Ab Initio Calculation of the Bonding in Nickel Tetracarbonyl

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Summary The results of an all-electron ab initio SCF–MO calculation of the electronic structure of $Ni(CO)_4$ are described.

ALTHOUGH the bonding in transition metal carbonyls has been the subject of a number of semi-empirical molecular orbital calculations,[1] no consistent picture of the bonding and charge distribution in these molecules has emerged. For this reason we here describe the results of an all-electron ab initio SCF–MO calculation of the electronic structure of $Ni(CO)_4$.

The calculation was performed in a basis of contracted Gaussian type functions (GTFs). For all core orbitals, carbon and oxygen 2s and nickel 4s orbitals, Slater type orbitals (STOs) with the best atom exponents of Clementi and Raimondi[2] were fitted using three GTFs per STO.[3] Nickel 3d STOs with exponents of 5·75 and 2·0, and 4p STOs with an exponent of 1·17 were taken,[4] fitted by three GTFs per STO. Carbon and oxygen 2p atomic orbitals (AOs) were taken from Stewart, each AO being expanded in 4 GTFs.[5] The calculation was carried out on the Atlas Computers of Manchester University and the S.R.C. Computer Laboratory using the ATMOL system of programs.

The results of the calculation, together with those for CO in the basis described here, are summarized in the Table. The orbital populations obtained by a Mulliken analysis show that the majority of the metal valence electrons occupy the 3d orbitals, the diffuse orbitals having rather larger populations than the more contracted ones. The metal 4s orbital has a negligible population and that of the 4p orbitals is quite small. These populations result in a small positive charge ($\sim$0·5) on the nickel atom. The change in electron distribution of the CO ligand on co-ordination occurs predominantly at the carbon atom, the population of the oxygen orbitals being essentially unaltered. The population of the carbon 2s orbital decreases by less than 0·1e whilst that of the 2p orbitals increases by more than 0·2e, resulting in a decrease in the formal positive charge on the carbon atom by $\sim$0·15. The concepts of σ-donation and π-back bonding may be qualitatively discussed in terms of these population changes. The decrease in carbon 2s population reflects the σ-donation from the 5σ orbital of CO, having a carbon 2s component of 51%, and the increase in carbon 2p population reflects the π-back bonding into the 2π orbital, empty in CO, having a carbon 2p component of 74%.

The energies, symmetry designations, and atomic components of the valence molecular orbitals of $Ni(CO)_4$ are also shown in the Table. The highest filled orbitals are the $9t_2$ and $2e$, of predominantly nickel 3d character. The

TABLE

Electronic structure of $Ni(CO)_4$

Orbital populations

		$Ni(CO)_4$	CO
Ni	4s	−0·0345	
	4p	0·3517	
	3d(ζ = 5·75)	2·4897 (t_2)	
		1·6826 (e)	
	(ζ = 2·0)	2·9743 (t_2)	
		2·0836 (e)	
C	2s	1·5568	1·6311
	2p	2·2124	1·9994
O	2s	1·8345	1·8393
	2p	4·5188	4·5342

Valence molecular orbitals

Symmetry	Orbital energy (a.u.)	Ni 4s	Ni 4p	3d	C 2s	C 2p	O 2s	O 2p
$9t_2$	−0·42924		9	65	11	7		8
$2e$	−0·49627			90		1		9
$8t_2$	−0·67919		2	21	23	29	3	21
$1t_1$	−0·68648					27		73
$1e$	−0·69703			4		31		66
$7t_2$	−0·69714		−2	2		32		68
$8a_1$	−0·72038	1		16	37		8	39
$6t_2$	−0·82956		−2	3	29	1	23	46
$7a_1$	−0·85479	−3		46	9		18	29

Overlap populations

		$Ni(CO)_4$	CO
Ni–C	4s–2s	−0·020	
	4s–2p	−0·003	
	4p–2s	0·127	
	4p–2p	−0·020	
	3d(t_2)–2s	−0·044	
	3d(t_2)–2p	0·030	
	3d(e)–2p	0·046	
C–O	2s–2s	−0·149	−0·177
	2s–2p	0·091	−0·050
	2p–2s	0·120	0·145
	2p–2p	1·127	1·138

orbital energies of 11·7 and 13·5 eV may be compared with the experimental vertical ionization potentials of 8·9 and 9·8 eV.[6] Our calculated order of these metal orbitals is in agreement with the degeneracies deduced from the photoelectron spectrum.[6] Each of these orbitals has nearly

equal amounts of the two nickel $3d$ orbitals in the basis, although, as might be expected, the $2e$ orbitals have a greater amount of the more diffuse component. The remaining valence orbitals are composed predominantly of ligand orbitals. The overlap populations (Table) show that although the population of the metal $4p$ orbitals is small, the contribution to the metal–carbon bond overlap population is larger than that of the metal $3d$ orbitals, the diffuse components of the latter contributing more than the contracted ones to the nickel–carbon bonds.

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