

The Importance of Correlation Effects in the Calculation of the Valence Ionization Energies of Bis(π -allyl)nickel

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The calculation of the valence ionization energies of bis(π -allyl)nickel by an *ab initio* Green's function method yields an interpretation of the photoelectron spectrum of this molecule in good agreement with experiment, in contrast to that given by Δ S.C.F. calculations.

Although Koopmans' theorem has often proved extremely useful in assigning molecular photoelectron (P.E.) spectra of organic molecules,¹ the situation is more complicated for transition metal complexes,^{2,3} since this approximation is often totally inadequate owing to the considerably larger orbital relaxation which may arise from metal, compared to ligand, ionization. For a range of transition metal complexes, Δ S.C.F. calculations, which include such differential orbital relaxation, have been extremely useful in assignment of their P.E. spectra. However, for one of the simplest, and most studied^{4,5} transition metal sandwich complexes, bis(π -allyl)nickel, there is evidence that Δ S.C.F. calculations do not provide a correct assignment of the P.E. spectrum. For this reason we here describe *ab initio* calculations of the valence ionization energies (I.E.) of this molecule by a Green's function technique which includes both relaxation and correlation effects and allows for the calculation of all the states observed in the low-energy P.E. spectrum. In this method the ionization energies appear as the poles of the one-particle Green's function and can thus be calculated directly, instead of as the difference of the energies resulting from two independent calculations for the neutral ground state and for the various ionic states, as in Δ S.C.F. methods. This approach has been successful in yielding ionization energies accurate to ~ 0.5 eV for a range of organic molecules, and accurate to

~ 0.2 eV for smaller molecules for which extended basis sets can be used.

The calculations were carried out using contracted Gaussian functions. For carbon, the (9s5p) basis of Huzinaga⁶ was contracted to (3s2p).⁷ For hydrogen, the (4s)⁷ primitive basis, contracted to (2s) with a scale factor of 1.2, was used. The nickel basis was constructed from the (12s6p4d) functions of Roos *et al.*⁸ The two most diffuse s functions were replaced by those having exponents of 0.32 and 0.08, and additional p and d functions with exponents 0.32 and 0.1481⁹ respectively, were added. These functions were contracted (6s3p2d) giving a close to double zeta representation in the valence region. Bis(π -allyl)nickel was taken to have a staggered arrangement of the allyl moieties (C_{2h} symmetry), with experimental bond lengths taken from that of bis(π -methylallyl)nickel,¹⁰ the allyl groups being taken to be planar and to have idealized bond angles of 120°.

Restricted Hartree-Fock calculations were carried out on the 1A_g ground state of the neutral molecule, and lowest 2A_g , 2B_g , 2A_u , and 2B_u states of the ion to yield the Koopmans' theorem and Δ S.C.F. I.E.s shown in Table 1. To take account of both orbital relaxation and correlation effects, the valence I.E.s were also calculated by a Green's function method. In the case of the molecule studied herein, bis(π -allyl)nickel, where there is strong relaxation for the orbitals of a_g and b_g

Table 1. Ionization energies (eV) of the valence orbitals of bis(π -allyl)nickel.

Orbital	Character	Ionization energy			
		Koopmans' theorem	Δ S.C.F.	Extended 2ph-TDA	Expt. ^a
7a _u	$\pi(L)$	7.5	6.8	6.4	7.7(1)
6b _g	3d _{xz} ; $\pi(L)$	9.0	5.6	7.7	8.1(2)
11b _u	$\pi(L)$	11.8	11.0	10.3	10.3(5)
13a _g	3d _{xy} ; $\pi(L)$	11.7	5.5	7.6	8.1(2)
12a _g	$\sigma(L)$	14.0		13.5	12.7(7)
5b _g	3d _{yz}	14.0		8.5	8.5(3)
11a _g	3d _{x²-y²}	14.2		8.2	
6a _u	$\sigma(L)$	14.6		13.3	12.7(7)
10b _u	$\sigma(L)$	14.6		13.4	
4b _g	$\sigma(L)$	15.0		13.7	9.4(4)
10a _g	3d _{z²}	15.3		8.8	
9a _g	3d _{xy} ; $\pi(L)$	16.4		11.5	11.5(6)
5a _u	$\sigma(L)$	16.5		14.9	14.2(8)
3b _g	$\sigma(L)$	17.3		15.1	
9b _u	$\sigma(L)$	18.0		16.2	15.6(9)
8a _g	$\sigma(L)$	19.0		16.5	

^a The band number is given in parentheses.

symmetry^{4,5} the extended two-particle-hole Tamm-Dancoff method¹¹⁻¹³ (extended 2ph-TDA) was used. In this calculation all the filled valence orbitals, including the carbon 2s and 20 virtual orbitals, were employed. The valence I.E.s thus calculated are given in Table 1.

The P.E. spectrum of bis(π -allyl)nickel shows nine bands below 17 eV, and has been assigned as follows on the basis of a comparison of the P.E. spectra of a series of nickel, palladium, and platinum bis(π -allyl) derivatives.¹⁴ Bands (1) and (5) arise from the $7a_u$ and $11b_u$ ligand π M.O.s, bands (2) and (3) from the mainly metal $9a_g$, $10a_g$, $11a_g$, and $5b_g$ M.O.s, and bands (4) and (6) from the $6b_g$ and $13a_g$ M.O.s respectively having significant ligand π -character. Bands (7)–(9) are assigned to orbitals of allyl σ -character. The Δ S.C.F. results shown in Table 1 conflict with this assignment giving the first two ionic states, which are closely spaced, to be 2A_g and 2B_g , whereas the P.E. spectrum indicates the ground ionic state to be 2A_u arising from ligand ionization. However, when both correlation and relaxation effects are included in the Green's function calculation close agreement between the experimental and theoretical assignment results (Table 1). In particular the ground ionic state is now predicted to be 2A_u . Any differences between the experimental and theoretical assignments arise from interchanging orbitals of similar character such as $9a_g$ and $13a_g$, where any distinction between the resulting states must be somewhat arbitrary.

The results presented here are the first to interpret the full P.E. spectrum of a transition metal complex, including both correlation and relaxation effects by a Green's function technique, and show the importance of correlation effects for a correct assignment of the spectrum.

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