

DIRECT MEASUREMENT OF THE KINETIC ENERGY SHIFT BETWEEN THE MOLECULAR AND ATOMIC $M_{4,5}N_{4,5}N_{4,5}$ AUGER SPECTRA OF IODINE

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The $M_{4,5}N_{4,5}N_{4,5}$ Auger electron spectrum of iodine has been measured from molecular and atomic iodine vapours. The energy shift of 3.25 ± 0.10 eV between molecular and atomic Auger spectra has been determined using a least-squares fitting procedure to spectra containing both molecular and atomic contributions. Different initial and final state splittings for atomic and molecular spectra, as well as the extra-atomic relaxation energy, are discussed.

1. Introduction

During the past few years there has been considerable theoretical interest in electronic reorganization accompanying core ionization in simple molecules [1–6]. These relaxation phenomena are, as such, very important in the interpretation of experimental binding-energy shifts obtained by X-ray photoelectron spectroscopy. Extra-atomic relaxation phenomena via the shifts of the kinetic energies of Auger electrons have not been studied so extensively until recently. The relaxation shifts of the emitted Auger electrons are expected to be considerably greater than the shifts of photoelectrons due to more extensive polarizing of the double-hole final state of the Auger process. Thus the Auger energy shifts can provide important complementary information for a better understanding of extra-atomic relaxation phenomena in molecules and solids.

Iodine vapour consists of diatomic molecules at room temperature but the molecules dissociate with increasing temperatures. Already at temperatures somewhat below 400°C the contributions of molecular and atomic iodine are about equal and simultaneous observation of Auger electron spectra from both is possible. This provides a convenient means for the experimental determination of the shift between molecular and atomic Auger spectra. Due to the fact that there is no change in the oxidation num-

ber between I_2 and I, the ground-state properties should be the same and the observed shift should arise almost exclusively from extra-atomic relaxation effects.

The $M_{4,5}N_{4,5}N_{4,5}$ spectra in iodine are well suited for the study of extra-atomic relaxation shifts because these transitions have high intensity and because the orbitals of the final-state holes are well in the core (binding energies 57–60 eV).

2. Experimental procedure and results

The measurements were done with a cylindrical mirror analyzer [7]. The spectrometer is equipped with a high-temperature oven. The iodine vapour is allowed to flow into the oven where the vapour is ionized by 2–3 keV primary beam electrons. A standard pulse-counting technique applying a multi-channel analyzer as the multiscaling mode was used.

The series of experimental spectra in different oven temperatures are shown in fig. 1. It can clearly be seen that the spectrum of atomic iodine increases on the low-energy side at the expense of the intensity of the molecular spectrum as the temperature increases. The corresponding purely molecular and almost entirely atomic vapours at room temperature and 800°C reveal that the overall structure of the spectra is similar. Especially the low-energy sides of the M_4 -groups

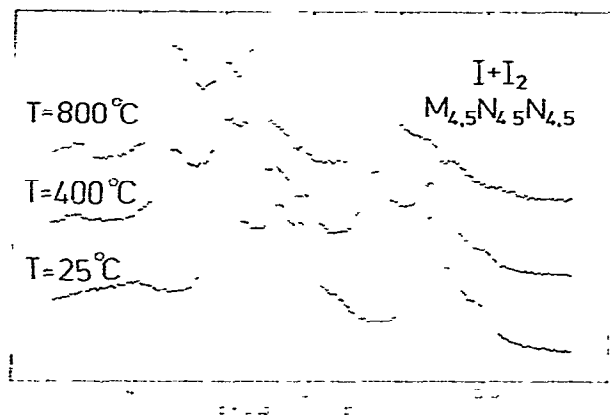


Fig. 1 $M_{4,5}N_{4,5}N_{4,5}$ Auger electron spectra from iodine vapour at temperatures of 25°C, 400°C and 800°C. The lowest spectrum is from pure molecular vapour and the highest from almost pure atomic vapour.

clearly show the shift between the spectra, because the M_4 -group of the atomic spectrum is increasing just at the minimum between the M_5 - and M_4 -groups of the molecular spectrum. Thus the energy shift could be determined in a first approximation directly from the energy difference between these intensity maxima.

3. Discussion

The $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of molecular iodine has previously been studied in detail [8]. The lines of molecular iodine were observed to be considerably broadened due to excitation of many different vibrational levels during the Auger process. At first sight it would be easy to assume that the Auger lines of atomic iodine are narrower. However, the spectra of fig. 1 do not support this expectation. The free iodine atom has a partially filled 5p shell ($\dots 5p^5$); one 5p electron missing from the closed xenon structure. The resulting 5p hole affects the splitting of the initial and final states of the Auger process. Actually the initial states are 3d5p two-hole and the final states 4d²5p three-hole states with the corresponding terms. For molecular iodine the single-hole initial and two-hole final state model is more valid. Hence the number of possible line components is much higher in the atomic iodine spectrum.

The terms of initial and final states and their re-

lative splittings can easily be calculated in LS coupling. Free iodine atoms have an initial configuration ($\dots 3s^2 3p^6 3d^9 4s^2 4d^{10} 5s^2 5p^5$) which splits into levels $^1P_1$, $^1D_2$, $^1F_3$, $^3P_{0,1,2}$ and $^3D_{1,2,3}$ from which the levels ^1P and ^3D (having the highest and lowest energy) are separated in LS coupling by 0.47 eV.

From the final states only the $\dots 4d^8 5s^2 5p^5 (1S)^2P$ remains as a single level in LS coupling. All other levels of the two-vacancy final state $4d^{-2}$ split into several levels due to the appearance of the third vacancy in the open 5p shell. The splitting between the lowest and highest energies of the final-state levels caused by the third hole is rather small (≤ 2 eV) and can be compared with the inherent atomic line width (0.6 eV). Thus in the case of the atomic spectrum there are many unresolved components in a narrow energy range (inherent line width) around the corresponding pure two-hole final-state component. This qualitatively explains why the overall shape of the atomic spectrum is about the same or slightly smoother than that of the molecular spectrum.

The intensity of molecular lines is distributed in the atomic spectrum into the several components discussed above. Without detailed intensity calculations it is not possible to determine the shift between corresponding molecular and atomic line components unambiguously. In order to obtain as accurate average shift values as possible the spectrum taken at 400°C was least-squares fitted both with 20 separate lines of equal width and the shape of the Voigt function and using as the standard lines fitted shapes of M_4 and M_5 groups obtained from separate fits to molecular and atomic spectra. The fit with the four latter standard lines is shown in fig. 2. The mean value 3.25 ± 0.10 eV has been obtained from several fits for the shift between corresponding components in atomic and molecular spectra. The shift values have been determined from the spectrum containing both atomic and molecular spectra, because then both spectra were taken simultaneously in identical experimental conditions and the observed shifts are not affected, e.g. by the shifts arising from vapour-pressure variations with temperature as they could be if pure molecular and atomic spectra were compared.

To our knowledge there are no ab-initio self-consistent-field calculations for the electronic relaxation energies in the I_2 molecule. With the aid of measured Auger and binding energies of molecular iodine and

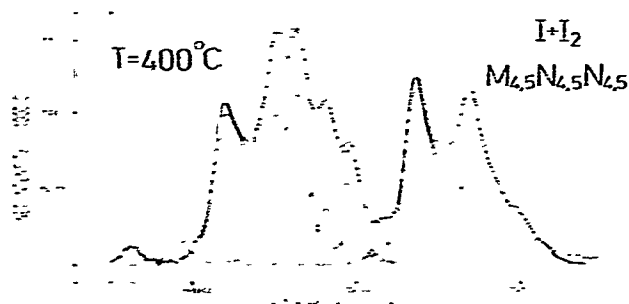


Fig. 2. Separation of the atomic-molecular Auger spectrum into the atomic and molecular Auger line groups. As the standard lines the fits to the experimental $M_{4,5}$ - and $N_{4,5}$ -line groups of the molecular ($T = 25^\circ\text{C}$) and atomic ($T = 800^\circ\text{C}$) spectra were used.

atomic xenon, the extra-atomic relaxation energy in the $M_{4,5}N_{4,5}N_{4,5}$ spectrum of I_2 was estimated [8] using the simple equation

$$F(jkl) = B(i) - B(k) - B(l) \\ - F(kl) + R^a(kl) + R^{\text{ex}}(kl), \quad (1)$$

where $F(jkl)$ is the Auger kinetic energy, $B(i)$ the binding energies, $F(kl)$ the hole-hole interaction energy and $R^a(kl)$ and $R^{\text{ex}}(kl)$ the formal atomic and extra-atomic parts of the relaxation energy in the double-hole final state of the iodine molecule. The value 3.3 eV was obtained for the extra-atomic part in eq. (1). Another simple estimate of the extra-atomic part $R^{\text{ex}}(kl)$ can be based on comparison of the calculated free-atom binding energies of iodine with the experimental molecular binding energies and on the observed Auger shift. If we assume that the calculated binding energies deviate from the experimental values by the same amount for atomic iodine as for the neighbouring element xenon, whose experimental values are accurately known, "semi-empirical" free-atom binding energies of iodine can be obtained. We used the relaxed-orbital electron binding energies of Huang et al.

[9]. Experimental binding energies for xenon were taken from ref. [10] and those of iodine from ref. [8]. By correcting the calculated free-atom binding energies of iodine by the difference between experimental and calculated values for xenon it is found that from molecular iodine vapour measured values are 1.18 and 0.56 eV lower for $M_{4,5}$ and $N_{4,5}$ levels, respectively. Assuming that the hole-hole interaction is the same for I_2 and I we obtained 3.2 eV for the extra-atomic relaxation energy term in eq. (1). In this case it is close to the observed shift between the molecular and atomic Auger spectra, but it is achieved by the cancellation of the binding energy shifts in eq. (1). The estimated binding energy shift of 1.18 eV between atomic and molecular $M_{4,5}$ levels correlates rather well with the shift of 1.05 eV for bromine calculated by Martin and Davidson [11], whereas the difference in the shifts, 0.6 eV, between $M_{4,5}$ and $N_{4,5}$ levels is probably too large.

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