization
direction of the emitted x rays. The curved crystal of the
emission spectrometer was positioned to transmit x rays
whose polarization vectors were either parallel or perpen-
dicular to this plane. The x-radiation patterns were
characterized by two sets of measurements of the emission
intensities as a function of $\theta$. $I_\parallel(\theta)$ denotes the an-
gular distribution observed for emitted x rays polarized
parallel to the reference plane, and $I_\perp(\theta)$ denotes the an-
gular distribution for emitted x rays polarized perpendicu-
lar to this plane.

As shown in Fig. 2, the parallel-polarized Cl $K$-$\nu$ spec-
tra display strong angular variations of the branching ra-
tios for the different valence MOs when the excitation en-
ergy is tuned to a subthreshold absorption resonance as-
signed [9] to the Cl 1s-to-valence transition $1a_1 \rightarrow 11a_1$.
Similar variations in relative peak intensities are observed
[10] at fixed emission angle ($\theta=90^\circ$) when parallel- and
perpendicular-polarized Cl $K$-$\nu$ spectra are compared for
resonantly excited molecules.

A quantum-theoretical formulation for the polar-
ization-dependent angular distribution of photon emission
from atoms and molecules has been developed by Fano
and Macek [3] and by Greene and Zare [4]. This formu-
lation adopts a two-step model of the excitation and radi-
ative decay. We assume here that x-ray absorption and
emission may be described as electric dipole processes.
The theoretical formulation relates the multipole
moments of the spatial distributions of angular momenta in
the initial, photoexcited, and final states of the target to
the propagation directions and polarizations of the in-
cident and emitted photons [3,4]. Photoabsorption by ran-
domly oriented target molecules can give rise to an en-
ssemble of excited states whose rotational angular momen-
tum vectors are directed in space anisotropically. This
excited-state anisotropy is described by an alignment pa-
rameter, and the polarization and angular distribution
of the emitted photons depend on the alignment and on a
geometrical factor determined by the rotational quantum
numbers of the excited and final states [3,4]. In the
present case, the angular distributions can be expressed by

\begin{equation}
I_\parallel(\theta) = I_0 [1 + R (3 \sin^2 \theta - 1)]
\end{equation}

and

\begin{equation}
I_\perp(\theta) = I_0 [1 - R],
\end{equation}

where $I_0$ is proportional to the total intensity emitted in
all directions and summed over polarizations, and $R$ is
the polarization anisotropy. The parameter $R$ charac-
terizes the radiation pattern and relates measurements to
theory [11,12]. In the quantum-theoretical model [3,4],
$R$ is given by $\frac{1}{2}$ of the product of the alignment param-
eter and geometrical factor [11,12].

It can be seen from Eqs. (1) and (2) that the radiation
patterns have simple symmetry properties. Because of
the cylindrical symmetry with respect to the polarization
vector of the incident x-ray beam, no dependence on az-
imuthal angle is expected. Also, $I_\perp$ is isotropic, and
$I_\parallel(\theta)=I_\perp$. It follows that $R$ can be determined by mea-
asurements either of the anisotropy of the parallel com-
ponent $I_\parallel(\theta)$ or of the polarization $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ measured at $\theta=90^\circ$ as in Ref. [10].

Application of the quantum-theoretical version of the
two-step model to molecular targets is complicated by the
need to account for rotational transitions in absorption
and emission [11]. However, while typical vacuum-
ultraviolet (VUV) emission lifetimes ($\sim 10^{-9}$ s) are slow
compared with rotational periods ($\sim 10^{-12}$ s), the time
scale of x-ray processes ($\sim 10^{-11}$ s) is fast compared
with rotational motion. This consideration brings into
question the application of a two-step model to x-ray ab-
sorption and emission processes in molecules. A more
accurate picture may be that of a one-step, inelastic-
scattering process [13] by molecules essentially fixed in
space during the time scale of the process. However, it is
useful to retain the basic two-step picture in order to de-
scribe how x-ray absorption selectively excites an aniso-
tropic distribution of target molecules and how the polar-
ization and anisotropy of the emitted x rays depend on
the symmetries of the electronic states involved.

We make use of the classical model [14,15] in which
the absorption and emission dipole moments are replaced
by classical dipole oscillators treated as rigidly attached
to the molecular framework. The polarization and an-
isotropy of the emitted radiation are obtained from the

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig2.png}
\caption{Parallel-polarized Cl $K$-$\nu$ emission spectra from
CF$_3$Cl recorded on resonance at emission angles $\theta=0^\circ$ (top)
and $90^\circ$ (bottom). The solid curves are the results of a peak
fitting procedure used to obtain emission intensities for transi-
tions involving the $10a_1$ and $7e$ molecular orbitals.}
\end{figure}
relative directions of the absorption and emission oscillators averaged over molecular orientations. Defining γ to be the ensemble average of the angle between the absorption and emission oscillators, the polarization anisotropy is given by [15] $R = \frac{1}{2} (3 \cos^2 \gamma - 1)$. This result can be used to predict $R$ values for particular rotational transitions by referencing the directions of the transition dipole moments to the rotational angular momentum vectors and by taking account of the relative time scales of radiative lifetimes and rotational periods [15]. We disregard rotational motion in the present application of the classical model, treat the target molecules as fixed in space during the time scale of the x-ray absorption-emission process, and consider only the symmetries of the electronic states involved.

Applying the classical model to the $1a_1 \rightarrow 11a_1$ resonant excitation of CF$_3$Cl, the absorption dipole moment lies parallel to the molecular figure axis (the C-Cl bond axis), and a $\cos^2 \theta$ distribution of the figure axes with respect to the incident polarization vector is selectively excited. In the emission step, valence MOs having $a_1$ symmetry give rise to emission dipole moments also directed parallel to the figure axis, so $\gamma = 0^\circ$ and $R(a_1) = \frac{1}{2}$. MOs having $e$ symmetry are associated with emission dipole moments directed perpendicular to the figure axis, so $\gamma = 90^\circ$ and $R(e) = -\frac{1}{3}$.

In order to compare measured angular distributions with theory, a peak fitting procedure was used to obtain the emission intensities of the transitions involving the 10a$_1$ and 7e MOs indicated in Fig. 2. The MO assignment of the CI $K$ absorption and emission spectra of CF$_3$Cl is discussed in Ref. [9]. The collection efficiency of the emission spectrometer varied as a function of $\theta$ due to the geometry of the interaction region and due to the difficulty of maintaining precise mutual alignment of the incident x-ray beam, the gas cell, and the emission spectrometer. However, the relative collective efficiency was determined and corrected for at each $\theta$ by recording CI $K-V$ spectra far above ($\sim 50$ eV) the CI $K$-ionization threshold. Above threshold, degenerate continuum channels having $a_1$ and $e$ symmetries both contribute, and the absorption dipole moment may lie parallel or perpendicular to the molecular figure axis. Only a small alignment of the core-vacancy state is expected to be produced above threshold, and the anisotropy and polarization of x-ray emission are therefore relatively weak. It has been demonstrated using VUV emission spectroscopy that measurements of the small alignments produced above threshold provide dynamical information on the photoionization of valence orbitals [11,16,17]. We anticipate that precise measurements of the polarizations and anisotropies of emitted x rays produced above threshold will provide similar information on the photoionization of core orbitals. However, in the present study we emphasize measurements of the much stronger anisotropies which result when x-ray absorption and emission involve states having well-defined symmetries. For purposes of determining the relative collection efficiency of the spectrometer, we have assumed that the x-ray emission far above threshold is essentially isotropic and unpolarized. This assumption has been confirmed to within experimental uncertainties by measurements [10] of the polarization of CI $K-V$ emission at $\theta = 90^\circ$. The uncertainties in the results reported here represent 1 standard deviation due to counting statistics of the x-ray spectra.

Using the classical values for $R(a_1)$ and $R(e)$ in Eqs. (1) and (2) and normalizing to the perpendicular component ($I_{\perp} = 1$) in each case, the predicted anisotropies of the parallel components are $I_{\parallel}(a_1) = 1 + 2 \sin^2 \theta$ and $I_{\parallel}(e) = \frac{1}{2} (1 + \cos^2 \theta)$. The measured values of $I_{\parallel}(90^\circ)/I_{\parallel}(0^\circ)$ are $2.7 \pm 0.2$ and $0.50 \pm 0.02$ for the 10a$_1$ and 7e MOs, respectively, in good agreement with the classical-model predictions of 3 and $\frac{1}{2}$. For the perpendicular components, which should be isotropic, we obtained $I_{\perp}(90^\circ)/I_{\perp}(0^\circ) = 0.90 \pm 0.10$ and $0.88 \pm 0.05$ for the 10a$_1$ and 7e MOs, respectively. In Fig. 3 the 10a$_1$:7e intensity ratios are plotted for both parallel- and perpendicular-polarized measurements. Also plotted is the intensity ratio for parallel polarization predicted by the classical model and normalized to the measured ratio at $\theta = 90^\circ$. While the perpendicular-polarized intensity ratio is isotropic, as expected, the parallel-polarized intensity ratio varies by a factor of 6. This comparison demonstrates the distinct difference in the radiation patterns for the two MO symmetries. The simple classical model is in fairly good quantitative agreement with the observed anisotropies.

Finally, the determination of total intensities $I_0$ is of interest in many applications of x-ray emission spectrometry. For the present study, Eq. (1) shows that an intensity proportional to $I_0$ is given by $I_1$ at the “magic angle,” $\theta_m = \sin^{-1}(3^{-1/2}) \approx 35.3^\circ$. For example, the
resonant oscillator-strength ratio for the $10a_1$ and $7e$ transitions is given by the parallel-polarized $10a_1:7e$ intensity ratio at $\theta_m$. Using the measurements and theoretical curve plotted in Fig. 3, we obtain $I_0(10a_1):I_0(7e) = 0.14 \pm 0.01$.

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