

STIELTJES IMAGING TECHNIQUE APPLIED TO INNER SHELL IONIZATION PHENOMENA IN MOLECULES

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ABSTRACT

We devise Stieltje's imaging techniques for high-energy electronic continua in molecules and demonstrate some applications for Auger resonances, shake-off spectra, lifetime broadening and discrete-continuum interaction energy shifts.

1. INTRODUCTION

Theoretical descriptions of bound-continuum electronic transitions in molecules are complicated by the anisotropy of molecular ionic field. L^2 methods, especially the Stieltjes imaging method, have been quite promising in overcoming these problems, and have lately been applied to shape resonances and cross sections in molecular photoelectron spectra [1,2]. However, except for photoionization at low photon energies, the use of these methods has been rather sparse.

In the present work we show how Stieltjes imaging can be generalized to include high energy electronic continua and also other types of inner shell ionization phenomena in molecules. This means that both shape resonances (open channels) and "delta-" or Auger resonances (closed channels) can be addressed with the same, Stieltjes imaging, approach.

The technique is applied to shake-off transitions, Auger resonances, lifetime broadening and to discrete-continuum interaction energy shift and results are also used to analyse fine structure in the emission spectra emerging from lifetime-vibrational interference and variation of lifetime with nuclear conformation. Sample calculations on these phenomena for the water molecule are presented.

2. THEORY AND APPLICATIONS

Stieltjes imaging is a moment theory method, which utilizes spectral moments $S(-k)$ obtained by integrable basis set calculations of a theoretical spectrum in the discrete and continuous energy regions. Spectral distributions describing the transition from a discrete initial state to a final state in the electronic continuum are obtained by the Stieltjes derivative (SD)

$$\frac{d F^{(n)}(X)}{d X} = (1/2) \frac{I_{\ell+1}^{(n)} + I_{\ell}^{(n)}}{X_{\ell+1}^{(n)} + X_{\ell}^{(n)}} \quad \text{at } X = (1/2)(X_{\ell}^{(n)} - X_{\ell+1}^{(n)})$$

of a function $F^{(n)}(X) = \sum_{\chi} X_{\chi} I^{(n)}$ deriving from the principal spectral representation of order n [$X_{\chi}^{(n)}$; $I_{\chi}^{(n)}$] that reproduces the first $2n$ spectral moments

$$S(-k) = \sum_{i=1, n} I_i^{(n)} (X_i^{(n)})^{-k} \quad k = 0, 1, 2, \dots, (2n-1).$$

In the usual photoionization cross section calculations [1,2], the discretized theoretical spectrum, from which the $S(-k)$ are computed, consists of excitation energies and oscillator strengths. In the present contest, it is defined by the Fermi Golden Rule for the Auger decay

$$[\sqrt{2\epsilon_\nu} ; 2\pi | \langle \tilde{\varphi}_F^{N-2} | \hat{a}_{\epsilon_\nu} (\hat{H} - E) | \tilde{\varphi}_h^{N-1} \rangle |^2]$$

and by the Sudden Approximation for the shake-off process

$$[(\epsilon_\nu + E_f) ; | \langle \tilde{\varphi}_F^{N-2} | \hat{a}_{\epsilon_\nu} \hat{a}_h | \tilde{\varphi}_0^N \rangle |^2]$$

where $\tilde{\varphi}_0^N$ is the molecule ground state, $\tilde{\varphi}_h^{N-1}$ is a core hole state, $\tilde{\varphi}_F^{N-2}$ is the appropriate double ionized final state, ϵ_ν is the energy of the secondary emitted electron and E_f is the shake-off threshold [3,4].

The many-electron continuum is basically approximated by an antisymmetrized product of a fixed target function for the molecular ion and a continuum orbital for the outgoing electron obtained by diagonalizing a static-exchange hamiltonian [2-4], projected on a L^2 basis set containing special oscillating functions [2], that, for the water molecule, has the following expressions

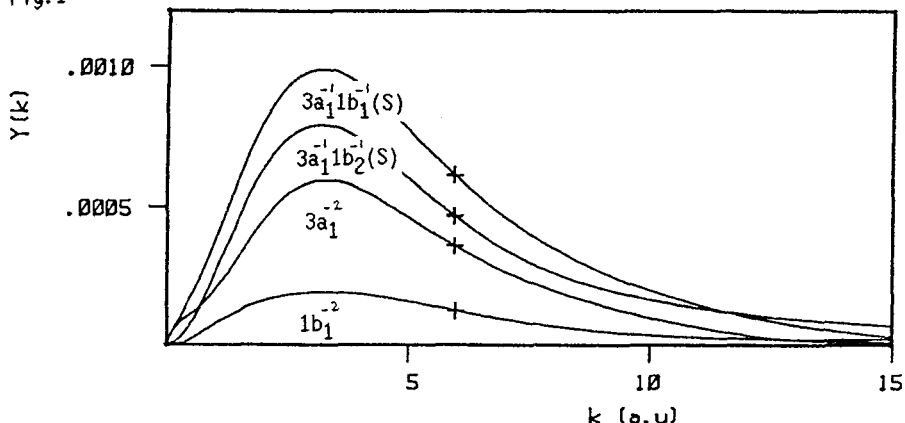
$$\hat{h}^S = \hat{T} + \hat{V} + \sum_{i=(x,y)} (2\hat{J}_i - \hat{K}_i) + [\hat{J}_x + \hat{J}_y - (1/2)\hat{K}_x - (1/2)\hat{K}_y](1 - \delta_{xy})$$

$$\hat{h}^T = \hat{T} + \hat{V} + \sum_{i=(x,y)} (2\hat{J}_i - \hat{K}_i) + [\hat{J}_x + \hat{J}_y + (1/2)\hat{K}_x + (1/2)\hat{K}_y]$$

where S(singlet) and T(triplet) specify the spin of the ion final state (double hole in the orbitals x and y), \hat{T} , \hat{V} , \hat{J} and \hat{K} are the kinetic, nuclear attraction, Coulomb and exchange operators respectively.

In contrast to photoionization or shake-off transitions [1,2,4], where the cross sections are obtained from the SD on a continuous range of energies, the Auger process, refers to only one energy value ϵ_0 corresponding to the resonance energy of the considered decay channel [3].

Fig.1



In Fig.1 the continuous functions $Y(k) = dF^{(n)}(k)/dk$ (where $k = \sqrt{2\epsilon}$ is the outgoing electron momentum) corresponding to the d-wave contribution to the channels $3a_1^1$, $3a_1^1 1b_2^1(S)$, $3a_1^1 1b_1^1(S)$, $1b_1^1$ in the Auger decay of the H_2O core hole state, are reported for example; the resonance condition is marked by crosses. By these functions, the energy shift of the core hole state due to the interaction with the Auger continua can be computed

$$\Delta E = P \int_0^\infty d\epsilon \frac{Y(\sqrt{2\epsilon})}{\sqrt{2\epsilon}(\epsilon_0 - \epsilon)}$$

the total value obtained amounts to ≈ 0.06 eV.

The described approach has been applied at several approximation levels starting with the SCF approximation for the initial and final states and the independent wave approximation for the emitted electron. The effect of the electronic relaxation for the ionic states and of the different channel interaction has been subsequently investigated; this last effect was found rather important especially towards the low kinetic energy part of the Auger spectrum.

Fig.2 CORE ELECTRON SHAKE-OFF SPECTRUM OF WATER
INDEPENDENT CHANNEL CALCULATION
RELAXED ORBITAL SHAKE-OFF EDGES

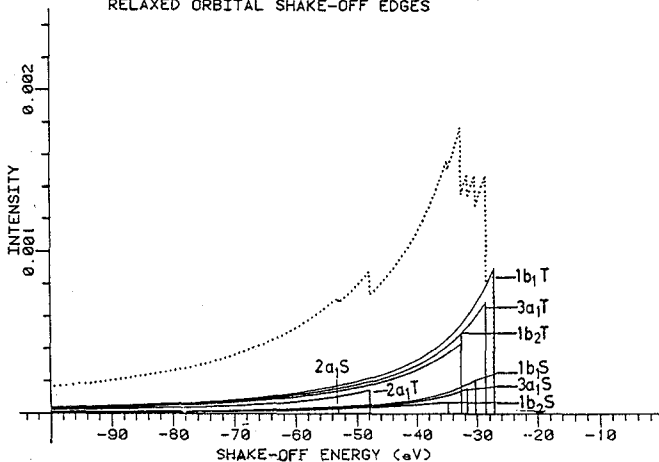
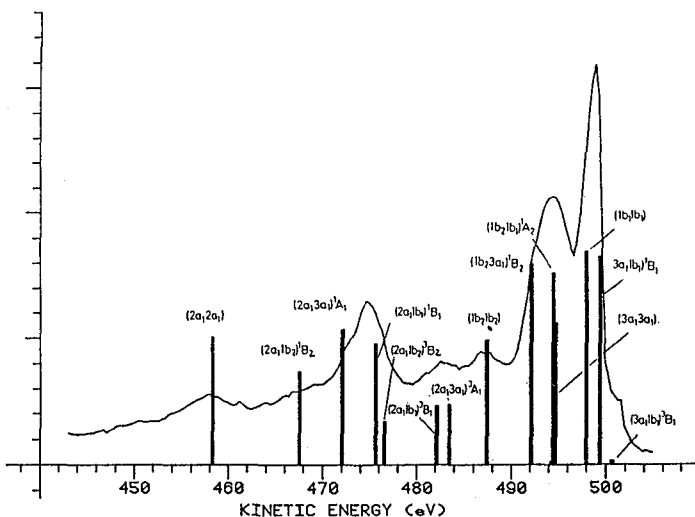
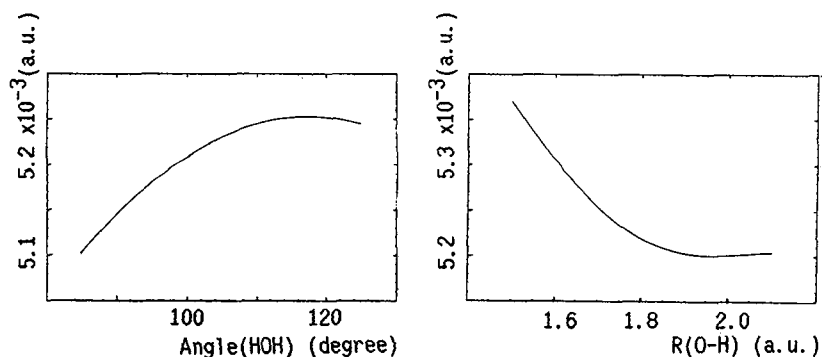


Fig.3 AUGER SPECTRUM OF WATER: HOLE-MIXING CALCULATIONS



The 4 figures are a short review of different applications of the Stieltjes method for inner shell ionization processes in the water molecule. Fig. 2 reports the total core electron shake-off spectrum (broken line) together with partial contributions from several channels identified by the label of the valence orbital involved in the shake-off and the spin label of the final ionic state [4]. In Fig.3 the theoretical Auger spectrum including the interaction of the 16 different decay channels is compared with the experimental spectrum [5]. Since the fluorescence yield is very small for core hole state of water as for inner vacancies of all small-Z elements, the lifetime (and lifetime broadening) is directly given by the total Auger rate. Summing all the theoretical independent channel rates we obtain a lifetime broadening of 0.15 eV for the core hole state of water.

Fig.4 TOTAL AUGER DEACY RATE (LIFETIME WIDTH)



In Fig.4 we display the dependence of the lifetime on the nuclear conformation [6]. It is seen that most of the variation (from united atom (Ne) to the free atom (O) limits) is allocated to internuclear distances short of the equilibrium geometry. The 'constant resonance approximation' seems thus to hold for core ionization of water. Although the lifetime variation only marginally influences the band shape in the core emission spectra of water, (viz. Auger and X-ray emission spectra) the total lifetime gives rise to non-negligible distortions of the bands due to vibrational-lifetime interference effects. A formalism for band shape analysis including lifetime interference and lifetime geometry variation has recently been derived and applications to water core emission spectra are in progress.

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