

## A Green's Function Approach to the Photoelectron Spectrum of Bis( $\pi$ -allyl)nickel<sup>[1]</sup>

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The vertical ionization potentials of bis( $\pi$ -allyl)nickel (see **(1)** in Fig. 1) are calculated by means of the Green's function approach within a semiempirical INDO extension to the first transition metal series. The computed ionization potentials are in good agreement with an experimentally deduced assignment. In contrast to earlier theoretical and experimental studies, the  $7a_u(\pi)$  level is predicted on top of the levels corresponding to the Ni  $3d$  orbitals. Our approach leads to a complete assignment of the PE spectrum of **(1)** in the outer valence region.

**Key words:** INDO calculations – relaxation and correlation contributions.

### 1. Introduction

Discussing the photoelectron (PE) spectra of metalorganic compounds in the valence region, bis( $\pi$ -allyl)nickel **(1)** has become an often quoted example for large Koopmans' defects [3]. Since its first publication in 1972 [4], the PE spectrum of **(1)** has been the subject of controversial discussion and several divergent assignments have been put forward [5]. A comparison between the PE spectrum of **(1)** and the spectra of the various methyl derivatives on one side [6] and the spectra of the Ni, Pd and Pt bisallyl systems on the other [7] has led to a consistent assignment except for the first bandsystem. On the basis of alkyl shifts and arguments from perturbation theory, it was concluded that the first transitions

are due to ionization events from Ni  $3d$  orbitals ( $13a_g$ ,  $12a_g$ ,  $5b_g$ ,  $11a_g$ ) closely followed by the ionization from the  $7a_u$  orbital [6]. Correlation within the bis( $\pi$ -allyl) series of Ni, Pd and Pt as well as results of  $\Delta$ SCF and transition operator (TO) calculations within an INDO extension [8] to the first transition metal series has lead to the sequence  $7a_u$  on top of  $13a_g$ ,  $12a_g$ ,  $5b_g$  and  $11a_g$  [7]. For a further investigation of the relaxation and correlation contributions to the ionization energies of metalorganic compounds we have applied the Green's function technique [9, 10] to bis( $\pi$ -allyl)nickel. This approach, based on many body perturbation theory, has been successfully used in recent years to calculate vertical ionization potentials of small and medium sized molecules of the complete first [11] and second period [12] within the computational framework of an *ab initio* Hamiltonian. Although the accuracy and sophistication of the *ab initio* calculations mentioned exceeds the capacity of a semiempirical approach, we feel that our INDO model combined with the Green's function formalism is a useful tool for the determination of ionization energies in those molecules where the application of accurate *ab initio* methods (Hartree-Fock Limit) is not possible at present.

## 2. Calculations

To calculate ionization potentials beyond Koopmans' approximation [13] via the one particle Green's function approach we have to determine those  $\omega$  values for which the matrix of the inverse Dyson equation (1) has eigenvalues equal to zero [14].

$$G^{-1} = (G^0)^{-1} - \Sigma(\omega) = \omega I - \varepsilon - \Sigma(\omega). \quad (1)$$

In (1)  $G$  is the matrix of the Green's function, while  $G^0$  is the matrix of the free Green's function associated with the set of canonical Hartree-Fock (HF) orbitals with orbital energies  $\varepsilon$ .  $I$  symbolizes the unit matrix of proper size. The expression  $\Sigma(\omega)$  is the self-energy part which can be expanded in different orders of perturbation as indicated in (2):

$$\Sigma(\omega) = \Sigma^{(1)}(\omega) + \Sigma^{(2)}(\omega) + \dots + \Sigma^{(n)}(\omega), \quad n = \infty. \quad (2)$$

If canonical HF orbitals are used as a starting point the first order correction  $\Sigma^{(1)}(\omega)$  vanishes [10, 15]. To compute the energy parameter  $\omega$  we have introduced approximations used in most semiempirical Green's function approaches [16]. Thus  $\Sigma(\omega)$  is developed up to second order, assumed to be diagonal [17] and a Taylor series expansion about the Koopmans' pole is performed [18]. The detailed expressions of the matrix elements of  $\Sigma_{ij}^{(2)}(\omega_i)$  within the INDO formalism for  $3d$  elements are derived in the Appendix. The semiempirical MO calculation with a recently developed INDO extension to the first transition metal series [8] was performed by using the experimentally determined geometry of bis( $\pi$ -methallyl)nickel [19]. In the expansion of the self-energy part 19 hole-states and 7 particle-states were considered.

### 3. Results

The measured PE spectrum of (1) is shown in Fig. 1 [6]. The calculated ionization potentials together with the assignment of the PE bands are given in Table 1. According to our calculation the first ionization event is due to the ejection of electrons from the  $7a_u(\pi)$  orbital, a purely ligand MO. The following four

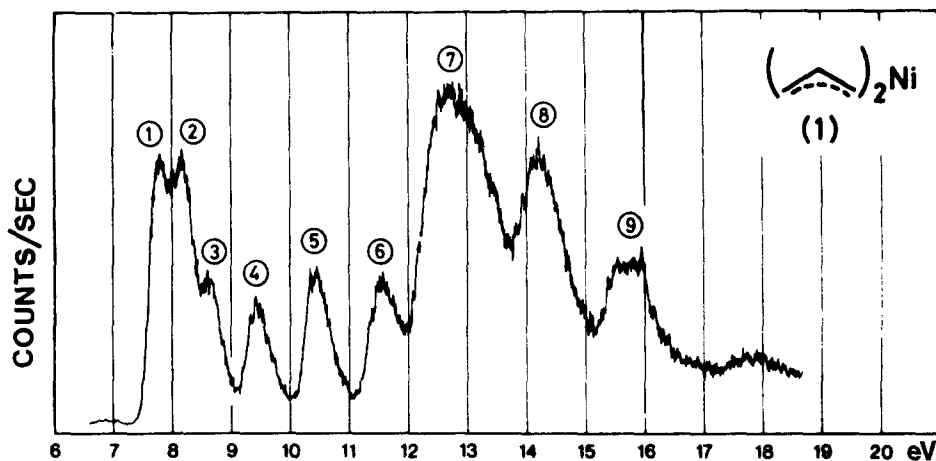


Fig. 1. He(I) PE spectrum of bis( $\pi$ -allyl)nickel (1) [6]

**Table 1.** Comparison between the experimentally determined vertical ionization potentials,  $I_{v,j}^{\text{exp}}$ , of bis( $\pi$ -allyl)-nickel (1) and the calculated ones, assuming the validity of Koopmans' theorem,  $I_{v,j}^{\text{K}}$ , and using the inverse Dyson equation ( $I_{v,j}^{\text{K}} + \sum_{ij}^{(2)}(\omega_i)$ ). All values in eV. (L = allyl ligand)

Band	$\Gamma_j$	MO-type	$I_{v,j}^{\text{K}}$	$I_{v,j}^{\text{K}} + \sum_{ij}^{(2)}(\omega_i)$	$I_{v,j}^{\text{exp}}$
①	$7a_u$	$a_2(\pi)_L$	9.12	8.75	7.76
②	$\left\{ \begin{array}{l} 13a_g \\ 5b_g \end{array} \right\}$	$\left\{ \begin{array}{l} \text{Ni } 3d_{yz}, b_1(\pi)_L \\ \text{Ni } 3d_{xy} \end{array} \right\}$	11.15	8.91	8.19
			12.48	9.19	
③	$\left\{ \begin{array}{l} 12a_g \\ 11a_g \end{array} \right\}$	$\left\{ \begin{array}{l} \text{Ni } 3d_z^2 \\ \text{Ni } 3d_{x^2-y^2} \end{array} \right\}$	12.44	9.21	8.58
			12.51	9.47	
④	$6b_g$	$\text{Ni } 3d_{xz}, a_2(\pi)_L$	11.04	10.07	9.40
⑤	$11b_u$	$b_1(\pi)_L$	11.42	10.88	10.38
⑥	$9a_g$	$b_1(\pi)_L, \text{Ni } 3d_{yz}$	14.44	12.16	11.55
⑦	$\left\{ \begin{array}{l} 6a_u \\ 10a_g \\ 10b_u \\ 4b_g \end{array} \right\}$	$\left\{ \begin{array}{l} \text{CC}\sigma_L \\ \text{CC}\sigma_L \\ \text{CC}\sigma_L \\ \text{CC}\sigma_L \end{array} \right\}$	13.92	13.02	12.70
			14.27	13.05	
			14.09	13.09	
			14.41	13.25	
⑧	$\left\{ \begin{array}{l} 3b_g \\ 5a_u \end{array} \right\}$	$\left\{ \begin{array}{l} \text{CH}\sigma_L \\ \text{CH}\sigma_L \end{array} \right\}$	16.87	15.43	14.20
			16.76	15.65	
⑨	$\left\{ \begin{array}{l} 9b_u \\ 8a_g \end{array} \right\}$	$\left\{ \begin{array}{l} \text{CH}\sigma_L \\ \text{CH}\sigma_L \end{array} \right\}$	18.43	16.96	15.60
			19.06	17.18	

ionization processes are predicted to arise from the MO's  $13a_g$ ,  $5b_g$ ,  $12a_g$  and  $11a_g$ . All four are mainly localized at the metal. The calculated difference between the centers of gravity of the first ionization potential and the four ionization events from the Ni  $3d$  functions amounts to 0.35 eV. This value is in good agreement with the experimental separation of 0.43 eV. The ionization potential of  $6b_g$  is predicted at 10.07 eV. The calculated energy difference between bands ②, ③ and band ④ amounts to 0.60 eV. This result is close to the observed separation (0.82 eV).

Bands ⑤ and ⑥ are predicted to result from ionizations out of the two remaining ligand  $\pi$ -orbitals  $11b_u$  and  $9a_g$  (strong Ni  $3d$  participation). Due to the larger reorganization predicted for the ionization out of  $9a_g$  the corresponding band is significantly separated from the four  $\sigma$  combinations  $10a_g$ ,  $10b_u$ ,  $6a_u$  and  $4b_g$ , as compared with a prediction based on the orbital energies of the ground state. The calculated Koopmans' defect of  $9a_g$  (2.29 eV) is found to be 1 eV smaller than the corresponding corrections of the strongly localized MO's  $13a_g$ ,  $5b_g$ ,  $12a_g$  and  $11a_g$ . Also the separation of the remaining PE bands is reproduced satisfactorily by the present approach. A pictorial representation of the calculated Koopmans' defects is given in Fig. 2. The standard deviation between the measured ionization potentials and the calculated values for the first 12 ionization events of (1)

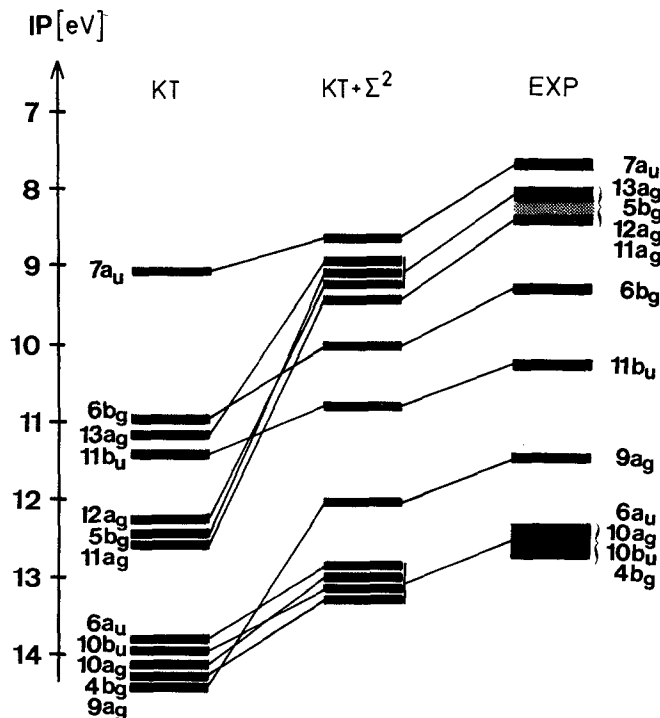


Fig. 2. Comparison between the first bands in the PE spectrum of (1) (EXP) with the calculated ionization potentials assuming the validity of Koopmans' theorem (KT) and using the inverse Dyson equation ( $KT + \Sigma^2$ ).

amounts to 0.08 eV with a regression coefficient of 0.9989. The linear relation between the calculated,  $I_{v,j}^{\text{cal}}$ , and the experimental,  $I_{v,j}^{\text{exp}}$ , values is given by (3).

$$I_{v,j}^{\text{cal}} = 1.56 + 0.91 \times I_{v,j}^{\text{exp}}. \quad (3)$$

The limitation to 19 hole-states explains why the extension to all ionization potentials in the outer valence region is not so good. For all 16 ionization events one calculates a standard deviation of 0.30 eV and a regression coefficient of 0.9939. The linear relation between  $I_{v,j}^{\text{cal}}$  and  $I_{v,j}^{\text{exp}}$  follows:

$$I_{v,j}^{\text{cal}} = 0.33 + 1.04 \times I_{v,j}^{\text{exp}}. \quad (4)$$

#### 4. Conclusions

The results presented confirm an earlier assignment based partly on correlation techniques in the series of selected bis( $\pi$ -allyl) complexes of Ni, Pd and Pt and partly on calculation procedures taking into account relaxation contributions only [7]. Within our semiempirical INDO Hamiltonian the calculated Koopmans' defects amount up to 3.3 eV in the case of strongly localized MO's. If the wave function is delocalized by about equal amounts on the metal and the ligands, the corresponding deviations in the ionization potentials are calculated to be about 2.2 eV. Typical Koopmans' defects of ligand MO's span a range of 0.5–1.0 eV. As a result of this large variation of the Koopmans' defects the orbital energies in the electronic ground state differ drastically from the measured ionization potentials.

The main advantage of the simplified Green's function approach in comparison with relaxation techniques ( $\Delta$ SCF, TO) is that the wave functions and orbital energies of the ground state are used in the computational procedure. Thus, inherent convergence problems of the  $\Delta$ SCF [20] and TO method [21] can be avoided.

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#### Appendix

The diagonal-elements of the self-energy part are given to second order by (5):

$$\begin{aligned} \Sigma_{jj}^{(2)}(\omega_j) &= \sum_i \sum_a \sum_b \frac{(2V_{jaib} - V_{jbia})V_{jaib}}{\omega_j + \varepsilon_i - \varepsilon_a - \varepsilon_b} \\ \sum_i \sum_a \sum_b &= \sum_i \sum_a \sum_b^{\text{occ vir vir}} + \sum_a \sum_b \sum_j^{\text{occ occ vir}}. \end{aligned} \quad (5)$$

The interaction integrals  $V_{ijkl}$  are defined as follows:

$$V_{ijkl} = \langle i(1)j(1) | \frac{1}{r_{12}} | k(2)l(2) \rangle \quad (6)$$

To compute  $V_{ijkl}$  one has to perform the four-index transformation (7) from the AO-basis  $\alpha, \beta, \gamma, \delta$  to the MO-basis  $i, j, k, l$ .

$$V_{ijkl} = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} c_{i\alpha} c_{j\beta} c_{k\gamma} c_{l\delta} \langle \alpha(1) \beta(1) | \frac{1}{r_{12}} | \gamma(2) \delta(2) \rangle. \quad (7)$$

Under the zero differential overlap (ZDO) approximation of the CNDO formalism [22] Eq. (7) is simplified to (8).

$$V_{ijkl}^{\text{CNDO}} = \sum_{\alpha} \sum_{\gamma} c_{i\alpha} c_{j\alpha} c_{k\gamma} c_{l\gamma} \langle \alpha(1) \alpha(1) | \frac{1}{r_{12}} | \gamma(2) \gamma(2) \rangle. \quad (8)$$

Within the INDO model [22] all one-center exchange-integrals have to be added in a rotationally invariant manner to the CNDO expression. For a  $s, p, d$  basis the following formulas were derived for the various exchange-integrals  $K'_{\mu\nu}$  [23]:

$$K'_{sp} = G_1^{sp} \quad (9)$$

$$K'_{pp'} = 3F_2^{pp'} \quad (10)$$

$$K'_{sd} = G_2^{sd} \quad (11)$$

$$K'_{pd} = 2G_1^{pd} + 21G_3^{pd} \quad (12)$$

$$K'_{dd'} = 2.5F_2^{dd'} + 22.5F_4^{dd'} \quad (13)$$

In (9)–(13) the  $G$ - and  $F$ -integrals correspond to the well-known Slater–Condon-parameters [24]. The transformation within the INDO approximation is then given by Eq. (14), where the AO indices  $\alpha, \gamma$  and  $s$  belong to a common atom  $A$ .

$$\begin{aligned} V_{ijkl}^{\text{INDO}} = V_{ijkl}^{\text{CNDO}} &+ \left[ \sum_{\alpha \in p} (c_{i\alpha} c_{j\alpha} + c_{is} c_{j\alpha}) (c_{k\alpha} c_{l\alpha} + c_{ks} c_{l\alpha}) \right] \times G_1^{sp} \\ &+ \left[ \sum_{\alpha} \sum_{\gamma \neq \alpha} (c_{i\alpha} c_{j\gamma} + c_{i\gamma} c_{j\alpha}) (c_{k\alpha} c_{l\gamma} + c_{k\gamma} c_{l\alpha}) \right] \times 3F_2^{pp'} \quad * \\ &+ \left[ \sum_{\alpha \in d} (c_{i\alpha} c_{j\alpha} + c_{is} c_{j\alpha}) (c_{k\alpha} c_{l\alpha} + c_{ks} c_{l\alpha}) \right] \times G_2^{sd} \\ &+ \left[ \sum_{\alpha} \sum_{\gamma \neq \alpha} (c_{i\alpha} c_{j\gamma} + c_{i\gamma} c_{j\alpha}) (c_{k\alpha} c_{l\gamma} + c_{k\gamma} c_{l\alpha}) \right] \times (2G_1^{pd} + 21G_3^{pd}) \quad ** \\ &+ \left[ \sum_{\alpha} \sum_{\gamma \neq \alpha} (c_{i\alpha} c_{j\gamma} + c_{i\gamma} c_{j\alpha}) (c_{k\alpha} c_{l\gamma} + c_{k\gamma} c_{l\alpha}) \right] \times (2.5F_2^{dd'} + 22.5F_4^{dd'}) \quad *** \end{aligned}$$

\*  $\alpha \in p \quad \gamma \in p$   
 \*\*  $\alpha \in p \quad \gamma \in d \quad \alpha, \gamma, s \in A$   
 \*\*\*  $\alpha \in d \quad \gamma \in d$

(14)

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