1. Atomic and Molecular Science

1-1. Dynamics of Two Auger Electron Emission in Xe 4d Photoionization [1]

The creation of an inner-shell hole in an atom or molecule is usually followed by the emission of an Auger electron, a characteristic signature of both the hole and the species:

\[ h\nu + M \rightarrow M^+ + e^-_{\text{innershell photoelectron}} \]

followed by \[ M^+ \rightarrow M^{2+} + e^-_{\text{Auger}} \]

When the photon energy is close to the threshold of the inner-shell hole creation, the subsequent Auger decay may be influenced by the photoelectron still existing in the vicinity of the \( M^+ \) ion. The Auger peak becomes asymmetric and broadened, and its maximum is shifted to a higher energy. This so-called postcollision interaction (PCI) is explained in terms of an interaction among the two outgoing electrons and the ion.

Our interest here goes to the much-less common, but richer, process where two Auger electrons are emitted. We chose to study the decay of the 4d hole in xenon atoms:

\[ h\nu + Xe \rightarrow Xe^{+}(4d^-) + e^-_{4d \text{ photoelectron}} \]

\[ \rightarrow Xe^{3+} + e^-_{4d \text{ photoelectron}} + e^-_{\text{Auger1}} + e^-_{\text{Auger2}} \]

The two Auger electrons are emitted either simultaneously (double Auger: DA) or in sequence (cascade Auger: CA):

**DA:** \( Xe^+(4d^-) \rightarrow Xe^{3+} + e^-_{\text{Auger1}} + e^-_{\text{Auger2}} \)

**CA:** \( Xe^+(4d^-) \rightarrow Xe^{2+} + e^-_{\text{Auger1}} \]

\[ \rightarrow Xe^{3+} + e^-_{\text{Auger1}} + e^-_{\text{Auger2}} \]

It is a four-body dissociation as a whole process, in which one can expect a strong electron correlation. In order to gain insight into the dynamics of this decay, we detect the two Auger electrons in coincidence in the 4d photoionization threshold region where the PCI effect may be enhanced. Following the Xe energy level diagram in Fig. 1, the total energy of the two Auger electrons is 5.4 eV for the decay of the \( Xe^+ \) of the \( 4d_{3/2} \) hole to the \( Xe^{3+} 4S \) ground state. In our experimental setting, we have two electron energy analyzers: one is for threshold electrons with practically zero kinetic energy; the other is a hemispherical-type analyzer with a position-sensitive detector for energetic electrons. Figure 2 shows the electron spectrum measured at BL-16B with the hemispherical analyzer in coincidence with the threshold electron in the region where the photoelectron energy varies from near zero to 7.5 eV. All of the spectra reveal PCI effects that shift and broaden the line shapes, this distortion decreasing with increasing excess photon energy.

In the case of the DA process, the energy distribution of the two Auger electrons is continuous from 0 to 5.4 eV. However, the distribution will be discrete in the CA process depending on the energy levels of \( Xe^{2+} \). Furthermore, two possibilities exist in the CA process: 1) the CA1 process, where an initial fast electron forms an intermediate state of the \( Xe^{2+} \) ion, which decays to \( Xe^{3+} \) yielding a zero energy electron, and 2) the CA2 process, where the initial emission of a zero-energy electron forms \( Xe^{2+} \) and its decay to \( Xe^{3+} \), a fast electron. The theoretical
Highlights

The pulsed-field ionization zero-kinetic-energy photoelectron (PFI-ZEKE) technique has made possible rotationally resolved spectroscopic studies of ions. These high-resolution studies have shown to provide valuable insight into the basic photoelectron dynamics of diatomic molecule. Most of the PFI-ZEKE studies were performed using lasers as the light source. Due to the difficulty of tuning lasers over a wide energy range, laser-based PFI-ZEKE studies generally cover only a few vibrational levels near a molecule’s first ionization threshold. Hsu et al. [1] recently developed a new PFI-ZEKE detection scheme using multi-bunch synchrotron radiation. In their scheme, molecules are excited to high-n Rydberg states just below the ionization threshold using high-resolution monochromatized multi-bunch synchrotron radiation. A pulse electric field is then applied in the storage-ring dark gap to field-ionize the decaying molecule. The electric field ionizes the Rydberg electron and selects the Auger electron that is released, allowing the study of Auger electron emission.

The coincidence spectra shown in Figure 2 illustrate the energy selection of the slow Auger electron and provide information about the intermediate states involved. The calculations shown in the figure agree well with the experimental data, suggesting that the dominant process is cascade emission of a slow Auger electron followed by a rapid one, in both 4d\_3/2 and 4d\_5/2 decay, and the existence of intermediate Xe^{2+} states very close to the Xe\(^+\) 4d\_3/2 and 4d\_5/2 states.

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References

the Rydberg states. The electrons are collected with a steradiancy analyzer and a hemispherical energy analyzer. We used a penetrating field threshold electron analyzer instead of the steradiancy analyzer (Onuma et al. [2]) to eliminate any undesired hot electrons more efficiently. The rotationally resolved PFI-ZEKE spectra of the $B^2Σ_u^+(v^\prime=0)$ state of $N_2^+$ were first recorded at BL-20A using the PF synchrotron radiation dark gap [3]. Figure 3 shows in the upper part the ZEKE spectrum obtained at a resolution of 2.5 cm$^{-1}$ and in the lower part a spectral simulation using the BOS model [4]. The transition from the $X^2Σ_g^+$ state to the $B^2Σ_u^+$ state involves a change in the rotational angular momentum by an odd quantum number, i.e., $ΔJ = ±1, ±3, ...$ etc. It was found that this selection rule is valid for our observations. In Fig. 3, the P and R branches dominate and the N and T branches are weak. This result is supported by a previous study (Baltzer et al. [5]). However, the ZEKE spectrum is remarkably different from the simulated one in the low-energy side of the band origin. The enhancement of the L, N, and P branches can be attributed to field-induced rotational autoionization, like the autoionization mechanism of the Rydberg states converging to the $N_2^+ X^2Σ_g^+$ vibrational states.

The relative intensities ($σ(N^+ ← N^\prime)$) for rotationally resolved structures in individual vibrational bands were simulated using the Buckingham-Orr-Sichel (BOS) model [4], which is described by the formula

$$σ(N^+ ← N^\prime) \propto \sum Q(\lambda; N^+, N^\prime) C_\lambda,$$

where $N^+$ and $N^\prime$ are the rotational quantum numbers of the ion and the neutral ground state, respectively.

This model was derived to predict the rotational line strengths $σ(N^+ ← N^\prime)$ observed in the single-photon ionization of diatomic molecules. The factor $C_\lambda$ is associated with the electric transition moments, which is a linear combination of the electron transition amplitudes for the possible angular momenta $λ$ of the ejected electron. The other factor (Q) is determined by the angular-momentum coupling scheme. The parameter $λ$ can be interpreted as the orbital angular-momentum quantum number of the electron partial waves before photoexcitation. Since the

Figure 3. (Black line) PFI-ZEKE photoelectron spectra of nitrogen ($N_2^+ B^2Σ_u^+(v^\prime=0) ← N_2 X^2Σ_g^+(v^\prime=0)$) recorded with an extraction field of 0.8 V/cm between the dark gap of PF synchrotron. (Blue line) A simulation by the BOS model.
BOS model can be thought as a linear combination of spectra weighted by a set of the $C_\lambda$ coefficients, these coefficients are determined by the measured spectrum least-squares fit. The ratio $C_3/C_1$ of the BOS coefficient obtained by the simulation was 0.35. Baltzer et al. [5] have obtained a branching ratio 0.18 for the T and R branches of the photoelectron spectrum of the $\text{B} ^2\Sigma_u^+ (v=0)$ band using the He I resonance line. If we converted the ratio $C_3/C_1$ to the branching ratio (T/R), the ratio was $0.17\pm0.02$. This ratio agrees well with that of the Baltzer et al. study. This result suggests that relative ionization cross section can be evaluated if the effects due to the autoionization are negligibly small in the ZEKE spectrum.

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References

1-3. Effects of Light Polarizations on the $2\sigma_g$ Photoelectron Angular Distributions from Oriented $N_2$ Molecules

To perform a “complete” quantum-mechanical experiment, from which one can extract all of theoretical parameters describing the process under consideration, is an ultimate goal of all photoionization experiments. One way to obtain the necessary parameters is to measure the photoelectron angular distributions (PAD) from oriented molecules under three different experimental configurations and one light polarization state. The other way is to measure PAD under one experimental configuration and three different light polarization states. Here, the latter approach towards the complete experiment is discussed.

Experimental results on PAD from the $2\sigma_g$ inner valence shell of $N_2$ molecules are shown in Fig. 4. The photons emitted from the helical undulator beamline of BL-28A were monochromatized and tuned at 58.2 eV. The molecular axis is aligned to the vertical line, and the polarization ellipse is indicated in the figure. As can be seen from the figure, PAD

$$N_2 \ 2\sigma_g$$

$\hbar\nu = 58.2$ eV

Figure 4.
$2\sigma_g$ photoelectron angular distributions for $N_2$ molecules oriented along the vertical line: (a) left-elliptical polarization, $S_1 = 0.42$ and $S_3 = -0.91$ (b) right-elliptical polarization, $S_1 = 0.50$ and $S_3 = 0.87$, (c) linear polarization, $S_3 = 0.97$. 
is strongly dependent on the light polarization. PAD can be written as the incoherent sum of four contributions, \( d\sigma_x \) (\( d\sigma_x \) and \( d\sigma_y \) refer to linearly polarized light with the electric vector along the x-axis and the y-axis, and \( d\sigma_R \) and \( d\sigma_L \) to right- and left-circularly polarized light):

\[
d\sigma_{\text{tot}} = \frac{1}{2}(d\sigma_x + d\sigma_y) + \frac{S_1}{2}(d\sigma_x - d\sigma_y) + \frac{S_3}{2}(d\sigma_R - d\sigma_L),
\]

(1)

where \( S_1 \) and \( S_3 \) are the Stokes parameters describing the light polarization, and the individual \( d\sigma_i \) includes the electric-dipole matrix elements and phase shifts describing the photoionization process and the angle between the molecular axis and the major axis of the polarization ellipse. The difference between Fig. 4(a) and Fig. 4(b) is caused by the opposite sign of \( S_3 \) and the major axes of the polarization ellipses being nearly orthogonal to each other. In other words, one can say that the difference is the mixture of, so-called, linear and circular dichroism. The circular dichroism already appears in the electric-dipole approximation, and arises solely from interferences between degenerate photoelectron continua with \( m \) values differing by \( \pm 1 \). Since the matrix elements and phase shifts have been determined by analyzing the experimental results of Fig. 4, every contribution, i.e., the first term (PI) independent on polarization of Equation (1), the second term (LD) dependent on \( S_1 \), and the third term (CD) dependent on \( S_3 \) are reconstructed as shown in Figure 5. The difference between the second terms in Figs. 5(a) and (b) gives the linear dichroism, and the difference between the third terms gives the circular dichroism. Because the circular dichroism in PAD appears in the electric-dipole approximation, as mentioned above, the magnitude of the circular dichroism is appreciably strong and of the same order of magnitude as the photoelectron intensity.

The interpretation of the PAD patterns for adsorbed molecules has been based on theoretical calculations for oriented free molecules. As discussed above, the theoretical parameters describing the photoionization process for free molecules can be determined experimentally. Using the determined parameters, one can simulate the PAD patterns for the relevant adsorbed molecules under the given geometrical condition and polarization properties. The difference between the simulated and experimental PAD patterns would be attributed to a surface effect, which is expected to be appreciable for chemisorbed molecules. The PAD measurements for free oriented molecules are quite useful for understanding the nature of the adsorbed molecules.

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