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Chemical Physics Letters 410 (2005) 423–429

CHEMICAL PHYSICS LETTERS

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The influence of relativistic effects on the ionization spectra of the alkali iodides

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Received 3 May 2005
Available online 21 June 2005

Abstract

Fully relativistic ionization spectra of hydrogen iodide (HI) and the alkali iodides MI (M = Li, Na, K, Rb) are calculated using the one-particle propagator technique in the four-component framework. The algebraic diagrammatic construction (ADC) technique up to third order is hereby used for the matrix construction. Comparison to experimental results is made and the trends in the ionization spectra with increasing ionicity of the species investigated. The spin–orbit splitting in the outer valence and sub-valence ionization peaks is well reproduced in all cases.

1. Introduction

Photoelectron (PE) spectra provide valuable information about the electronic structure and bonding in a specific system and their accurate prediction by ab initio methods still is a challenging task. In the PE spectra of systems containing heavy elements a subtle interplay of relativistic effects and electron correlation can be observed necessitating a balanced description of both effects and purely nonrelativistic or scalar relativistic treatments often do not yield satisfactory results. If spin–orbit splitting is pronounced a fully relativistic treatment is the method of choice. For the calculation of the ionization energies the one-particle propagator (Green's function) technique [1,2] was employed. In this method the ionization energies and spectral intensities are calculated as eigenvalues and eigenvectors of a Hermitian matrix whose elements are determined by the algebraic diagrammatic construction (ADC) scheme [3]. For the correct description of systems containing heavy elements we embedded the ADC scheme into the four-component framework [4,5] resulting in Dirac–Hartree–Fock-ADC (DHF-ADC). Compounds containing iodine will exhibit considerable relativistic effects necessitating an appropriate treatment via DHF-ADC.

In this work our focus lies on the study of the alkali iodide valence PE spectra in order to reproduce experimental valence ionization spectra. Also for the inner valence 4d ionization high-resolution PE spectra of iodine compounds are available [6] showing considerable ligand-field and spin–orbit splitting. The theoretical description of these spectral features within the propagator framework was not accessible before and the third-order implementation of DHF-ADC has also been successfully applied to the calculation of the $PtCl_6^{2-}$ [7] and XeF_n ($n = 2, 4, 6$) spectra [8].

Vibrational effects on the various ionization processes are hereby not considered. They can be distinguished from ligand-field effects that lead to a $d_{3/2}$ doublet and a $d_{5/2}$ triplet whereas vibrational splitting affects both d components in the same manner.

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doi:10.1016/j.cplett.2005.05.104

2. Methodology

In the following we will briefly outline the method of the fully relativistic one-particle propagator method DHF-ADC(3) for the calculation of PE spectra and refer to review articles and more detailed presentations where necessary.

The calculation of nonrelativistic and relativistic ionization energies including electron correlation is based on the formalism of the one-particle Green's function $G_{pq}(t,t')$ (electron propagator) which is defined [9] by the equation,

$$G_{pq}(t,t') = -\mathrm{i}\langle \Psi_0^N | c_p(t) c_q^\dagger(t') | \Psi_0^N \rangle \Theta(t-t') + \mathrm{i}\langle \Psi_0^N | c_q^\dagger(t') c_p(t) | \Psi_0^N \rangle \Theta(t-t'). \tag{1}$$

$|\Psi_0^N\rangle$ is the exact (non-degenerate) ground state of the considered N-particle system, $c_r^\dagger(t)$ $[c_r(t)]$ denote creation (destruction) operators for one-particle states $|\Phi(r)\rangle$ and $\Theta(\tau)$ is the Heavyside step function. In the energy representation G_{pq} takes on the form

$$G_{pq}(\omega) = G_{pq}^+(\omega) + G_{pq}^-(\omega), \tag{2}$$

where:

$$G_{pq}^+(\omega) = \langle \Psi_0^N | c_p(\omega - \hat{H} + E_0^N + i\eta)^{-1} c_q^\dagger | \Psi_0^N \rangle, \tag{3}$$

$$G_{pq}^-(\omega) = \langle \Psi_0^N | c_q^\dagger(\omega + \hat{H} + E_0^N + i\eta)^{-1} c_q | \Psi_0^N \rangle. \tag{4}$$

Here, $\hat{H}$ is the Hamiltonian of the system and E_0^N is the ground state energy, η is a positive infinitesimal required to define the Fourier transform between the time and energy representation of Eqs. (1) and (2). The parts $G^+(\omega)$ and $G^-(\omega)$ contain physical information on the $(N+1)$ and $(N-1)$ particle systems, respectively. This becomes explicit in the spectral representation [9,10], which for the $(N-1)$ particle part reads as

$$G_{pq}^-(\omega) = \sum_n \frac{x_{nq}^* x_{np}}{\omega - \omega_n - \mathrm{i}\eta}. \tag{5}$$

The pole positions

$$\omega_n = -\left(E_n^{N-1} - E_0^N\right) \tag{6}$$

are the (negative) ionization energies of the system, while the residue amplitudes

$$x_{np} = \langle \Psi_n^{N-1} | c_p | \Psi_0^N \rangle \tag{7}$$

are related to spectral intensities. In Eq. (5) summation is carried out over all $(N-1)$-particle states $|\Psi_n^{N-1}\rangle$.

In the ADC method [3], the pole positions ω_n and residue amplitudes x_{np} are obtained as eigenvalues and eigenvectors of an Hermitian matrix whose entries are determined by comparison of the diagrammatic expansions of $\mathbf{G}$ with the terms of an algebraic series expansion of the nondiagonal resolvent matrix that is related to the spectral representation of $\mathbf{G}$.

It should be noted that in the ADC(3) scheme the ionization energies are treated consistently through third order within a 1h/2h1p configuration space and those classes of Feynman diagrams that derive from the first n orders are implicitly summed up to infinity by application of the Dyson equation for the Green's function:

$$\mathbf{G}(\omega) = \mathbf{G}^{(0)}(\omega) + \mathbf{G}^{(0)}(\omega)\mathbf{\Sigma}(\omega)\mathbf{G}^{(0)}(\omega) + \ldots \tag{8}$$

The Dyson equation is a concise expression for the infinite diagrammatic expansion of the full Green's function that contains the dynamic self energy part $\mathbf{\Sigma}(\omega)$ consisting of all irreducible diagrams. $\mathbf{\Sigma}(\omega)$ itself is the sum of a purely dynamic and an ω-independent part according to

$$\mathbf{\Sigma}(\omega) = \mathbf{M}(\omega) + \mathbf{\Sigma}(\infty). \tag{9}$$

Beyond the second-order treatment the ω-independent diagrams $\mathbf{\Sigma}(\infty)$ occur and their determination is based on a self-consistent procedure starting from the equation,

$$\sum_{pq}(\infty) = \sum_{rs} V_{pr,qs}\left[\frac{1}{2\pi\mathrm{i}} \oint G_{sr}(\omega)\mathrm{d}\omega - n_r\delta_{rs}\right] \tag{10}$$

with the occupation numbers n_r taking on the value +1 for hole states and 0 for particle states. The totally antisymmetric two-electron integral $V_{pq,rs}$ is hereby defined as

$$V_{pq,rs} = \langle pq|rs\rangle - \langle pq|sr\rangle. \tag{11}$$

In contrast to the full Dyson formulation where the $(N-1)$ and $(N+1)$ part of $\mathbf{G}(\omega)$ are treated simultaneously [3] one can also resort to the $(N-1)$ particle part exclusively and apply the ADC scheme to $\mathbf{G}^-(\omega)$ directly (non-Dyson formulation) [11]. Because we consider ionization energies only we will confine ourselves to $\mathbf{G}^-(\omega)$ in the following.

Once the ADC matrix is diagonalized one obtains the energetic positions (ionization energies) of the spectral lines as the eigenvalues where each line corresponds to an individual eigenstate of the cation. If we worked in the independent particle picture exclusively the resulting cationic spectrum would give one line with a spectroscopic factor of 1 for each occupied molecular orbital (MO) $|\varphi_i\rangle$. The energies of these lines would then correspond to the orbital energies ε_i according to Koopmans' theorem. Actually, the electrons exhibit correlation not described by the independent particle model of ionization and the resulting cationic state is to be seen as a linear combination of 1h, 2h1p, 3h2p, ... excited configurations. The ADC matrix up to a certain order is constructed within a subset of these configurations and the resulting eigenvectors then provide information about the contributing configurations, i.e., the strength of the coupling of a 1h configuration to other excited configurations. If the eigenvector component is close to 1 in the 1h space then the corresponding line in ionization spectrum is called a *main line* and the molecular