

Electronic Structure of the Nickel Tetracyanonickelate $\text{Ni}(\text{CN})_4^{2-}$ and Nickel Carbonyl $\text{Ni}(\text{CO})_4$. An *ab-initio* LCAO–MO–SCF Calculation

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The electronic structure of the $\text{Ni}(\text{CN})_4^{2-}$ ion in its ground and first excited states and of the $\text{Ni}(\text{CO})_4$ molecule in its ground state have been investigated through an LCAO-MO-SCF calculation with a gaussian basis set (12, 8, 5/8, 4) contracted to a [5, 4, 2/3, 2 (C)/2, 1 (N or O)] set. The sequence of ionization potentials (I.P.) computed for $\text{Ni}(\text{CO})_4$ from the Koopmans' theorem is in agreement with previous assignments for the experimental spectrum. On the contrary, Koopmans' theorem turns out to be not valid for the $\text{Ni}(\text{CN})_4^{2-}$ ion, that is the sequence of I.P. computed as the difference of the total energy for this ion and the mononegative ion is different from the sequence of orbital energies for $\text{Ni}(\text{CN})_4^{2-}$. The computed I.P. turn to be rather sensitive to the electrostatic potential of the crystal represented through a set of point charges. The Ni atom in $\text{Ni}(\text{CO})_4$ bears a small positive charge of $0.24e$, as a result of π back-bonding to the ligands. Charge transfer upon coordination and the nature of the ligand-metal bonding is compared in these two complexes through the results of a population analysis and a description in terms of localized orbitals. Separate SCF calculations have been performed for the lowest excited states of $\text{Ni}(\text{CN})_4^{2-}$. Although $\pi \rightarrow \pi^*$ transitions would be expected as the lowest ones on the basis of orbital energy values, the lowest computed transitions correspond to $d \rightarrow d$ excitations, in agreement with previous assignments for the experimental spectrum. This is traced to the role of Coulomb and exchange terms in the computed transition energies together with the importance of electronic relaxation upon excitation.

Mit Hilfe einer LCAO-MO-SCF Rechnung unter Verwendung eines Gauß-Basisatzes (12, 8, 5/8, 4), der zu einem [5, 4, 2/3, 2 (C)/2, 1 (N oder O)] Satz kontrahiert wurde, wurden Untersuchungen über die Elektronenstruktur des $[\text{Ni}(\text{CN})_4]^{2-}$ -Ions im Grundzustand und in den ersten angeregten Zuständen und des $\text{Ni}(\text{CO})_4$ -Moleküls im Grundzustand durchgeführt. Die mit dem Koopmanschen Theorem berechnete Reihenfolge der Ionisationspotentiale des $\text{Ni}(\text{CO})_4$ stimmt mit früheren Zuordnungen zum experimentell erhaltenen Spektrum überein.

Für $[\text{Ni}(\text{CN})_4]^{2-}$ gilt dieses Theorem dagegen nicht, das heißt, die Reihenfolge der I.P., die als Differenz der Gesamtenergie dieses Ions und des einfach negativen Ions bestimmt werden, unterscheidet sich von der Reihenfolge der Orbitalenergien von $[\text{Ni}(\text{CN})_4]^{2-}$.

Die berechneten I.P. sind in hohem Maße von dem elektrostatischen Potential des Kristalls, der durch einen Satz von Punktladungen dargestellt wird, abhängig. Aufgrund der π -Rückbindung zu den Liganden trägt das Nickelatom in $\text{Ni}(\text{CO})_4$ eine geringe positive Ladung ($0,24e$). "Charge Transfer" durch Koordination und Natur der Ligand-Metall-Bindung werden in beiden Komplexen anhand der Resultate einer Populationsanalyse und mit Hilfe von lokalisierten Orbitalen verglichen. Für den niedrigsten angeregten Zustand von $[\text{Ni}(\text{CN})_4]^{2-}$ wurden gesonderte SCF Rechnungen durchgeführt. Obwohl aufgrund der Orbitalenergien $\pi \rightarrow \pi^*$ Übergänge die niedrigste Energie haben sollten, ergeben die Rechnungen in Übereinstimmung mit dem Experiment $d \rightarrow d$ Anregungen. Diese Tatsache wird auf Coulomb- und Austauschsterme in den berechneten Übergangsenergien und den Einfluß der Elektronenrelaxation bei der Anregung zurückgeführt.

La structure électronique de l'ion $\text{Ni}(\text{CN})_4^{2-}$ dans l'état fondamental et dans les premiers états excités ainsi que celle de la molécule $\text{Ni}(\text{CO})_4$ dans l'état fondamental ont été étudiées par la méthode LCAO-MO-SCF avec une base de fonctions gaussiennes (12, 8, 5/8, 4) contractée en [5, 4, 2/3, 2(C)/2, 1 (N ou O)]. La séquence des potentiels d'ionisation calculée pour $\text{Ni}(\text{CO})_4$ d'après le théorème de Koopmans est en accord avec celle proposée antérieurement pour l'interprétation du spectre expérimental. Par contre le théorème de Koopmans ne paraît pas valable pour l'ion $\text{Ni}(\text{CN})_4^{2-}$. En effet, la séquence des potentiels d'ionisation calculés comme la différence des énergies de cet ion et de l'ion $\text{Ni}(\text{CN})_4^-$ est différente de la séquence des énergies d'orbitale pour $\text{Ni}(\text{CN})_4^{2-}$. Les valeurs calculées pour les potentiels d'ionisation de cet ion sont très sensibles à l'effet du potentiel électrostatique du cristal, représenté par un ensemble de charges ponctuelles. L'atome de Ni dans $\text{Ni}(\text{CO})_4$ porte une charge positive de $0,24e$, conséquence du transfert en retour π vers les ligands. L'importance du transfert de charge au cours de la coordination et la nature de la liaison métal-ligand sont comparées dans ces deux complexes à partir des résultats de l'analyse de population et d'une description en termes d'orbitales localisées. Les états excités les plus bas de $\text{Ni}(\text{CN})_4^{2-}$ ont donné lieu à des calculs SCF distincts. Bien que les plus hautes orbitales occupées et les plus basses orbitales virtuelles dans l'état fondamental de $\text{Ni}(\text{CN})_4^{2-}$ soient des orbitales π et π^* des ligands, les transitions calculées les plus basses correspondent aux excitations $d \rightarrow d$. Ceci est lié au rôle joué par les termes coulombiens et d'échange dans les énergies d'excitation ainsi qu'à l'importance de la relaxation électronique au cours de l'excitation.

Introduction

Transition metal complexes may be classified into σ complexes and π complexes [1]. In the σ complexes, coordination of the ligand to the metal atom is insured through a σ lone pair of the ligand group¹. In the π complexes, coordination is achieved through the π electrons of the ligand, like in the ferrocene molecule or in the silver-ethylene complex. Ligands which coordinate through their σ electrons may be further classified according to their acceptor ability with respect to donation from the metal atom (or backbonding). This property is associated with the presence of empty π orbitals (which are sometimes π^* antibonding orbitals) on the ligand. For instance, while the chlorine ion Cl^- has no acceptor ability as long as one does not introduce $3d$ and higher orbitals of the chlorine atom, the cyanide and carbonyl ligands CN^- and CO have empty π^* orbitals and are susceptible of π back-bonding from the metal atom.

We present here a study of the coordination in the two complexes nickel tetracyanonickelate $\text{Ni}(\text{CN})_4^{2-}$ and nickel carbonyl $\text{Ni}(\text{CO})_4$. Studies of the coordination of the ligand Cl^- in the tetrachlorocuprate complex CuCl_4^{2-} and of π coordination in the ferrocene and nickel bis-(π -allyl) molecules will be reported later [2]. The choice of the $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$ complexes is based on a number of reasons. Both the cyanide ion and the carbonyl molecule are susceptible of π back-bonding, however to a different extent. The cyanide ion is considered as a good σ electron donor and a poor π electron acceptor while the carbonyl ligand should be a poorer σ donor and a better π acceptor [3]. Both complexes are representative of two important types of structures, corresponding respectively to the square-planar arrangement (D_{4h} symmetry) and to the tetrahedral arrangement (T_d symmetry). Both have been the subject of a fairly extensive experimental work in relation with the electronic structure in the

¹ We assume that the ligand is a linear or planar molecule, hence the possible classification into σ and π orbitals; however it is usually extended to molecules of any geometry like for instance the phosphines PR_3 .

ground and excited states. The photoelectron spectrum has been reported for both complexes [4–6]. The experimental absorption spectrum of the $\text{Ni}(\text{CN})_4^{2-}$ ion has been investigated by many authors [7–13].

Many theoretical studies, either qualitative or semi-empirical, have been reported previously for these two complexes. Qualitative energy level schemes have been put forward for the $\text{Ni}(\text{CN})_4^{2-}$ ion mostly in connection with the interpretation of the electronic spectrum. Although they may differ in small details like the relative ordering of the filled $3d$ orbitals, most of these schemes rely on the assumption that each molecular orbital of the complex may be correlated with a metal $3d$ orbital or with a ligand σ or π orbital and have agreed on the following sequence of energy levels in the complex [9, 13, 14]

$$\pi(\text{CN}^-) < \sigma(\text{CN}^-) < 3d_{z^2}, 3d_{xz}, 3d_{yz}, 3d_{xy} \ll 3d_{x^2-y^2} < \pi^*(\text{CN}^-).$$

However, on the basis of an extended Hückel calculation, Piepho *et al.* have suggested that the $3d_{x^2-y^2}$ level lie above some $\pi^*(\text{CN}^-)$ levels [13]. Sometimes ago, one of us (A.V.), on the basis of a Wolsberg-Helmholz type calculation with partial inclusion of the Coulomb repulsion, concluded that the π levels of the cyanide ligands should be above the $3d$ levels in the complex [15].

Semi-empirical calculations have been reported for the $\text{Ni}(\text{CO})_4$ complex [16–17]. Nieuwpoort performed a non-empirical calculation for this molecule but had to rely on various approximations for the evaluation of the three- and four-center integrals [18]. Most calculations have agreed that the highest occupied orbitals are the $2e$ and $9t_2$ orbitals which correspond to the splitting of the metal $3d$ orbitals under the tetrahedral ligand field. However Nieuwpoort calculation gives the highest filled orbital to be $2e$ followed by $9t_2$, whilst this order is reversed in other calculations. Both calculations by Nieuwpoort [18] and Hillier [17] give a formal negative charge on the Ni atom close to one electron. When this work was completed [19], Hillier has reported a non-empirical calculation with a basis of contracted Gaussian type functions [20]. The order of the highest filled orbitals is $9t_2$ followed by $2e$ and the population analysis now indicates a small positive charge on the nickel atom.

Computations

The present calculations are of the SCF-LCAO-MO type using a basis set of Gaussian functions. For the Ni atom, a $12s$, $8p$, $5d$ Gaussian basis set is built by starting from a $12s$, $6p$, $4d$ set with its exponents optimized for the ground state of Ni0 [21]. The lowest two exponents for the s functions (which may be considered as describing the $4s$ atomic orbital) are set equal to 0.32 and 0.08 (the lowest two exponents optimized for the atom correspond to a $4s$ atomic orbital which is too diffuse for the molecular wavefunction). This basis set is incremented with two p functions of exponents 0.32 and 0.08 in order to describe the $4p$ atomic orbital and one additional $3d$ function of exponent 0.2 (this allows the atomic $3d$ function to expand upon formation of the complex). A $8s$, $4p$ basis set was used for the atoms of the ligands [22]. These atomic sets are contracted to a $5s$, $4p$, $2d$ set for the Ni atom, a $3s$, $2p$ set for the C atom and a $2s$, $1p$ set for

the N and O atoms. Within some limitations, emphasis has been put on a better description of the valence shells. For this reason, the valence shells $3d$, $4s$ and $4p$ of Ni, $2s$ and $2p$ of C are described by two contracted functions, while only one contracted function is used for the inner shells. However, due to some limitations on the total number of contracted functions, only one contracted function has been used for each orbital of the N and O atoms. Although this may introduce a slight lack of balance between the two atoms of the ligands, this should not alter the description of the ligand-metal bond.

The interatomic distances were taken as

$$\text{Ni} - \text{C} = 1.86 \text{ \AA} \quad \text{C} - \text{N} = 1.15 \text{ \AA} \quad \text{in Ni(CN)}_4^{2-} (D_{4h}) [23],$$

$$\text{Ni} - \text{C} = 1.84 \text{ \AA} \quad \text{C} - \text{O} = 1.15 \text{ \AA} \quad \text{in Ni(CO)}_4 (T_d) [24].$$

The choice of the coordinate axis and the numbering of the atoms are the ones given in Fig. 1 and 2.

Open-shell calculations for the ionized and excited states of the Ni(CN)_4^{2-} ion have been performed in the Restricted Hartree-Fock formalism as given by Roothaan [25]. The corresponding vector coupling coefficients for the various states may be found in Ref. [26].

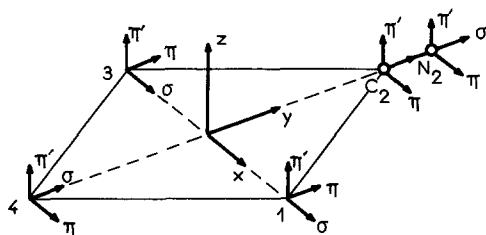


Fig. 1. Choice of the coordinate axis and numbering of the atoms for Ni(CN)_4^{2-}

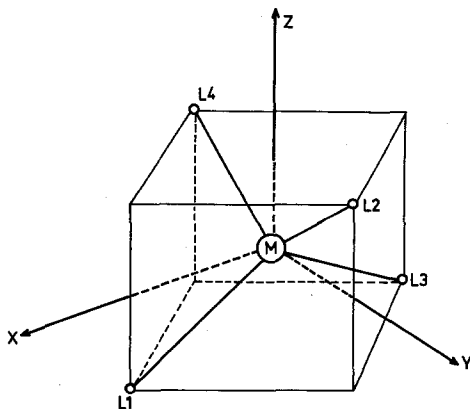


Fig. 2. Choice of the coordinate axis for Ni(CO)_4

Table 1. Total energy (in a.u.)

	This calculation	Previous calculation
$\text{Ni}^{2+} (3d^8 \ ^3F)$	-1502.975	-1506.028 ^{a, b}
$\text{Ni}^0 (3d^{10} \ ^1S)$	-1503.614	
CN^-	- 92.138	- 92.323 ^{a, c}
CO	- 112.550	- 112.789 ^{a, d}
$\text{Ni}(\text{CN})_4^{2-}$	-1872.496	
$\text{Ni}(\text{CO})_4$	-1953.949	

^a Value close to the Hartree-Fock limit.

^b Ref. [27].

^c Ref. [28].

^d Ref. [29].

Results and Discussion

The Ground State of $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$

Preliminary results for the ground state of the $\text{Ni}(\text{CN})_4^{2-}$ ion have been previously reported [19] and will not be repeated here.

Total Energy and Binding Energy

The total energy computed is reported in Table 1 together with the values for the metal atom, the ion and the ligands. The energy values for the ligands CN^- and CO may be compared with previous estimates of -92.323 and -112.789 a.u., which are probably close to the Hartree-Fock limit.

A binding energy of 608 kcal/mole is computed for the $\text{Ni}(\text{CN})_4^{2-}$ ion with respect to the ion Ni^{2+} and the ligands CN^- . However it should be realized that most of this computed binding energy corresponds to the electrostatic energy associated with the ion-ion interaction. For this reason it is not possible to compare the computed value with the experimental estimate of -43 kcal/mole for solvated ions [30].

For the nickelcarbonyl molecule, the computed binding energy of 86 kcal/mole may be compared to the experimental value of 140 kcal/mole in the gaz phase [31].

Orbital Energies and Ionization Potentials

The sequence of orbital energies for the $\text{Ni}(\text{CN})_4^{2-}$ ion has already been reported [19]. One important result was that this sequence may be represented as

$$3d \sim \sigma(\text{CN}^-) < \pi(\text{CN}^-)$$

and is different from the one which has been commonly assumed

$$\pi(\text{CN}^-) < \sigma(\text{CN}^-) < 3d.$$

According to Koopmans' theorem [32], the ionization potential associated with the removal of one electron from a given orbital of a closed-shell system is

Table 2. Orbital energies and overlap populations for the ground state of Ni(CO)₄

Orbital	Orbital energy (in a.u.) ^a	Overlap population		Nature
		Ni-C	C-O	
9t ₂	- 0.395	-0.061	-0.073	3d _{x²-y², xz, yz}
2e	- 0.471	0.007	-0.004	3d _{xy} , 3d _{z²}
8t ₂	- 0.644	0.225	-0.108	5σ
1t ₁	- 0.653	—	0.294	π
7t ₂	- 0.662	0.007	0.292	π
1e	- 0.665	0.009	0.196	π
8a ₁	- 0.693	0.019	-0.025	5σ
6t ₂	- 0.793	-0.043	0.234	4σ
7a ₁	- 0.809	-0.117	0.062	4σ
6a ₁	- 1.530	0.001	0.124	3σ
5t ₂	- 1.530	0.004	0.372	3σ
4t ₂	- 3.103	0.017	—	3p _{x, y, z}
5a ₁	- 4.482	-0.017	—	3s
4a ₁	- 11.419 (- 11.396)	—	—	2σ
3t ₂	- 11.419 (- 11.396)	—	—	2σ
3a ₁	- 20.657 (- 20.632)	—	—	1σ
2t ₂	- 20.657 (- 20.632)	—	—	1σ
1t ₂	- 32.615 (- 32.288)	—	—	2p _{x, y, z}
2a ₁	- 36.802 (- 36.472)	—	—	2s
1a ₁	- 304.746 (- 304.438)	—	—	1s

^a The values between parenthesis refer to the free metal or to the ligand.

merely the opposite of the corresponding orbital energy. Before we discuss the validity of Koopmans' theorem for the Ni(CN)₄²⁻ ion and the influence of the crystal lattice upon the computed ionization potentials, we will first discuss the orbital energies associated with the molecular orbitals of Ni(CO)₄.

The orbital energies of Ni(CO)₄ are given in Table 2. The sequence of the highest orbital energies

$$8a_1(\sigma_L) < 1e(\pi_L) \sim 7t_2(\pi_L) \sim 1t_1(\pi_L) \sim 8t_2(\sigma_L) < 2e(d_M) < 9t_2(d_M)$$

(with the subscripts *M* and *L* standing for metal and ligand) is similar to the one reported by Hillier [20] except for an interversion of the 1e and 7t₂ levels which are nearly degenerate. The experimental ionization potentials are compared in Table 3 with the values computed according to Koopmans' theorem. Our calculation supports the assignment proposed previously for the first three ionization potentials (I.P.) corresponding to the 9t₂, 2e and 8t₂ orbitals. However a few words of caution appear necessary. Five orbitals, from 8t₂ to 8a₁, have their orbital energy in a range of 0.05 a.u. (1.4 eV). That the third experimental I.P. corresponds to the 8t₂ orbital seems to be supported by the photoelectron spectrum of Ni(PF₃)₄ [33]. Through a comparison of the I.P. for this complex and the free ligand, Hillier has established that the I.P. associated with an orbital which is chiefly a ligand lone pair (then corresponding to the 8t₂ orbital of Ni(CO)₄) is lower than the I.P. for molecular orbitals which are mostly fluorine 2p orbitals (then corresponding to the 1t₁, 7t₂ and 1e orbitals of Ni(CO)₄). However, any assignment beyond the 8t₂ orbital based on Koop-

Table 3. Computed and experimental ionization potentials in $\text{Ni}(\text{CO})_4$ (in eV)

This calculation		Previous calculation ^a		Experimental ^b	
$-\varepsilon_i$	Assignment	$-\varepsilon_i$	Assignment		Assignment
10.75	$9t_2$	11.67	$9t_2$	8.8	t_2
12.82	$2e$	13.50	$2e$	9.7	e
17.52	$8t_2$	18.47	$8t_2$	14.8	t_2
17.77–18.09	$1t_1, 1e, 7t_2$	18.67–18.96	$1t_1, 1e, 7t_2$		
18.86	$8a_1$	19.59	$8a_1$	18.2	a_1

^a Ref. [2].

^b Ref. [5] and [6].

mans' theorem may be considered as dubious given the approximations involved: neglect of the electronic relaxation upon ionization and of the change in correlation energy between the molecule and the ion. We will discuss in detail (cf. below) the importance of the electronic relaxation during ionization for the $\text{Ni}(\text{CN})_4^{2-}$ ion. These approximations, together with the limitation in the basis set used, will also explain the difference between the computed and experimental values of the I.P., which is never less than 2 eV. The basis set seems to play a major role with this respect, since there is a significant improvement, of about 1 eV, between our computed values and the ones of Ref. [20].

Some information may be derived from the change in orbital energy when going from the metal and the ligands to the complex. The corresponding values for the metal and the ligands are also given in Table 2. For the inner-shells of the Ni atom, the orbital energies are lowered by 0.3 a.u. upon complexation. This stabilization is indicative of an electron transfer from the metal to the ligand (cf. the population analysis below). One would then expect an increase of the electron density on the C atom and a corresponding destabilization of the $1s$ orbital. Unexpectedly one finds a very slight stabilization of these orbitals (by 0.023 a.u. = 0.62 eV), which we have been unable to explain. Barber *et al.* have reported a computed chemical shift of 0.3 eV for the carbon and 0.4 eV for the oxygen $1s$ orbitals in qualitative agreement with an experimental destabilization of respectively 2.2 and 1.4 eV compared to free CO [34]. Slightly different experimental values, corresponding to a shift of respectively 1.7 and 0.3 eV to lower binding energy, have been reported by Clark and Adams [35].

The good agreement between the sequence of orbital energies and the experimental I.P. for $\text{Ni}(\text{CO})_4$ indicates that Koopmans' theorem is probably valid for this molecule. This may not be true for the $\text{Ni}(\text{CN})_4^{2-}$ ion. A somewhat similar situation has been encountered for the ferrocene molecule, with the highest occupied orbitals being π ligand orbitals rather than metal $3d$ orbitals [36]. However, it has been shown that Koopmans' theorem is not valid for this molecule and that the lowest ionization potentials computed as the difference of the energy for the molecule and the ion are associated with orbitals which have a $3d$ orbital character, in good agreement with the experimental evidence [36]. For this reason we have decided to investigate further

the problem of the ionization potentials of the ion $\text{Ni}(\text{CN})_4^{2-}$ by computing separately the energy of the mononegative species $\text{Ni}(\text{CN})_4^-$.

Calculations have been carried out for the electronic states of $\text{Ni}(\text{CN})_4^-$ corresponding to removal of one electron from the orbitals $8e_u(\pi_L)$, $1a_{2g}(\pi_L)$, $9a_{1g}(3d_{z^2})$, $1e_g(3d_{xz}, 3d_{yz})$ and $1b_{2g}(3d_{xy})$ of $\text{Ni}(\text{CN})_4^{2-}$. The geometry for $\text{Ni}(\text{CN})_4^-$ in its various electronic states has been kept the same as the one used for $\text{Ni}(\text{CN})_4^{2-}$, hence the computed ionization energies may be compared to vertical I.P. The corresponding energies are reported in Table 4, together with the I.P. according to Koopmans' theorem and the I.P. computed as the difference of the energy for the two species. The main conclusion, similar to the one reached for ferrocene, is that it is not possible to rely on Koopmans' theorem to establish the sequence of I.P. The lowest ionization energies, when computed as the difference of the energy for the two species, correspond to removal of one electron from the metal $3d$ orbitals and not from the π ligand orbitals. In fact, Koopmans' theorem turn to be approximately valid for the π ligand orbitals (for instance the orbital energy of the $8e_u$ orbital, 0.121 a.u., is not very different from the I.P. of 0.113 a.u. computed as the difference of the energy values) but not for the metal $3d$ orbitals (compare for instance the energy orbital of +0.182 a.u. for the $9a_{1g}$ orbital and the computed I.P. of -0.033 a.u.). The computed I.P. corresponding to the removal of one electron from the $9a_{1g}$ and $1e_g$ orbitals is negative, namely the $\text{Ni}(\text{CN})_4^-$ ion in its ${}^2A_{1g}$ and 2E_g electronic states is computed to be more stable than the $\text{Ni}(\text{CN})_4^{2-}$ ion in its ground state. This increased stability associated with the removal of one negative charge from the dinegative ion is merely an artefact due to the neglect of the surrounding crystal, which exerts a stabilizing effect on the negative ion through the corresponding positive charge. We have carried out additional calculations which try to account for the electrostatic potential of the crystal. The crystal has been represented in the SCF calculation by a set of point charges occupying the positions of the atomic nuclei within a sphere of a given radius. In a first set of calculations (hereafter called Lattice I), the radius of the sphere was taken as 4.8 Å and the point charges were the ones which result from the population analysis for the free ion [19]. The positions of the atomic nuclei in the crystal have been derived from the structure of $\text{K}_2\text{Ni}(\text{CN})_4$ [43]. In a second set of calculations (called Lattice II), the radius of the sphere was increased to 6.2 Å and the point charges used were taken as the ones given by the population analysis corresponding to the Lattice I calculation.

The corresponding results are also reported in Table 4. Inclusion of the crystal potential results in a stabilization of both the orbital energies and the I.P. It also stabilizes the $\text{Ni}(\text{CN})_4^{2-}$ ion compared to the $\text{Ni}(\text{CN})_4^-$ ion. As a result, I.P. computed as the difference of the energy for both ions turn now to be positive and much larger. The lowest I.P. corresponds to the removal of an electron from orbitals which have mainly a metal $3d$ character and the corresponding sequence, which seems to be independent of the inclusion of crystal effects, is

$$\text{I.P.}(9a_{1g}) < \text{I.P.}(1e_g) < \text{I.P.}(1b_{2g}).$$

On the contrary, the magnitude of the computed I.P. turns to be extremely sensitive to the inclusion of the crystal effect and the convergence of the computed

values with the number of point charges included in the calculation seems to be slow. The experimental photoelectron spectrum of $\text{Ni}(\text{CN})_4^{2-}$ shows a peak around 9.0 eV which corresponds probably to the 3d orbitals, followed by a broad absorption region in the range 11–14 eV corresponding probably to the ligand π orbitals [4].

Two major conclusions may be drawn from the above results. The first one is that Koopmans' theorem is not always valid. The rigorous and sometimes only satisfactory way of estimating I.P. is to compute separately the energy associated with the two species. This appears to be especially true whenever the orbital energies associated with the ligand π orbitals are higher than the ones associated with the metal 3d orbitals, as it occurs for both the $\text{Ni}(\text{CN})_4^{2-}$ ion and for the ferrocene molecule [36]. In these two cases, the sequence of I.P. computed as the difference of the energy for the two species is different from the sequence of I.P. according to Koopmans' theorem (i.e. from the sequence of orbital energies). The other conclusion is that the crystal potential has to be taken into account for the calculation of the I.P. of an ionic species.

*The Wavefunction and Electron Density Associated
with the Ground State of $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$*

The wavefunction for the $\text{Ni}(\text{CN})_4^{2-}$ ion in terms of symmetry adapted orbitals has been previously reported and discussed briefly [19]. We will not report the wavefunction of the $\text{Ni}(\text{CO})_4$ molecule but rather give in Table 5 the results of a population analysis [37] for the highest molecular orbitals. For the sake of comparison, the population analysis for the free ligand CO is given in Table 6. The orbitals $5t_2$ to $1t_1$ are nearly pure ligand orbitals. The orbital $8t_2$ is a bonding combination (with an overlap population of 0.225) of the lone pair orbital 5σ of the C atom with the 3d metal orbitals, with 26% of metal orbital. The $9t_2$ orbital is the corresponding antibonding combination (with an overlap population of -0.061), with 74% of metal orbital. The $2e$ orbital is a nearly pure metal 3d orbital with no metal-carbon bonding character.

The electron transfer corresponding to the formation of the metal-ligand bond may be discussed in terms of gross atomic and orbital populations. These are reported in Table 7 for the $\text{Ni}(\text{CO})_4$ and CO molecules. We will refer to the Ni atom in its $3d^{10} 1S$ state, this is a common and convenient assumption [38]. The Ni atom in the complex bears a formal positive charge of $0.24e$. This is the result of a loss of $0.77e$ from the d orbitals ($0.57e$ for the d functions belonging to the t_2 representation and $0.20e$ for the ones belonging to the e representation) with a gain of $0.57e$ in the 4p orbitals (mostly through the $8t_2$ and $9t_2$ orbitals). The population associated with the 4s orbital is close to zero, this is in agreement with the result reported by Hillier [20]. The configuration obtained for the Ni atom $4s^{-0.02} 4p^{0.57} 3d^{9.23}$ is close to the one given by Hillier $4s^{-0.04} 4p^{0.35} 3d^{9.22}$. The largest change in the populations of the ligand CO upon formation of the complex is the decrease in the population of the 2s orbital of the C atom, from $1.67e$ to $1.53e$. This is a consequence of the sharing of the lone pair of the C atom, namely the 5σ orbital which is built

Table 6. Population analysis for the ligand CO

Orbital	Overlap population C–O	C				O			
		s	x	y	z	s	x	y	z
5 σ	–0.295	1.17	0.46		0.23		0.10		0.05
1 π	0.748		0.16	0.49	0.33		0.50	1.51	1.01
4 σ	0.260	0.26	0.07		0.03	0.43	0.81		0.40
3 σ	0.510	0.23	0.12		0.06	1.39	0.13		0.06
Total	1.223	1.66	0.81	0.49	0.65	1.82	1.54	1.51	1.52

Table 7. Gross atomic and orbital populations for $\text{Ni}(\text{CO})_4$ and CO

	$\text{Ni}(\text{CO})_4$			CO	
	Ni	C ₁	O ₁	C	O
4s/2s	–0.02	1.53	1.79	1.67	1.81
4p _x /2p _x	0.19	0.88	1.53	0.81	1.54
4p _y /2p _y	0.19	0.57	1.51	0.49	1.51
4p _z /2p _z	0.19	0.72	1.52	0.65	1.52
3d _{x²–y²}	1.81				
3d _{xy}	1.90				
3d _{xz}	1.81				
3d _{yz}	1.81				
3d _{z²}	1.90				
Formal charge	+0.24	+0.29	–0.35	+0.37	–0.37

mostly from the 2s orbital of the C atom. This decrease in the 2s population is more than balanced by an increase in the 2p populations of the C atom, as a result of the π backbonding from the Ni atom to the ligand. It is observed that there is little change in the populations on the O atom².

² The electronic structure of $\text{Ni}(\text{CO})_4$ has been investigated recently by the SCF-X α -SW method [46]. The results are at variance with ours with respect to the interpretation of the bonding. In agreement with our calculation, the highest occupied level is 9t₂ followed by the 2e level, both corresponding principally to Ni 3d-like orbitals. The levels immediately below are

$$7a_1(5\sigma) < 6t_2(4\sigma) < 8a_1(4\sigma) < 7t_2(5\sigma) < 1e(1\pi) < 8t_2(4\sigma) < 1t_1(1\pi).$$

The 8t₂, 8a₁ and 6t₂ levels are described as almost exclusively CO 4 σ orbitals. This interpretation is certainly erroneous for either the 8t₂ or the 6t₂ level, one of these levels, probably the 8t₂, has to be a CO 1 π orbital. The stability of the molecule is attributed to the 7a₁ and 7t₂ orbitals which are described as strong covalent admixtures of Ni 4s-like and 3d-like partial waves with the 5 σ carbon “lone-pair” orbitals of the CO ligands. This is at variance with our conclusion that the Ni 4s orbital does not participate to the bonding in $\text{Ni}(\text{CO})_4$. Finally it is stated without much proof that there is no evidence for any significant metal-to-ligand π back-donation, which is also at variance with our conclusions. π back-bonding is evidenced in our calculation through the formal positive charge of the Ni atom and through the decrease in the formal positive charge of the C atom compared to CO (which results from an increase in the populations of the 2p orbitals). This π back-bonding seems to be the result of an intricate process at the molecular orbital level. The 2e molecular orbital shows no contribution of the carbon 2p orbitals but rather one from the oxygen 2p orbitals. Through the 7t₂ and 1e molecular orbitals, there is a small electronic transfer from the oxygen 2p orbitals to the carbon 2p orbitals, compared to the electron distribution in the free CO. The whole process is equivalent to a transfer from the 3d $_{\pi}$ orbitals of the Ni atom to the carbon 2p orbitals.

A comparison of the populations associated with the two complexes $\text{Ni}(\text{CN})_4^{2-}$ (see Table 3 of Ref. [19]) and $\text{Ni}(\text{CO})_4$, and of the charge transfer upon formation of these complexes, point to some significant similarities and differences:

- in both complexes the metal atom bears a formal positive charge but, as expected, this one remains larger for the NiIII of $\text{Ni}(\text{CN})_4^{2-}$ than for the Ni⁰ of $\text{Ni}(\text{CO})_4$;

- in $\text{Ni}(\text{CN})_4^{2-}$ the NiIII ($3d^8$) gains d electrons while the Ni⁰ ($3d^{10}$) of $\text{Ni}(\text{CO})_4$ can only lose d electrons³;

- the population of the $4s$ orbital is important in $\text{Ni}(\text{CN})_4^{2-}$ but is close to zero in $\text{Ni}(\text{CO})_4$. On the contrary the population of the $4p$ orbitals is larger in $\text{Ni}(\text{CO})_4$, with the three orbitals equally populated while only the $4p_x$ and $4p_y$ orbitals are appreciably populated in $\text{Ni}(\text{CN})_4^{2-}$;

- the above results are not incompatible with the "old" concepts of dsp^2 and sp^3 hybridizations respectively, although the $4s$ orbital does not seem to participate to the bonding in $\text{Ni}(\text{CO})_4$;

- while the cyanide ion behaves only as a σ -donor, the carbonyl molecule acts simultaneously as a σ -donor and a π -acceptor;

- the σ charge-transfer is much smaller for the CO molecule than for the CN^- ion (compare for instance the variation of the $2s$ orbital population of the C atom from CN^- to $\text{Ni}(\text{CN})_4^{2-}$ and from CO to $\text{Ni}(\text{CO})_4$).

A more familiar picture of the bonding may be obtained in terms of localized bonds. These have been derived from the canonical SCF orbitals through a unitary transformation according to the localization criterion proposed by Boys [39]. We have reported in Tables 8 and 9 some characteristics of the localized orbitals corresponding to the lone pairs and bonds of the complexes and the free ligands. Most significant is the change in the coordinates of the center of gravity for the electronic distribution (hereafter called "charge center") of the localized orbitals upon formation of the complex. Electron density

Table 8. Localized orbitals of $\text{Ni}(\text{CO})_4$ and CO

Localized orbital	Coordinates of the charge center ^{a, b, c}			Overlap population ^b	
	x	y	z	Ni-C	C-O
Ni-C ^d	2.126 (2.200)	-0.016 (0.000)	-1.503 (-1.556)	0.066	-0.164 (-0.248)
C-O	3.816 (3.845)	0.020 (0.234)	-3.317 (-3.264)	-0.022	0.454 (0.442)
C-O	4.238 (4.114)	-0.448 (-0.503)	-2.709 (-2.884)	-0.022	0.457 (0.442)
C-O	4.259 (4.347)	0.429 (0.269)	-2.681 (-2.553)	-0.022	0.457 (0.442)
O:	5.073 (5.079)	0.000 (0.000)	-3.586 (-3.591)	-0.030	0.204 (0.149)

^a In a.u.

^b The numbers in parenthesis refer to the free ligand CO.

^c The coordinates of the nuclei are:

Ni 0., 0., 0. C 2.839, 0., -2.008 O 4.613, 0., -3.262.

^d C: for the free ligand CO.

³ If one would consider the Ni atom in its ground state $3d^8 4s^2$, one would conclude that it gains d electrons, but one should introduce a loss of two electrons from the $4s$ orbitals.

Table 9. Localized orbitals of $\text{Ni}(\text{CN})_4^{2-}$ and CN^-

Localized orbital	Coordinates of the charge center ^{a, b, c}			Overlap population ^b	
	x	y	z	Ni-C	C-N
Ni-C ^d	2.478 (2.640)	0.000 (0.000)	0.003 (0.000)	0.489	-0.151 (-0.307)
C-N	4.729 (4.779)	-0.006 (-0.015)	-0.584 (-0.588)	-0.011	0.581 (0.570)
C-N	4.780 (4.779)	-0.505 (-0.502)	0.298 (0.307)	-0.015	0.580 (0.570)
C-N	4.782 (4.779)	0.511 (0.517)	0.286 (0.281)	-0.015	0.580 (0.570)
N:	6.370 (6.383)	0.000 (0.000)	-0.003 (0.000)	-0.117	0.331 (0.208)

^a In a.u.

^b The numbers in parenthesis refer to the free ligand CN^-

^c The coordinates of the nuclei are:

Ni 0., 0., 0. C 3.515, 0., 0. N 5.688, 0., 0.

^d C: for the free ligand CN^- .

contours for the localized orbital corresponding to the σ metal-ligand bond are given in Figs. 3 and 4. The difference in the coordination of the ligand to the metal for the two complexes is apparent both from Figs. 3 and 4 and from Tables 8 and 9. From the figures, one may see that the $3d_{x^2-y^2}$ orbital participates to the bonding in $\text{Ni}(\text{CN})_4^{2-}$, while clearly there is less participation of a $3d$ orbital to the σ bonding in $\text{Ni}(\text{CO})_4$. There is also a difference in the degree of coordination and bonding. The Ni-C overlap population for the localized orbital is 0.489 in $\text{Ni}(\text{CN})_4^{2-}$ and only 0.066 in $\text{Ni}(\text{CO})_4$. Upon coordination, there is a shift in the position of the "charge center" for the lone pair of the

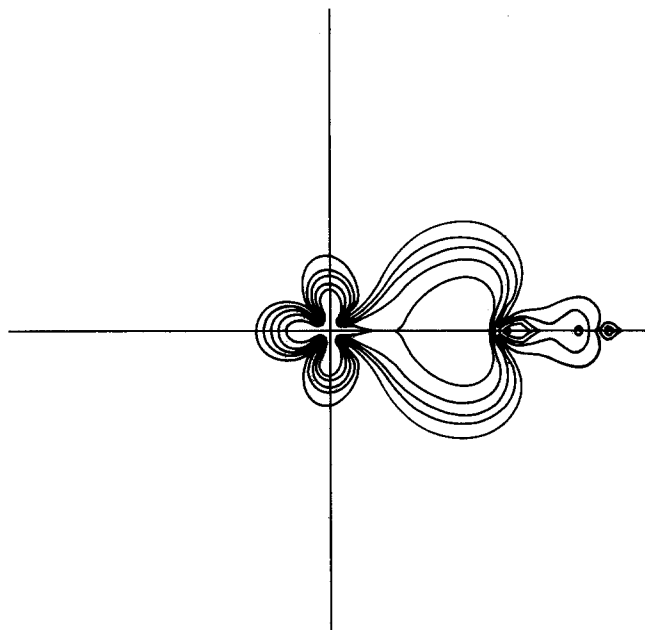


Fig. 3. Electron density contours for the Ni-C localized orbital in $\text{Ni}(\text{CN})_4^{2-}$

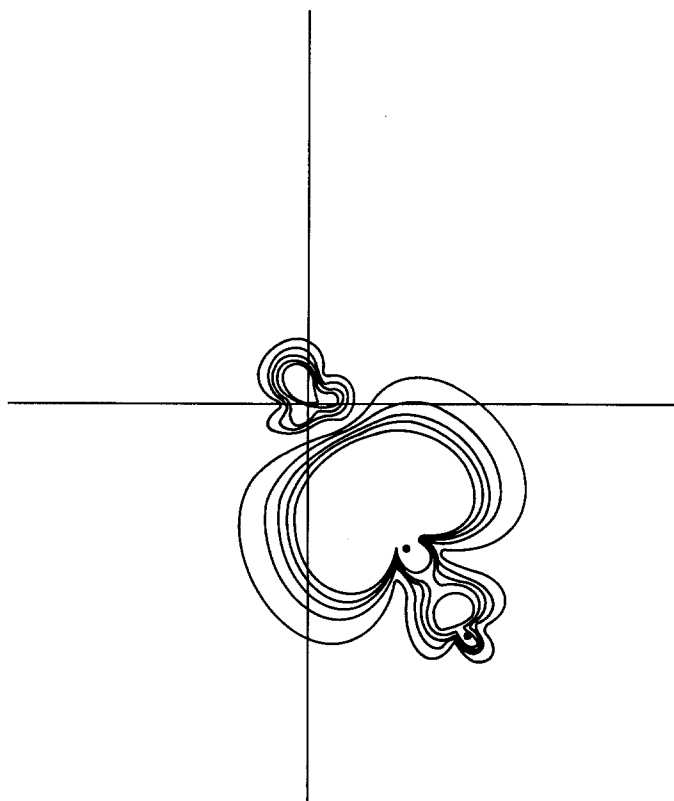


Fig. 4. Electron density contours for the Ni-C localized orbital in $\text{Ni}(\text{CO})_4$

C atom. This shift amounts to 0.162 a.u. in $\text{Ni}(\text{CN})_4^{2-}$ and to only 0.090 a.u. in $\text{Ni}(\text{CO})_4$. Although the charge center corresponding to the lone pair of the C atom is appreciably shifted during the formation of the complex, at least for $\text{Ni}(\text{CN})_4^{2-}$, it still remains in the complex relatively close to the C atom (the charge center is at 2.478 a.u. from the Ni atom and at 1.037 a.u. from the C atom in $\text{Ni}(\text{CN})_4^{2-}$): this has been previously considered as a characteristic of the dative bond [40].

The effect of the coordination on the binding of the CO and CN^- ligands has been discussed by several authors. It has been pointed out that the 5σ orbital is antibonding in both ligands, so that removal of electron density from this orbital should result in σ -bond strengthening [47]. From CNDO calculations for a series of XCO molecules, the CO σ bond order was found to increase very slightly and the CO π bond order to decrease (except for HCO^+), with the π decrease considerably larger than the σ increase in some instances [48]. Similar conclusions were reached for the CN^- ligand, with the σ bond order increasing only slightly and the π bond order very much reduced when the substituent was a backbonding atom.

From Tables 2 and 6, it is found that the CO total overlap raises from 1.223 for the free ligand to 1.358 in $\text{Ni}(\text{CO})_4$. There is a similar increase for the CN^- ligand, from 1.592 for the free ion to 1.889 in $\text{Ni}(\text{CN})_4^{2-}$. The σ overlap population raises for both ligands, mostly as the result of an increase in the overlap population of the 5σ orbital (the value of -0.295 for the free CO should be compared to the sum of the overlap populations for the $8a_1$ and $8t_2$ orbitals in $\text{Ni}(\text{CO})_4$, which is -0.133), together with a small increase for the 4σ orbital and a small decrease for the 3σ orbital (see Tables 2 and 6). In $\text{Ni}(\text{CN})_4^{2-}$, where the σ and π contributions are exactly separable, there is a small decrease in the π overlap population of 0.939 compared to the value of 1.054 for the free ligand. The changes in the σ electron distribution of the ligands appear as important, if not more, as the ones in the π electron distribution.

Excited States and Electronic Transitions in $\text{Ni}(\text{CN})_4^{2-}$

We report in this section some results relative to the excited states of $\text{Ni}(\text{CN})_4^{2-}$. The purpose of this work was not to compute accurate (i.e. within one thousand cm^{-1}) values of the transition energies for this ion, but rather to provide with a *semi-quantitative model* of the sequence of excited states. This was prompted by the results obtained for the ground state of the ion, with the π ligand orbitals lying higher than the occupied d orbitals of the metal. At first such a result would conflict with the usual assignment of the lowest transitions as $d-d$ or ligand field transitions [8]. This study was also started with a number of questions in mind:

– what is the relationship between the sequence of occupied and virtual orbitals obtained for the ground state and the sequence of electronic transitions? In many semi-empirical calculations which do not introduce *explicitly* the electron repulsion, excitation energy may be written as the difference of the orbital energies for the two orbitals i and j involved in the excitation

$$\Delta E_{i \rightarrow j} = \varepsilon_j - \varepsilon_i.$$

Conversely, a sequence of energy levels has been sometimes advanced for the ground state of the molecule or ion on the basis that it does account for the sequence of electronic transitions [14];

– such an hypothesis may be valid as long as the transition energy $\Delta E_{i \rightarrow j}$ parallel $\varepsilon_j - \varepsilon_i$. However, the rigorous way to calculate $\Delta E_{i \rightarrow j}$ is to achieve a separate minimization of the ground state and excited state energies E_i and E_j , with the transition energy given as the difference

$$\Delta E_{i \rightarrow j} = E_j - E_i. \quad (\text{I})$$

An equally common approximation is the use of virtual orbitals from the ground state calculation to describe the excited states. Then the excitation energy may be written as [41]

$$\left. \begin{aligned} {}^1 E(i \rightarrow j) &= \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij} \\ {}^3 E(i \rightarrow j) &= \varepsilon_j - \varepsilon_i - J_{ij} \end{aligned} \right\}. \quad (\text{II})$$

Table 10. Highest occupied and lowest empty orbitals of $\text{Ni}(\text{CN})_4^{2-}$ (from the ground state calculation)

Orbital	Orbital energy ^a	Nature
$3e_g$	0.589	π^*
$6b_{1g}$	0.587	$d_{x^2-y^2}$
$9e_u$	0.576	$4p_x, 4p_y$
$10a_{1g}$	0.550	$4s$
$3b_{2g}$	0.527	π^*
$4a_{2u}$	0.402	π^*
$8e_u$	-0.121	π
$1a_{2g}$	-0.123	π
$2e_g$	-0.132	π
$1b_{2u}$	-0.136	π
$2b_{2g}$	-0.156	π
$3a_{2u}$	-0.160	π
$9a_{1g}$	-0.182	d_{z^2}
$5b_{1g}$	-0.182	5σ
$7e_u$	-0.195	5σ
$8a_{1g}$	-0.231	4σ
$4b_{1g}$	-0.263	4σ
$1e_g$	-0.267	$d_{xz, yz}$
$6e_u$	-0.278	4σ
$1b_{2g}$	-0.335	d_{xy}

^a In a.u.

How good is the approximation of building the excited wavefunction from virtual orbitals? Then how much important is the term J_{ij} or $J_{ij} - 2K_{ij}$ compared to the difference of orbital energies?

The sequence of orbital energies for the highest occupied and lowest empty ("virtual") orbitals, as given by the ground state calculation [19], is indicated in Table 10. Each excited state corresponding to a single excitation from one occupied to one empty orbital of Table 10 has been the subject of an independent SCF calculation in the RHF scheme. Separate SCF calculations have been performed for the singlet and triplet states. Excitations involving two orbitals belonging to the same irreducible representation (like the $8e_u \rightarrow 9e_u$ or $5b_{1g} \rightarrow 6b_{1g}$) have not been considered [25]. We have assumed for each excited state the same geometry as the one used for the ground state (cf. below).

The computed transitions energies are reported in Table 11. Excitations above $70\,000\text{ cm}^{-1}$ are not reported in this table. It is immediately apparent that the sequence of transition energies has no relationship with the sequence of orbital energies. On the basis of orbital energies, one would expect as lowest energy transitions the ones corresponding to the excitations $8e_u \rightarrow 4a_{2u}$, $1a_{2g} \rightarrow 4a_{2u}$, $8e_u \rightarrow 3b_{2g}$ which may be classified as $\pi \rightarrow \pi^*$ transitions. It turns out from Table 11 that the *lowest transitions correspond to $d \rightarrow d$ excitations* from the $9a_{1g}$, $1e_g$ and $1b_{2g}$ orbitals to the $6b_{1g}$ orbital. Further confirmation of the lack of relationship between orbital energies and excitation energies is provided

by the fact that the sequence of energy transitions corresponding to the excitation from a given orbital X to the lowest empty orbitals ($4a_{2u}$, $3b_{2g}$, $10a_{1g}$, $9e_u$, $6b_{1g}$) always satisfy⁴

$$E(X \rightarrow 6b_{1g}) < E(X \rightarrow 4a_{2u}) < E(X \rightarrow 3b_{2g}) < E(X \rightarrow 10a_{1g}) < E(X \rightarrow 9e_u)$$

despite the fact that the $6b_{1g}$ orbital has the highest orbital energy. Conversely, if one considers the sequence of energy transitions corresponding to the excitation from the highest occupied orbitals (from $1b_{2g}$ to $8e_u$) to a given empty orbital X , it is found that (consider for instance the case $X = 4a_{2u}$)

$$E(9a_{1g} \rightarrow X) < E(1e_g \rightarrow X) < E(1b_{2g} \rightarrow X) < E(8e_u \rightarrow X)$$

despite the fact that the $9a_{1g}$, $1e_g$ and $1b_{2g}$ are not the highest occupied orbitals. A more careful analysis shows that the sequence of orbital energies may parallel the sequence of transition energies as long as the comparison deals with orbitals of the same nature (for instance the three $3d$ orbitals $1b_{2g}$, $1e_g$ and $9a_{1g}$, or the ligand π orbitals from $3a_{2u}$ to $8e_u$), but breaks down when it involves both the metal $3d$ and the ligand orbitals.

Table 11. Computed transition energies (in cm^{-1}) in $\text{Ni}(\text{CN})_4^{2-}$

Transition	Excited state ^a	Transition energy	Nature of the transition
$9a_{1g} \rightarrow 6b_{1g}$	<u>${}^1B_{1g}$</u>	20 600	$d_{z^2} \rightarrow d_{x^2-y^2}$
	${}^3B_{1g}$	4 000	
$1e_g \rightarrow 6b_{1g}$	<u>1E_g</u>	21 900	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$
	3E_g	7 700	
$1b_{2g} \rightarrow 6b_{1g}$	<u>${}^1A_{2g}$</u>	22 500	$d_{xy} \rightarrow d_{x^2-y^2}$
	${}^3A_{2g}$	14 700	
$9a_{1g} \rightarrow 4a_{2u}$	<u>${}^1A_{2u}$</u>	33 900	$d_{z^2} \rightarrow \pi^*$
	${}^3A_{2u}$	30 300	
$1e_g \rightarrow 4a_{2u}$	<u>1E_u</u>	37 900	$d_{xz}, d_{yz} \rightarrow \pi^*$
	3E_u	36 000	
$1b_{2g} \rightarrow 4a_{2u}$	<u>${}^1B_{1u}$</u>	46 900	$d_{xy} \rightarrow \pi^*$
	${}^3B_{1u}$	46 700	
$9a_{1g} \rightarrow 3b_{2g}$	<u>${}^1B_{2g}$</u>	58 500	$d_{z^2} \rightarrow \pi^*$
	${}^3B_{2g}$	62 300	
$1e_g \rightarrow 3b_{2g}$	<u>1E_g</u>	62 300	$d_{xz}, d_{yz} \rightarrow \pi^*$
	3E_g	61 700	
$8e_u \rightarrow 6b_{1g}$	<u>1E_u</u>	68 600	$\pi \rightarrow d_{x^2-y^2}$
	3E_u	66 000	
$1a_{2g} \rightarrow 6b_{1g}$	<u>${}^1B_{2g}$</u>	69 700	$\pi \rightarrow d_{x^2-y^2}$

^a Excited states corresponding to allowed transitions from the ground state are underlined.

⁴ The full set of computed transition energies, including excitations above $70\,000\text{ cm}^{-1}$, may be found in Ref. [26].

Table 12. Transition energies computed as the difference of the energy for the two states and estimated from orbital energies, Coulomb and exchange integrals

Transition $i \rightarrow j$	$\varepsilon_j - \varepsilon_i^a$	J_{ij}^a	K_{ij}^a	Transition energy ^{b, c}	Transition energy ^{b, d}
$1a_{2g} \rightarrow 4a_{2u}$	0.525	0.185	0.001	75 170	71 700
$9a_{1g} \rightarrow 4a_{2u}$	0.584	0.248	0.015	80 330	33 900
$1a_{2g} \rightarrow 3b_{2g}$	0.650	0.226	0.034	108 000	106 000
$9a_{1g} \rightarrow 3b_{2g}$	0.709	0.247	0.005	103 600	58 500
$1a_{2g} \rightarrow 6b_{1g}$	0.710	0.209	0.002	111 000	69 700
$9a_{1g} \rightarrow 6b_{1g}$	0.769	0.529	0.023	62 770	20 600

^a In a.u.^b In cm^{-1} .^c Computed according to ${}^1E(i \rightarrow j) = \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij}$.^d Computed as the difference of the energy for the two states.

The reason for these inversions is to be found both in the fact that the excitation energy cannot be written as a difference of orbital energies (after assuming that the excited state may be represented through the occupied and virtual orbitals of the ground state) and in the fact that these occupied and virtual orbitals obtained for the ground state cannot provide a satisfactory description of the excited state. To investigate the relative importance of both effects, we have reported in Table 12, for a set of transitions, the values of $\varepsilon_j - \varepsilon_i$, of $\Delta E_{i \rightarrow j}$ computed as the difference of the energies for the ground state and the excited state, and of $\Delta E_{i \rightarrow j}$ as given by formula II (with the approximation that ε_i and ε_j are the orbital energies from the ground state calculation and that the integrals K_{ij} and J_{ij} are computed for the ground state orbitals). If one considers first the sequence of excitation energies as given by formula II and the difference of orbital energies $\varepsilon_j - \varepsilon_i$ (columns 5 and 2 of Table 12) they parallel approximately for five transitions out of six and the reason is that J_{ij} remain approximately constant, in a range 0.18–0.25 a.u., for these five excitations. However, the $d-d$ excitation $9a_{1g} \rightarrow 6b_{1g}$ which is the highest in energy if one considers the difference of orbital energies, is the lowest according to formula II. The reason is that the corresponding Coulomb integral J_{ij} raises to 0.53 a.u. for this excitation. This points to the importance of the Coulomb integral J_{ij} in the determination of the excitation energies. A similar conclusion has been previously reached by Basch *et al.* for the hypothetical compound NiF_4^{2-} [42]. Moreover, a comparison of the excitation energies as given by formula II and by the difference of the energies for the ground and excited states (Columns 5 and 6 of Table 12) indicate that the use of formula II (with integrals computed from the ground state wavefunction) may be a poor approximation. Whenever the transition $i \rightarrow j$ involves one metal $3d$ orbital as i or j , formula II may be in error by as much as $45\,000 \text{ cm}^{-1}$. From Table 12, it is apparent that formula II provides a satisfactory approximation only when both i and j are ligand orbitals. It has already been shown for the ferrocene molecule [36] that there is an important electronic relaxation upon ionization of an electron from a metal $3d$ orbital and that, on the contrary, there is little electronic rearrangement when the ionization

Table 13. A comparison of some “occupied” molecular orbitals ϕ_i from the ground state calculation and from some excited state calculations

Orbital	Nature of the excitation	LCAO coefficients ^{a, b}
<i>From the ground state calculation</i>		
$1a_{2g}$		$0.32\ 2p_C^1 + 0.22\ 2p_C^2 + 0.71\ 2p_N$
$9a_{1g}$		$0.36\ 4s_{\text{Ni}}^2 - 0.23\ 2p_C^1 + 0.42\ 2p_N + 0.72\ 3d_{z^2}^1$
<i>From the excited state calculation</i>		
$1a_{2g}$	$1a_{2g} \rightarrow 4a_{2u}$	$0.32\ 2p_C^1 + 0.22\ 2p_C^2 + 0.71\ 2p_N$
$1a_{2g}$	$1a_{2g} \rightarrow 3b_{2g}$	$0.31\ 2p_C^1 + 0.24\ 2p_C^2 + 0.70\ 2p_N$
$1a_{2g}$	$1a_{2g} \rightarrow 6b_{1g}$	$0.30\ 2p_C^1 + 0.21\ 2p_C^2 + 0.73\ 2p_N$
$9a_{1g}$	$9a_{1g} \rightarrow 6b_{1g}$	$0.95\ 3d_{z^2}^1$
$9a_{1g}$	$9a_{1g} \rightarrow 3b_{2g}$	$0.98\ 3d_{z^2}^1$
$9a_{1g}$	$9a_{1g} \rightarrow 4a_{2u}$	$0.99\ 3d_{z^2}^1$

^a Only coefficients greater than 0.2 are reported.

^b The notations $2p_C^1$, $2p_C^2$, $3d^1$, etc. ... refer to split orbitals.

Table 14. A comparison of some “excited” molecular orbitals ϕ_j from the ground state calculation and from some excited state calculations

Orbital	Nature of the excitation	LCAO coefficients ^{a, b, c}
<i>From the ground state calculation (“virtual” orbitals)</i>		
$6b_{1g}$		$-1.24\ 2s_C^2 + 0.26\ 2s_N + 0.23\ 2p_C^1 + 0.38\ 2p_C^2 - 0.28\ 2p_N + 0.85\ 3d^1 + 0.53\ 3d_{x^2-y^2}^2$
$9e_u$		$-1.73\ 2s_C^2 - 0.23\ 2s_N + 2.12\ 4p_{x,y}^2 + 0.60\ 2p_{1C}^2 + 0.22\ 2p_{2C}^2 - 0.54\ 2p_{2N}$
$10a_{1g}$		$-0.69\ 4s^1 + 4.46\ 4s^2 - 3.02\ 2s_C^2 - 0.40\ 2s_N + 1.88\ 2p_C^2 - 0.61\ 3d_{z^2}^2$
$3b_{2g}$		$-0.29\ 2p_C^1 - 0.58\ 2p_C^2 + 0.82\ 2p_N + 0.25\ 3d_{xy}^1$
$4a_{2u}$		$-0.94\ 4p_z^2 + 0.52\ 2p_N$
<i>From the excited state calculation</i>		
$6b_{1g}$	$1a_{2g} \rightarrow 6b_{1g}$	$-0.49\ 2s_C^2 + 0.99\ 3d_{x^2-y^2}^1$
$9e_u$	$5b_{1g} \rightarrow 9e_u$	$-1.39\ 2s_C^2 + 1.63\ 4p_{x,y}^2 + 0.46\ 2p_{1C}^2 + 0.30\ 2p_{2C}^1 + 0.23\ 2p_{2C}^2 - 0.68\ 2p_{2N}$
$10a_1$	$1e_g \rightarrow 10a_1$	$-0.64\ 4s^1 + 4.01\ 4s^2 - 2.70\ 2s_C^2 - 0.28\ 2s_N + 1.55\ 2p_C^1 - 0.40\ 3d_{z^2}^2$
$3b_{2g}$	$1a_{2g} \rightarrow 3b_{2g}$	$-0.31\ 2p_C^1 - 0.55\ 2p_C^2 + 0.75\ 2p_N + 0.28\ 3d_{xy}^1 - 0.25\ 3d_{x^2-y^2}^2$
$4a_{2u}$	$1a_{2g} \rightarrow 4a_{2u}$	$-0.86\ 4p_z^2 + 0.52\ 2p_N$

^a Only coefficients greater than 0.2 are reported.

^b The notations $2s_C^1$, $2s_C^2$, $2p_C^1$, etc. ... refer to split orbitals.

^c The notations $2p_{1C}$, $2p_{2C}$, etc. ... refer to orbitals centered on the carbon atoms C_1 and C_2 (Fig. 1).

involves an electron from a ligand orbital. A similar conclusion may be reached relative both to the importance of the electronic relaxation upon excitation (change in the “occupied” orbital ϕ_i) and to the significance of “virtual” orbitals compared to the orbitals optimized for each excited state (change in ϕ_j). We have reported in Tables 13 and 14 the expressions for some orbitals ϕ_i and ϕ_j

Table 15. Transitions and assignments in $\text{Ni}(\text{CN})_4^{2-}$, according to Refs. [8] and [10]

Energy ^a	Extinction coefficient ϵ	Assignment
22 400	2	${}^1A_{1g} \rightarrow {}^1A_{2g}$ $d_{xy} \rightarrow d_{x^2-y^2}$
23 000	50	$\rightarrow {}^1B_{1g}$ $d_{z^2} \rightarrow d_{x^2-y^2}$
27 000	100	$\rightarrow {}^1E_g$ $d_{xz, yz} \rightarrow d_{x^2-y^2}$
32 300	700	$\rightarrow {}^1B_{1u}$ $d_{xy} \rightarrow \pi^*$
35 200	4 200	$\rightarrow {}^1A_{2u}$ $d_{z^2} \rightarrow \pi^*$
37 600	10 600	$\rightarrow {}^1E_u$ $d_{xz, yz} \rightarrow \pi^*$

^a In cm^{-1} .

both from the ground state calculation and from some excited state calculation. An orbital ϕ_i like the $1a_{2g}$ orbital, which is a ligand π orbital, remains nearly unchanged when its occupation number changes from 2 to 1. On the contrary, an orbital ϕ_i like the $9a_{1g}$ orbital, which is a rather diffuse metal $3d$ orbital in the ground state, is strongly affected upon excitation and becomes a nearly pure $3d$ orbital. If we turn now to the ϕ_j orbital (Table 14), the difference between the virtual orbital and the corresponding orbital optimized for the excited state is more pronounced for the $6b_{1g}$ orbital (which appears to be less diffuse when optimized for the excited state) than for the other orbitals. Again the $6b_{1g}$ orbital is predominantly a metal $3d$ orbital.

So far, we have not discussed the relationship between the computed excitation energies and the experimental absorption spectrum. The experimental spectrum of $\text{Ni}(\text{CN})_4^{2-}$ has been studied by many authors. We shall refer mostly to the work of Ballhausen and coll. [8] and to the work of Piepho and coll. [13]. On the basis of the polarized spectra of crystals in conjunction with ligand-field theory, Ballhausen has proposed the assignments given in Table 15. This has been confirmed by Stephens on the basis of the magnetic circular dichroism spectrum [12]. It has been shown later that the introduction of spin-orbit coupling does not change basically the interpretation of the spectrum [13].

The experimental spectrum shows three weak bands in the range 22 000–27 000 cm^{-1} , which have been interpreted as symmetry-forbidden $d-d$ (or “ligand-field”) transitions [8]. The corresponding singlet excitations are computed (Table 11) as the lowest energy excitations, in the range 20 000 to 22 500 cm^{-1} . The next three bands of the experimental spectrum, in the range 32 000–37 600 cm^{-1} , have been considered as charge-transfer excitations from a $3d$ orbital (b_{2g} , a_{1g} , e_g) to the ligand antibonding orbital $4a_{2u}$. The computed energies corresponding to these excitations fall in the range 33 900–46 900 cm^{-1} and come next to the $d-d$ excitations. We might consider this agreement, which is semiquantitative, as satisfactory, especially when one is reminded of the rather severe limitations of this type of calculation: use of a limited basis set and neglect of the change in correlation energy⁵.

⁵ The assumption that the excited state retains the geometry of the ground state is not an approximation as long as the reported experimental energies correspond to vertical transitions. According to Ballhausen *et al.*, $\text{Ni}(\text{CN})_4^{2-}$ should remain square planar in the ${}^1A_{2g}$ state but should distort in the 1E_g and ${}^1B_{1g}$ state [8].

However, there is some disagreement between the assignment given for the experimental spectrum (Table 15) and the sequence of computed excitations (Table 11). According to the assignment of the experimental spectrum, the sequence for both the $d-d$ and $d-\pi^*$ excitations is

$$(b_{2g} \rightarrow X) < (a_{1g} \rightarrow X) < (e_g \rightarrow X)$$

where X stands for b_{1g} or a_{2u} . The sequence of computed excitations is different

$$(a_{1g} \rightarrow X) < (e_g \rightarrow X) < (b_{2g} \rightarrow X).$$

However, this disagreement may be not so severe. In fact, the band which has been assigned to the $b_{2g} \rightarrow b_{1g}$ excitation is observed at 22400 cm^{-1} only in the barium tetracyanonickelate. For other salts, this band would appear at highest frequencies and would be covered by the more intense charge-transfer bands [10]. In fact, according to Ballhausen *et al.*, this transition is expected to occur around 30000 cm^{-1} [8]. Then, the experimental sequence of excitations would be

$$(a_{1g} \rightarrow b_{1g}) < (e_g \rightarrow b_{1g}) < (b_{2g} \rightarrow b_{1g})$$

in agreement with the computed sequence of Table 11. The assignment of the charge-transfer bands above 30000 cm^{-1} is probably more difficult. Stephens *et al.*, on the basis of magnetic circular dichroism (MCD) measurements, have established the excited state order ${}^1A_{2u} < {}^1E_u$, in agreement with the computed energies of Table 11 [12]. Piepho *et al.*, also on the basis of the MCD spectrum, assign the band around 32300 cm^{-1} as a composite ${}^1B_{1u} + {}^3A_{2u}$ (due to explicit consideration of spin-orbit coupling) [13]. Their justification for assuming that this band arises partially from the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition is that its intensity seems too large to result from an ${}^1A_{1g} \rightarrow {}^3A_{2u}$ transition alone. However, the possibility of a sequence of excited states

$${}^1A_{2u} < {}^1E_u < {}^1B_{1u}$$

does not appear to have been ruled out definitely.

There is little indication in the literature, if any, on the triplet electronic states. The $d \rightarrow d$ transitions to a triplet state are predicted at 4000 , 7700 and 14700 cm^{-1} ⁶. Two very weak bands have been reported by Ballhausen *et al.* at 5600 and 7000 cm^{-1} but do not correspond to electronic transitions. Weak absorptions at 20000 cm^{-1} have also been assigned as spin-forbidden transitions [8]. For the $3d \rightarrow \pi^*$ excitations, the triplet state is found to be about $200\text{--}3600 \text{ cm}^{-1}$ below the singlet state. In the energy level scheme proposed by Piepho *et al.* in the absence of spin-orbit coupling, the corresponding triplet states lie some $2500\text{--}3500 \text{ cm}^{-1}$ below the singlet states [13].

We have reported in Table 16 the results of a population analysis for some excited states. For the three $d \rightarrow d$ transitions, there is a nearly constant increase in the formal charge of the Ni atom compared to the ground state. This is due to the fact that, when one $3d$ electron is excited into the $d_{x^2-y^2}$ orbital, the ease of σ -coordination of the ligands to the metal through the $d_{x^2-y^2}$ orbital is decreased.

⁶ The reason for the large difference between the energies of the singlet and triplet states ${}^1B_{1g}$ and ${}^3B_{1g}$ is to be found in the large value of K_{ij} (see Table 12).

Table 16. Population analysis for the ground state and some excited states of $\text{Ni}(\text{CN})_4^{2-}$

Ground state	${}^1B_{1g}, d_{z^2} \rightarrow d_{x^2-y^2}$	${}^1E_g, d_{xz}, yz \rightarrow d_{x^2-y^2}$	${}^1A_{2g}, d_{xy} \rightarrow d_{x^2-y^2}$	${}^1E_g, d_{xz}, yz \rightarrow \pi^*$	${}^1E_u, \pi \rightarrow d_{x^2-y^2}$
Ni 4s	0.41	0.35	0.39	0.43	0.43
4p _x	0.17	0.19	0.18	0.23	0.12
4p _y	0.17	0.19	0.18	0.23	0.12
4p _z	0.04	0.05	0.05	0.06	0.02
3d _{x^2-y^2}	0.91	1.58	1.58	1.36	1.30
3d _{xy}	1.95	1.95	1.95	2.15	1.92
3d _{xz}, 3d_{yz}}	1.97	1.97	1.48	1.49	1.95
3d _{z^2}}	1.96	1.01	1.98	1.97	1.92
q ^a	+0.46	+0.74	+0.73	+0.60	+0.27
C 2s	1.26	1.31	1.31	1.16	1.35
2p σ ^b	1.14	1.16	1.16	1.10	1.13
2p π	0.84	0.83	0.83	0.92	0.79
2p π'	0.91	0.92	0.92	0.90	0.84
q ^a	-0.14	-0.22	-0.22	-0.18	-0.11
N 2s	1.66	1.66	1.66	1.66	1.67
2p σ	1.53	1.54	1.54	1.54	1.53
2p π	1.18	1.19	1.19	1.16	1.09
2p π'	1.10	1.08	1.08	1.10	1.18
q ^a	-0.47	-0.47	-0.47	-0.47	-0.46

^a Formal charge.^b The orbitals 2p σ , 2p π , 2p π' are defined in Fig. 1.

Compared to the ground-state, the population of the $3d$ orbital from where the electron is excited is decreased by about one electron (one-half for the degenerate d_{xz} and d_{yz} orbitals). In a charge-transfer transition of the type $d_{xz,yz} \rightarrow \pi^*$, the change in the formal charge of the Ni atom is small (from +0.46 to +0.60). This is due to the fact that the π charge transfer from the metal to the ligand induces an increased σ charge transfer from the ligand to the metal, as it may be seen from the population of the $3d_{x^2-y^2}$, $4p_x$ and $4p_y$ orbitals. Excitations which are classified as ligand to metal charge transfer ($\pi \rightarrow d_{x^2-y^2}$) appear to have only a limited effect on the formal charge of the metal atom, since only a fraction of an electron is transferred from the ligand into the $d_{x^2-y^2}$ orbital.

Conclusion

We have used the LCAO-MO-SCF method to investigate the electronic structure of the $\text{Ni}(\text{CN})_4^{2-}$ ion and of the $\text{Ni}(\text{CO})_4$ molecule, with a medium size basis set of Gaussian orbitals. The sequence of orbital energies for the highest occupied orbitals is predicted to be

$$3d \sim \sigma(\text{CN}^-) < \pi(\text{CN}^-)$$

for the $\text{Ni}(\text{CN})_4^{2-}$ ion and

$$8a_1(\sigma_L) < 1e(\pi_L) \sim 7t_2(\pi_L) \sim 1t_1(\pi_L) \sim 8t_2(\sigma_L) < 2e(d_M) < 9t_2(d_M)$$

for the $\text{Ni}(\text{CO})_4$ molecule. For this molecule, our sequence is different from the one obtained by Nieuwpoort [18] which puts the $2e$ orbital as the highest filled orbital, but in agreement with the recent calculation of Hillier [20] and with previous assignment of the experimental spectrum [6]. We may infer that Koopmans' theorem is probably true for this molecule. If the same would be true for the $\text{Ni}(\text{CN})_4^{2-}$, the lowest I.P. would be associated with the removal of an electron from orbitals which are predominantly ligand π orbitals. Separate calculations for various electronic states of the mononegative ion $\text{Ni}(\text{CN})_4^-$ have indicated that the lowest ionization energies should correspond to removal of one electron from the metal $3d$ orbitals and not from the π ligand orbitals. Reasonable values of the corresponding I.P. can be achieved only when the electrostatic potential of the crystal is accounted for. A somewhat similar situation is found in the calculation of the lowest electronic transitions of $\text{Ni}(\text{CN})_4^{2-}$. Since the highest occupied and lowest virtual orbitals for this ion are π and π^* ligand orbitals, $\pi \rightarrow \pi^*$ transitions would be expected as the lowest ones on the basis of orbital energy values. Separate SCF calculations indicate that the lowest computed transitions are associated with $d \rightarrow d$ excitations. The disagreement between the sequence of computed transitions and the one expected on the basis of orbital energies may be traced to the role of Coulomb and exchange integrals in the computed transition energies together with the importance of electronic relaxation upon excitation. These conclusions are probably rather general when, in the sequence of orbital energy, some ligand orbitals are found above the metal $3d$ orbitals. This situation, with similar results, has been found

⁷ In the sequence of orbital energy, ligand orbitals have been equally found above the doubly occupied metal $3d$ orbitals in NiF_4^{2-} [42], CuF_4^{2-} [44], NiCl_4^{2-} [45].

also in the ferrocene molecule [36] and the CuCl_4^{2-} ion [2]. It is probably rather general when the ligand is either a negative ion like in $\text{Ni}(\text{CN})_4^{2-}$ or CuCl_4^{2-} or a neutral molecule with an extended π -electron system like in ferrocene. On the contrary, one may expect that the highest occupied orbitals will have a character of metal $3d$ orbitals when the ligand is a neutral molecule with a limited π system, like in $\text{Ni}(\text{CO})_4$. One major consequence is that it does not seem possible any more to discuss the electronic spectrum of this type of complexes on the basis of a molecular orbital scheme or conversely to derive an orbital scheme from the assigned transitions, as it has been currently assumed [14, 9].

Our results are in agreement with the chemical evidence that the cyanide ion is a better σ -donor and a poorer π -acceptor than the carbonyl ligand, with a negligible π back-bonding in $\text{Ni}(\text{CN})_4^{2-}$ and a weak σ bonding in $\text{Ni}(\text{CO})_4$. While both previous calculations by Nieuwpoort [18] and Hillier [17] gave a formal negative charge on the Ni atom close to one electron in $\text{Ni}(\text{CO})_4$, we find that the Ni atom bears a small positive charge as the result of a limited σ charge transfer opposed by π backbonding.

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References

1. See for instance: Cotton, F. A., Wilkinson, G.: Advanced inorganic chemistry, p. 719. New-York: Interscience Publishers 1968.
2. Demuyneck, J., Coutiere, M.-M., Veillard, A.: to be published.
3. Griffith, W. P.: Quart. Rev. **16**, 188 (1962).
4. Jørgensen, K.: private communication.
5. Lloyd, D. R., Schlag, E. W.: Inorg. Chemistry **8**, 2544 (1969).
6. Green, J. C., King, D. I., Eland, J. H. D.: Chem. Comm. 1121 (1970).
7. Kida, S., Fujita, J., Nakamoto, K., Tsuchida, R.: Bull. chem. Soc. Japan **31**, 79 (1958).
8. Ballhausen, C. J., Bjerrum, N., Dingle, R., Eriks, K., Hare, C. R.: Inorg. Chemistry **4**, 514 (1965).
9. Mason, R., Gray, H. B.: J. Amer. chem. Soc. **90**, 5721 (1968).
10. Dahl, J. P., Dingle, R., Vala, M. T.: Acta chem. scand. **23**, 47 (1969).
11. Haines, R. A., Smith, A. A.: Can. J. Chem. **46**, 1444 (1968).
12. Stephens, P. J., McCaffery, A. J., Schatz, P. N.: Inorg. Chemistry **7**, 1923 (1968).
13. Piepho, S. B., Schatz, P. N., McCaffery, A. J.: J. Amer. chem. Soc. **91**, 5994 (1969).
14. Gray, H. B., Ballhausen, C. J.: J. Amer. chem. Soc. **85**, 260 (1963).
15. Millie, P., Veillard, A.: J. Chim. physique **20** (1965).
16. Schreiner, A. F., Brown, T. L.: J. Amer. chem. Soc. **90**, 3368 (1958).
17. Hillier, I. H.: J. chem. Physics **52**, 1948 (1970).
18. Nieuwpoort, W. C.: Philips Res. Rept. Suppl. No. 6, 1 (1965).
19. Demuyneck, J., Veillard, A., Vinot, G.: Chem. Physics Letters **10**, 522 (1971).
20. Hillier, I. H., Saunders, V. R.: Chem. Comm. 642 (1971).
21. Roos, B., Veillard, A., Vinot, G.: Theoret. chim. Acta (Berl.) **20**, 1 (1971).
22. Whitman, D. R., Hornback, C. J.: J. chem. Physics **51**, 398 (1969).
23. Holt, E. M., Watson, K. J.: Acta chem. scand. **23**, 14 (1969).
24. Ladell, J., Post, B., Faulkuchen, I.: Acta crystallogr. **5**, 795 (1952).
25. Roothaan, C. C. J.: Rev. mod. Physics **32**, 179 (1960).
26. Demuyneck, J.: Thèse de Doctorat d'Etat, Strasbourg, 1972.
27. Clementi, E.: Atomic energy tables, Supplement to IBM J. of Res. Develop. **9**, 1 (1965).

28. Bonaccorsi, R., Petrongolo, C., Scrocco, E., Tomasi, J.: Chem. Physics Letters **3**, 473 (1969).
29. McLean, A. D., Yoshimine, M.: Tables of linear molecule wave functions, Supplement to IBM J. of Res. Develop., 1967.
30. Christensen, J. J., Izatt, R. M., Hale, J. D., Pack, R. T., Watt, G. D.: Inorg. Chemistry **2**, 337 (1963).
31. Fischer, A. K., Cotton, F. A., Wilkinson, G.: J. Amer. chem. Soc. **81**, 800 (1959).
32. Koopmans, T.: Physica **1**, 104 (1933).
33. Hillier, I. H., Saunders, V. R., Ware, M. J., Bassett, P. J., Lloyd, D. R., Lynaugh, N.: Chem. Comm. 1316 (1970).
34. Barber, M., Connor, J. A., Hillier, I. H., Saunders, V. R.: Chem. Comm. 682 (1971).
35. Clark, D. T., Adams, D. B.: Chem. Comm. 740 (1971).
36. Coutiere, M.-M., Demuynck, J., Veillard, A.: Theoret. chim. Acta (Berl.) **27**, 281 (1972).
37. Mulliken, R. S.: J. chem. Physics **23**, 1833 (1955).
38. Mulliken, R. S.: Molecular complexes, p. 281. London: Wiley Interscience 1969.
39. Boys, S. F.: Rev. mod. Physics **32**, 296 (1960).
40. Millie, P., Berthier, G.: In: La nature et les propriétés des liaisons de coordination, p. 31. Paris: Editions du Centre National de la Recherche Scientifique, 1970.
41. Roothaan, C. C. J.: Rev. mod. Physics **23**, 69 (1951).
42. Basch, H., Hollister, C., Moskowitz, J. W.: In: Sigma molecular orbital theory, p. 449; O. Sinanoglu and W. Kenneth, Ed. New Haven: Yale University Press 1970.
43. Vannerberg, N. G.: Acta chem. scand. **18**, 2385 (1964).
44. Tossell, J. A., Lipscomb, W. N.: J. Amer. chem. Soc. **94**, 1505 (1972).
45. Dedieu, A., Veillard, A.: unpublished results.
46. Johnson, K., Wahlgren, U.: Int. J. quant. Chemistry, in press.
47. Dekock, R. L., Sarapu, A. C., Fenske, R. F.: Inorg. Chemistry **10**, 38 (1971).
48. Purcell, K. F.: J. Amer. chem. Soc. **91**, 3487 (1969).

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Note added in proof. The reported binding energy of 86 kcal/mole for the nickelcarbonyl molecule is with respect to $\text{Ni}^0(3d^{10} 1S)$. A full account of the results of Ref. [20] has been given by Hillier and Saunders (Mol. Physics **22**, 1025 (1971)).