Photoelectron Spectrum of Bis-(π-allyl)nickel

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Summary The apparent discrepancy between the photoelectron spectrum of bis-(π-allyl)nickel and the results of a previous calculation is removed by taking into account the electronic relaxation upon ionization.

WE reported previously the results of an *ab initio* computation of the electronic wavefunction for bis-(π-allyl)-nickel.[1] The photoelectron spectrum of this compound has been discussed recently[2] and it was claimed that the conclusions derived from the spectrum are not consistent with the results of our calculation, namely that the highest-lying orbitals are ligand orbitals rather than metal 3*d*-orbitals. It was stated further that the only possible ordering of the orbital types is: metal 3*d*-type > ligand π-type > ligand σ-type. Our purpose is to emphasize that (i) the distinction between metal *d*-type orbitals, ligand π-type orbitals, and ligand σ-type orbitals is less clear-cut in bis-(π-allyl)nickel than has been assumed;[2] (ii) there is no relationship between the sequence of ionization potentials and the sequence of molecular orbital energies, contrary to the assumption in ref. 2, as the result of a breakdown of Koopmans' theorem.[3]

We allowed for electronic relaxation by performing an independent SCF calculation within the Roothaan restricted Hartree–Fock formalism for several possible electronic states of the $Ni(C_3H_5)_2^+$ ion.† Stationary values of the energy were achieved for all the mentioned states of the ion without any special precaution (although in other cases we observed a tendency of the SCF iterative procedure towards the state of lower energy within each symmetry species[4]) and it was found that each molecular wavefunction is approximately orthogonal to the wavefunction of the lower states.

The following conclusions emerge from the results reported in the Table: the near-degeneracy of the first three experimental I.P.'s (at 7·85, 8·17, and 8·59 eV) is well accounted for by our calculation (computed I.P.'s at 7·92, 8·03, 8·21, and 8·52 eV). The next I.P. is predicted at 8·92 eV (experimental 9·48 eV). Although this agreement may be partly fortuitous, it gives some credit to our calculation. It turns out that Koopmans' theorem breaks down for this molecule. This may be seen from the fact that the sequence of computed I.P.'s does not parallel the sequence of orbital energies. This is exemplified for the $3b_g$, $9a_g$, $10a_g$, and $11a_g$ orbitals which have relatively high orbital energies (0·60—0·69 a.u. in absolute values) and low I.P.'s (0·29—0·31 a.u.) as a consequence of electronic relaxation. These are mixed-metal 3*d*-ligand orbitals for the neutral molecule. As mentioned above, this points to the lack of any clear-cut distinction between metal 3*d*-type and ligand-type orbitals for the ground state of the neutral molecule (this is indicative of some covalency in the complex[2]). Upon ionization, these orbitals undergo a marked electronic rearrangement and become nearly pure metal 3*d*-orbitals. Only in this respect may one say that the lowest I.P.'s are associated with metal 3*d*-type orbitals. This is not contradictory with the fact that for the neutral molecule orbitals which are mostly metal 3*d*-orbitals have lower orbital energies than σ- or π-allyl orbitals. Koopmans' theorem is approximately valid for M.O.'s which are

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† The results reported here differ from the ones in ref. 1 by the use of only one contracted function to describe each of the 4*s* and 4*p* orbitals on the Ni atom and by the use of a 9*s*, 5*p*, 4*d* atomic set for the Ni atom instead of a 10*s*, 6*p*, 3*d*.

TABLE. *Orbital energies, I.P.'s, and population analysis for bis-(π-allyl)nickel and its ions*

Orbital	Orbital energy[a] (in a.u.)	Computed I.P.[b]		Composition of the M.O. in $Ni(C_3H_5)_2$[c]			Electronic state of $Ni(C_3H_5)^+$	Composition of the open-shell M.O. in $Ni(C_3H_5)_2^+$[c]		
		in a.u.	in eV	Ni 3*d*	Ligand π	Ligand σ		Ni 3*d*	Ligand π	Ligand σ
$7a_u$	−0·350	0·328	8·92	—	94	6	^2A_u	—	94	6
$6b_g$	−0·407	—	—	34	56	10	—	—	—	—
$13a_g$	−0·509	—	—	27	53	20	—	—	—	—
$11b_u$	−0·521	0·500	13·6	—	93	7	^2B_u	—	94	6
$12a_g$	−0·579	—	—	8	26	66	—	—	—	—
$5b_g$	−0·587	—	—	42	1	57	—	—	—	—
$6a_u$	−0·587	0·577	15·7	—	—	100	^2A_u	—	—	100
$10b_u$	−0·590	0·581	15·8	—	3	97	^2B_u	—	4	96
$11a_g$	−0·601	0·302	8·21	83	4	13	^2A_g	98	—	2
$4b_g$	−0·607	—	—	25	—	75	—	—	—	—
$10a_g$	−0·643	0·313	8·52	69	2	29	^2A_g	99	1	—
$5a_u$	−0·657	—	—	—	—	100	—	—	—	—
$9a_g$	−0·671	0·291	7·92	62	12	26	^2A_g	96	2	2
$3b_g$	−0·692	0·295	8·03	38	—	62	^2B_g	99	—	1
$9b_u$	−0·709	—	—	—	—	100	—	—	—	—
$8a_g$	−0·762	—	—	38	—	62	—	—	—	—

[a] From the SCF calculation for the ground state of the neutral molecule. [b] Difference of the total energy for the molecule and the ion. [c] In percentage.

nearly pure ligand orbitals, *i.e.*, the I.P.'s computed as a difference of total energies are not very different from the corresponding orbital energies (M.O.'s $7a_u$ and $11b_u$ which are π-allyl orbitals and M.O.'s $6a_u$ and $10b_u$ which are σ-allyl orbitals). Population analysis for these orbitals shows little, if any, electronic relaxation upon ionization.

It is now apparent that conclusions from the photoelectron spectrum are no longer in opposition to the results of our calculations. Currently there is interest in the photoelectron spectroscopy of organometallics like bis-(π-allyl)nickel[2,5] and the metallocenes.[6] Owing to the failure of Koopmans' theorem for these molecules,[7] it is not possible to draw any conclusion from these photoelectron spectra regarding the sequence of M.O.'s in the ground state of the neutral molecule.

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