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REMARKS ON RELATIONS BETWEEN X-RAY EMISSION AND AUGER TRANSITION
RATES AND MOLECULAR PROPERTIES: CHEMICAL EFFECT*

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ABSTRACT

Relations are pointed out that there exist between (1) the X-ray emission rate and the π bond order and (2) the Auger transition rate and the valence electron density (chemical effects) resulting from C 1s vacancy in carbon-containing molecules. Recognition of these relations is very important for analysis of experimental data and for prediction of these quantities, for which no data are available.

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Recently, Larkins and colleagues conducted an extensive, systematic theoretical study of X-ray emission and Auger transition spectra for some carbon-containing molecules [1-3]. Some of their major findings are the following: (i) the importance of intra- and inter-atomic transitions, (ii) the significant contribution in some cases of the vibrational motion of the nucleus to electronic transitions, (iii) the sensitivity of the electronic transition coupling matrix to the basis set used for the molecular orbital calculation, (iv) the relation between the Auger transition rate and the valence electron density, and (v) the finding of no simple relation between the X-ray emission rate and electron density.

This short note points out that in addition to the relation of the Auger transition rate to valence electron density, a relationship exists between the X-ray emission rate and the π bond order [4]. The π bond order is the property that describes π -electron density between nearest neighbor atoms. The π -bond order is known to have an inverse linear relationship with bond length. That is, as the π bond order increases (with greater electron density in the molecular orbitals between neighboring atoms), the bond length decreases. Figure 1 shows our results for the X-ray emission rate for C_2H_2 , C_2H_4 , and C_2H_6 along with the results of Larkins for different carbon-containing molecules as a function of π bond order. Figure 1 clearly suggests a correlation between these two quantities. The physical reason for this correlation is that for X-ray emission, π valence electrons should have a direct, strong overlap with an inner-core hole (a carbon 1s hole in the present case) to allow an effective transition. However, as the π bond order increases (as the electron density between neighboring atoms increases), the electron density is well localized within π molecular orbitals, increasing the bonding effect. This increase of electron localization reduces the effective overlap with a 1s hole state, leading to a smaller X-ray emission rate.

In contrast, for the Auger transition, the essential dynamics are due to electron-electron interaction. More electrons are in valence orbitals, so more electron-electron interactions per a molecule can be expected, suggesting a larger Auger transition rate.

Therefore, as suggested by Larkins [3], the Auger transition rate shows a correlation with electron density in a molecule.

These findings are useful for further analyses of X-ray emission spectra and the chemical effects.

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Figure Captions

Fig. 1a. X-ray emission rate as a function of π bond order. ■, present work; ●, Larkins and co-workers [1,2]. Solid line represents the least square fit of the data.

Fig. 1

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