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Correlation Effects in the Ground and Ionic States of Bis(π-allyl)nickel

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Correlation effects in the ground and ionic states of bis(π-allyl)nickel are investigated by the use of large-scale configuration interaction calculations. In the ^1A_g molecular ground state the dominant correlation involves the b_g metal–ligand bonding electrons and results in an increase in the metal 3d electron density compared to that at the RHF level of approximation. Calculations on the ionic states reveal differential electron correlation for the metal- and ligand-ionized states, which must be considered for an interpretation of the photoelectron spectrum of this molecule. We report the first ab initio Green's function calculation of the ionization energies of a transition-metal complex, which leads to a satisfactory assignment of the photoelectron spectrum of bis(π-allyl)nickel.

Introduction

Photoelectron (PE) spectroscopy has proved an invaluable aid to the study of molecular electronic structure, particularly when combined with theoretical calculations of molecular ionization energies.[1] For molecules consisting of first- and second-row atoms, ionization energies obtained from ab initio calculations,[2] suitably scaled,[3] often provide a satisfactory assignment of the experimental spectra. More accurate values may be calculated by considering not only orbital relaxation effects (ΔSCF method) but also the differential correlation between the unionized and ionized species.[4] For transition-metal complexes, the situation is more complicated since Koopmans' theorem is often totally inadequate due to the considerably larger orbital relaxation that may arise from metal, compared to ligand, ionization.[4,5] For a range of transition-metal complexes, ΔSCF calculations, which include such differential orbital relaxation, have been extremely useful in assignment of the PE spectra. However, to date, the question of the role of correlation effects in the prediction of the ionization energies of transition-metal complexes has been largely unanswered, although a recent ab initio calculation has shown that differential electron correlation is important in determining the order of the low-lying ionic states of (η^4-cyclobutadiene)tricarbonyliron(0).[6] One can divide the correlation energy change upon ionization into two parts: a change due to the loss of an electron and a change due to relaxation. If relaxation is very large, it may be expected that the associated correlation effects will also be large, particularly in the valence region, due to the complicated charge rearrangement.

In this paper, we investigate the role of correlation effects in the ground and ionic states of the simplest transition-metal sandwich complex, bis(π-allyl)nickel, which has been the subject of both ab initio[7,8] and semiempirical MO calculations[9-11] designed in large measure to aid the assignment of the PE spectrum of this molecule.

Theoretical Considerations

There are two, well-proven approaches to the accurate calculation of the ionization energies of molecules lacking a transition-metal atom. In the first, SCF calculations are carried out on both the ground state and various ionic states, correlation effects being included by carrying out configuration interaction (CI) calculations on each state. Ionization energies are then obtained as the energy difference between the ground and ionic state (ΔSCF–CI method)[4]. To avoid carrying out individual calculations on both the unionized and various ionic states, several authors have used the single-particle propagator or Green's function techniques to calculate ionization energies directly, taking account of both relaxation and correlation effects. Both approaches have been successful in yielding ionization energies accurate to ~0.5 eV for a range of organic molecules[12,13] and accurate to ~0.2 eV for smaller molecules for which extended basis sets can be used.[14]

However, the extension of these methods to realistic transition-metal complexes that may be studied experimentally, presents formidable technical difficulties. Thus, a double-ζ representation of the valence orbitals, which is generally deemed the minimum size needed for a meaningful discussion of correlation effects, may generate more than 100 basis functions. The four-index transformation for such a basis size is a nontrivial computational problem. Furthermore, the size of the CI expansion generated from the large number of valence electrons in the complex, and from a basis of this size, may be upward of 5×10^5, again presenting computational problems. However, the implementation of quantum chemistry codes on vector processors,[15] combined with the development of direct CI methods,[16] has now resulted in the possibility of carrying out calculations on transition-metal complexes that include correlation effects. We now describe such calculations for bis(π-allyl)nickel.

Computational Details

The calculations were carried out by using contracted Gaussian functions. For carbon, the (9s5p) basis of Huzinaga[17] was contracted to (3s2p).[18] For hydrogen, the (4s)[17] primitive basis, contracted to (2s),[18] with a scale factor of 1.2, was used. The ligand basis is thus minimal for the core orbitals but of double-ζ quality for the valence orbitals. Two different basis sets were used for the nickel atom. The first, designated B1, was constructed from the (12s6p4d) functions of Roos et al.[19] 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 of 0.32 and 0.1481,[20] respectively, were added. These functions were contracted

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Table I. Calculated Ionization Energies (eV) of the Valence Orbitals of Bis(π-allyl)nickel (Basis B2)

ground state		ionization energy				
orbital	character	Koopmans' theorem	ΔSCF	ΔSCF–CI	extended 2ph–TDA[a–d]	$\sum P_i^e$
$7a_u$	π(L)	7.7	7.1	6.9	6.4	0.86
$6b_g$	$3d_{xz}$; π(L)	8.8	5.8	6.4	7.7	0.68
$11b_u$	π(L)	11.9	11.2	10.9	10.3	0.74
$13a_g$	$3d_{xy}$; π(L)	12.0	5.7	6.3	7.6	0.78
$12a_g$	σ(L)	14.2			13.5	0.80
$5b_g$	$3d_{yz}$	14.3			8.5	0.70
$11a_g$	$3d_{x^2-y^2}$	14.3			8.2	0.75
$6a_u$	σ(L)	14.7			13.3	0.75
$10b_u$	σ(L)	14.7			13.4	0.47
$4b_g$	σ(L)	15.0			13.7	0.68
$10a_g$	$3d_{z^2}$	15.8			8.8	0.75
$9a_g$	$3d_{xy}$, π(L)	16.6			11.5	0.64
$5a_u$	σ(L)	16.6			14.9	0.78
$3b_g$	σ(L)	17.5			15.1	0.68
$9b_u$	σ(L)	18.1			16.2	0.41
$8a_g$	σ(L)	19.3			16.5	0.80

[a] Basis B1. [b] The OVGF value for the $7a_u$ ionization is 7.1; for the other ionizations this method cannot be used. [c] This list of ionization energies is incomplete even in the low-energy region because of the appearance of satellite lines; see text. [d] If a larger MO basis and the Davidson diagonalization method are used, the extended 2ph–TDA method gives the lowest ionization energies of each representation to be as follows: a_u, 6.8; b_g, 8.3; b_u, 10.5 eV. [e] Summed pole strengths (relative intensities), the sum being over all orbitals of this symmetry that contribute intensity to this line.

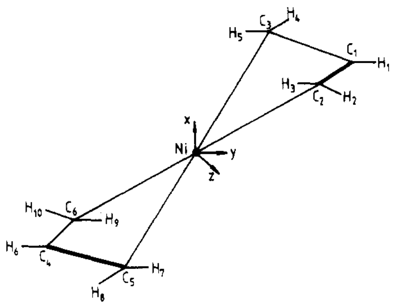

Figure 1. Choice of axis for bis(π-allyl)nickel.

(6s3p2d), giving close to a double-ζ representation of the valence region. The second and larger nickel basis, B2, was generated from the (14s9p5d) basis of Wachters,[21] with use of the contraction scheme outlined by Pitzer et al.[22] An additional *d* function was also appended,[20] giving a final contraction of (10s6p3d), close to a triple-ζ representation of the valence region. Basis B1 thus consisted of 99 contracted functions, and B2, 117 functions.

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,[23] the allyl groups being taken to be planar and to have idealized bond angles of 120°. The coordinate system used is shown in Figure 1.

Restricted Hartree–Fock (RHF) 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. Correlation effects were considered in all five states by carrying out CI calculations. In general, the CI expansion consisted of single and double excitations from a single root, the RHF configuration. All valence electrons, except the carbon 2s electrons were correlated in this way by using all the virtual orbitals.

The second method used in this paper to calculate the valence IEs is a Green's function method. The IEs and their relative intensities (pole strengths) appear as the poles and the residues 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 the ΔSCF–CI method. The method includes both correlation and relaxation effects. In the present work two distinct approximations to the one-particle Green's function are employed. These are discussed in detail in ref 24–27. In the outer-valence region where a one-particle picture holds for the physical description of the ionization process (i.e. where ionization can be reasonably well described by the ejection of an electron from a ground-state molecular orbital), the outer-valence Green's function (OVGF) may be used.[24,25] If there is very strong relaxation in the sense that the SCF orbitals for the ion are a strong mixture of the neutral ground-state SCF orbitals, plus the virtual orbitals, as is the case for bis(π-allyl)nickel for orbitals of a_g and b_g symmetry or if in a configurational expansion of the ionic wave function the single-hole configurations mix strongly with configurations involving ionization plus excitation, as is the case in the inner valence region, then the extended two-particle-hole Tamm–Dancoff method (extended 2ph–TDA) should be used.[26,27] This latter method is applicable in the entire valence region. Typical for the inner-valence region is the appearance of satellite lines, which borrow their intensity from the ionization processes that lead to simple hole states, and the possible disappearance of main lines with the intensity being distributed over many lines. This effect has been termed the breakdown of the molecular orbital model of ionization.[28] Both the OVGF and the extended 2ph–TDA methods are accurate to third order in the electron–electron interaction in the outer-valence region. However, in the inner-valence region, when the breakdown of the orbital model of ionization occurs, the structure of the ionization spectrum is only described qualitatively by the extended 2ph–TDA calculations. This is due to (a) the complicated configurational structure of the states and to the missing higher excitations and to (b) basis set inadequacies in the neighborhood of a continuum of states.

In the Green's function calculations all the filled valence orbitals, including the carbon 2s, and 20 or 37 virtual orbitals were employed. These calculations were carried out with basis B1. The extended 2ph–TDA calculations were performed in two ways. Firstly a calculation with 20 virtual orbitals was carried out to obtain all the ionic states up to about 30 eV IE (there are several hundred such states). In the second calculation, 37 virtual orbitals were employed to obtain a few of the lowest IEs by using the Davidson method for the diagonalization of large matrices.[29]

Computational Results

Ground State of Bis(π-allyl)nickel. The RHF calculations of the ^1A_g ground state yielded the same description of the bonding obtained previously by Veillard and co-workers,[7,8] the molecular energies obtained in bases B1 and B2, (−1736.7043 and −1739.5279 au respectively) being lower than those previously reported. The bonding picture that we find is similar to that given by these previous calculations, although the exact ordering of the closely spaced MOs is somewhat basis set dependent. The highest filled MO, $7a_u$, involves no metal character and derives from the

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Table II. Configuration Interaction Calculations on Bis(π-allyl)nickel (Basis B2)[a]

state	no. of confignsᵇ	total E	correln E
^1A_g	206 102	−1740.0215	0.4936
	410 594	−1740.0323	0.5044
^2A_g	472 203	−1739.7902	0.4721
	941 015	−1739.8008	0.4827
^2B_g	472 819	−1739.7873	0.4717
	942 259	−1739.7989	0.4833
^2A_u	472 822	−1739.7693	0.5017
	942 226	−1739.7842	0.5166
^2B_u	472 156	−1739.6196	0.5034
	940 912	−1739.6331	0.5169

[a] All energies are in atomic units. [b] The two entries for each state are for calculations using one and two reference configurations, respectively.

allyl a_2 π-MOs. The other MO involving these ligand orbitals, $6b_g$, is the second highest filled orbital and has the greatest contribution to the metal–ligand bonding, *via* interaction with the nickel $3d_{xz}$ orbital (we here use the conventional axis labeling in C_{2h}, rather than that used in ref 8). The antisymmetric combination of the ligand b_1 π-MOs, $11b_u$, is nonbonding, while the symmetric combination interacts with the metal $3d_{xy}$ orbital, leading to the $9a_g$ and $13a_g$ MOs. The $10a_g$, $5b_g$, and $11a_g$ MOs are mainly nonbonding, consisting of the metal $3d_{z^2}$, $3d_{yz}$, and $3d_{x^2-y^2}$ orbitals, respectively. The remaining valence orbitals involve mainly the σ-framework of the ligands. The energies of these valence orbitals are used in Table I, where it can be seen that Koopmans' theorem predicts the mainly metal ionizations to occur at considerably higher energy than the ligand π-ionizations.

A summary of the results of the CI calculations carried out by using atomic basis B2 on the neutral and ionized species is given in Table II. The results for basis B1 are similar. The first such calculation on the ^1A_g ground state used a single reference configuration, the RHF wave function and resulted in a CI expansion of length 206 102. It was found that the RHF configuration contributed 83% to this CI wave function, a value considerably less than that usually found for molecules lacking a transition-metal atom (>95%). The major correlating configurations were found to be the single and double excitations $6b_g \rightarrow 7b_g$, and $6b_g^2 \rightarrow 7b_g^2$. The $7b_g$ MO is the metal–ligand antibonding counterpart of the $6b_g$ bonding MO. Thus, the important $6b_g^2 \rightarrow 7b_g^2$ configuration yields the left–right correlation of the metal–ligand bonding electrons, a correlation effect absent in the isolated metal atom and allyl ligands. Both the $6b_g$ and $7b_g$ MOs are composed of Ni 3d and allyl π orbitals. However, the Ni 3d character is greater in $7b_g$ (43%) than in $6b_g$ (38%) so that this excitation corresponds to an increase in the population of the $3d(b_g)$ atomic orbitals. Although these two $6b_g \rightarrow 7b_g$ excitations are the most important, they contribute less than 2% of the total wave function. The effect of all the correlating configurations additional to the RHF configuration, which make up 18% of the total wave function, may be seen from a population analysis of the natural orbitals of this CI wave function. Such an analysis is shown in Table III. The major effects of correlation on the molecular charge distribution are (i) an increase in the $3d(b_g)$ populations and an associated decrease in the π-populations of the terminal carbon atoms of the allyl ligands, corresponding to correlation of the metal-ligand bonding electrons, and (ii) a smaller decrease in the population of the $3d(a_g)$ nonbonding electrons and an increase in the π-population of the central carbon atoms of the allyl ligands. This may be associated with in–out type correlation of the nonbonding 3d electrons.

The net result of these two effects is an increase in the metal 3d electron density and a decrease in the ligand π-density.

In view of the importance of the $6b_g^2 \rightarrow 7b_g^2$ correlating configuration, a second CI calculation was carried out, in which excitations from the RHF and from this second configuration were performed. As shown in Table II, this calculation consisted of >400 000 configurations, but yielded only an additional 0.01 au of correlation energy. Thus, the single-reference-configuration calculation is considered to give an adequate description of the correlation in this molecule.

Table III. Orbital Populations from RHF and CI Wave Functions for Bis(π-allyl)nickel

	population	
	RHF	CI
nickel orbital		
4s	0.417	0.420
4p	0.055	0.062
$3d_{xy}$	1.991	1.969
$3d_{xz}$	1.207	1.291
$3d_{yz}$	1.780	1.803
$3d_{x^2-y^2}$	2.029	2.015
$3d_{z^2}$	1.971	1.955
nickel atomic charge	+0.550	+0.485
carbon orbital[a]		
$2p_\pi$	0.892 (1.248)	0.922 (1.215)
$2p_\sigma$	1.877 (2.061)	1.868 (2.067)
carbon atomic charge	−0.040 (−0.656)	−0.064 (−0.628)
allyl charge	−0.273	−0.240

[a] The values are for the central carbon atom (C1), followed by those for the terminal carbon atom (C2) in parentheses.

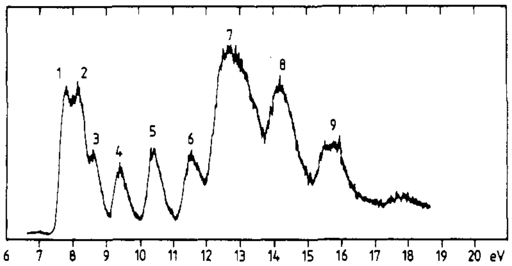

Figure 2. PE spectrum[30] of bis(π-allyl)nickel.

Calculated Ionization Energies of Bis(π-allyl)nickel. The valence ionization energies, calculated by the various methods, are summarized in Table I. As in previous studies,[7,8] Koopmans' theorem predicts the mainly metal 3d MOs ($10a_g$, $11a_g$, $5b_g$) to be considerably more tightly bound than the ligand π MOs ($7a_u$, $11b_u$). However, when direct SCF calculations are carried out on the ion states, the considerably greater reorganization energy associated with metal compared to ligand ionization, results in the ground state of the ion being predicted to be ^2A_g, arising from metal 3d ionization, in agreement with the calculations of Veillard and co-workers. The results of our CI calculations on the lowest four ion states of different symmetry are summarized in Table II. It is seen that considerably greater correlation energy is associated with the ^2A_u and ^2B_u states arising from ligand ionization than from the ^2A_g and ^2B_g states, which correspond to metal ionization. For the ^2A_u and ^2B_u states, the most important correlating configurations are similar to those in the ^1A_g ground state and involve the $7b_g$ MO, whose characters are similar in these ion states and in the ^1A_g ground state. Thus, the important correlation effects that we have identified in the ground state are also present in the ^2A_u and ^2B_u states and indeed appear to be slightly more important in the latter two, as witnessed by the somewhat greater correlation energy (Table II) and the slightly smaller contribution of the RHF configuration to the CI wave function (82%, compared with 83%). Thus, an increase in the nickel 3d correlation, associated with a decrease in ligand π-density, is indicated by these results.

Examination of both the metal orbital populations and the metal–ligand overlap populations in the RHF ^2A_u and ^2B_u states reveals values similar to those found in the ^1A_g ground state. Thus, similar correlation energies associated with the metal and metal–ligand bonding electrons in these three states are to be expected, as found by our CI calculations.

However, in the RHF ^2A_g and ^2B_g ion states, there is substantial electron reorganization accompanying metal electron ionization, leading to ligand → metal electron migration. As a result, the total metal 3d populations in the ^2A_g and ^2B_g ions are close to 9

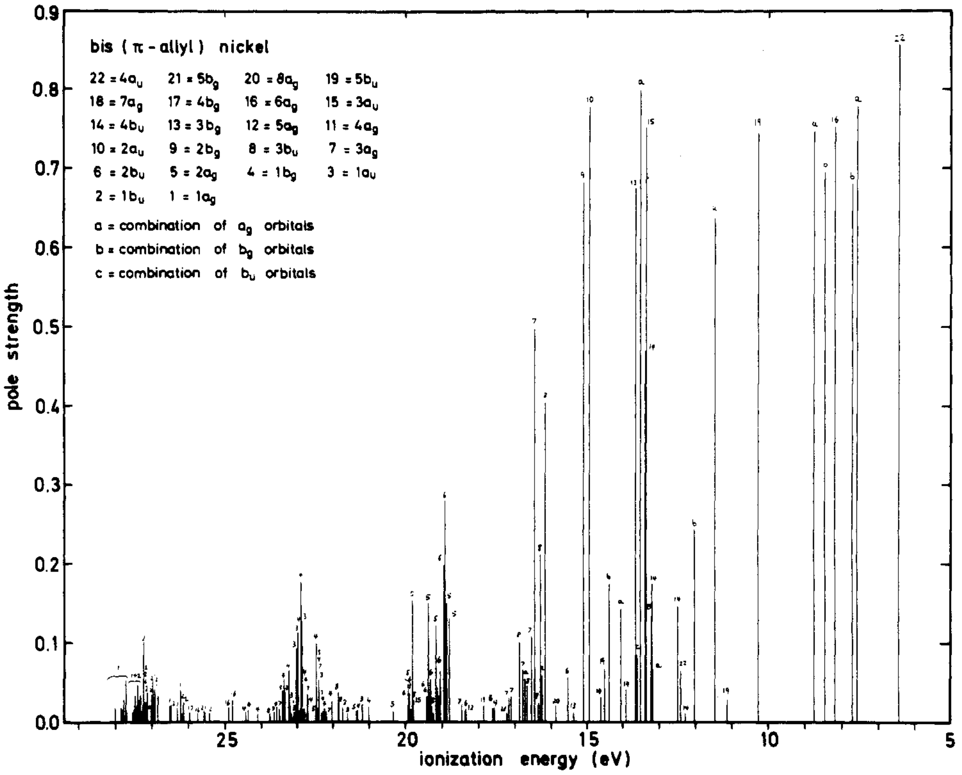

Figure 3. Theoretical ionization spectrum of bis(π-allyl)nickel in the entire valence region as calculated with the extended 2ph–TDA method. The numbering of the orbitals now refers to the valence orbitals and omits the core orbitals.

electrons (8.9 in both cases). The $3d_{xz}$ (b_g) population is 1.8 in the ^2A_g state and 1.4 in the ^2B_g state, so that there is no strongly metal–ligand bonding electron pair in either state, as witnessed by the decrease in the bond overlap populations in these two states compared with that in the ^1A_g ground state. There is thus a reduction of correlation energy in the ^2A_g and ^2B_g ion states compared to that found in the ^2B_u and ^2A_u ion states and in the ^1A_g ground state (Table II) associated mainly with the loss of the correlation energy associated with the metal–ligand bonding electrons in the $6b_g$ MO. The differential correlation energy associated with the ^2A_u, ^2B_u and ^2A_g, ^2B_g ion states is reflected in the ΔSCF–CI ionization energies shown in Table I. Thus, whereas the ^2A_g–^2A_u separation is 1.4 eV at the ΔSCF level, the introduction of electron correlation reduces this difference to 0.6 eV. However, at both the ΔSCF and ΔSCF–CI levels, the ground ionic state is predicted to be ^2A_g.

The ionization energies calculated by the extended 2ph–TDA approximation (Table I), are, as expected, closer to the ΔSCF–CI than to the ΔSCF results. However, the electron reorganization and correlation given by this method now places the ^2A_u as the ground ionic state, separated by 1.2 eV from the ^2A_g state. This method also allows all the valence ionization energies to be calculated, rather than just the first of each symmetry given by our ΔSCF–CI calculations.

We now discuss the valence PE spectrum of bis(π-allyl)nickel in the light of these calculations.

Photoelectron Spectrum of Bis(π-allyl)nickel. The PE spectrum of bis(π-allyl)nickel (Figure 2) shows nine bands below 17 eV and was originally assigned by Batich[30] on the basis of methyl substituent effects and by using both He I and He II radiation, as follows: The first, third and fourth bands are due to nickel 3d ionizations. The second is due to 3d plus a ligand π orbital, and the fifth and six are due to ligand π orbitals. On the basis of a comparison of the PE spectra of a series of nickel, palladium, and platinum bis(π-allyl) derivatives an alternative assignment has been presented.[10] Here the first and fifth bands arise from the $7a_u$ and $11b_u$ ligand MOs, respectively, bands two and three arise from the mainly metal $9a_g$, $10a_g$, $11a_g$, and $5b_g$ MOs, and bands four and six arise from the $6b_g$ and $13a_g$ orbitals, respectively, having significant ligand π-character. Bands seven–nine are assigned to orbitals of allyl σ-character. A Green's function approach based upon the semiempirical INDO method yields[11] an assignment in complete agreement with the above, although it is of interest to note that the INDO method predicts considerably smaller deviations from Koopmans' theorem than are given by ab initio methods. Our ab initio Green's function calculation yields an assignment of the PE spectrum close to that deduced by Böhm et al. In particular the ground ionic state is predicted to be ^2A_u. The major difference is an interchange of the $9a_g$ and $13a_g$ MOs. However, both MOs have similar atomic orbital characters so that any distinction between them must be somewhat arbitrary. In addition the ordering of the closely spaced states arising from the $6b_g$ and $10a_g$ MOs is inverted in our calculation.

Table IV. Assignments of the Photoelectron Spectrum of Bis(π-allyl)nickel

		assignment		
band	IE, eV	I[a]	II[b]	III[c]
1	7.7	3d, 3d	$7a_u$	$7a_u$
2	8.1	$\pi(a_u)$, 3d	$5b_g$, $9a_g$	$13a_g$, $6b_g$
3	8.5	3d	$10a_g$, $11a_g$	$11a_g$, $5b_g$
4	9.4	3d	$6b_g$	$10a_g$
5	10.3	$\pi(b_u)$	$11b_u$	$11b_u$
6	11.5	$\pi(a_g)$	$13a_g$	$9a_g$
7	12.7		$6a_u$, $10b_u$, $12a_g$, $4b_g$	$6a_u$, $10b_u$, $12a_g$, $4b_g$
8	14.2		$5a_u$, $3b_g$	$5a_u$, $3b_g$
9	15.6		$9b_u$, $8a_g$	$9b_u$, $8a_g$

[a] Reference 30. [b] Reference 10, with orbital labeling of Table I. [c] This work, extended 2ph–TDA (Basis B1).

The valence ionization spectrum as obtained by the extended 2ph–TDA method in the energy range up to about 30 eV is presented in Figure 3. The spectrum is drawn as a line spectrum with the numbers giving the orbitals from which the intensity is obtained. In the energy range up to 11 eV, the lines have a large relative intensity, but frequently the intensity is borrowed from many ground-state orbitals, particularly in the case of a_g and b_g symmetries. This is a reflection of the strong electron reorganization in the electron ejection from orbitals with a strong nickel

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d character. Already at about 11 eV, satellite lines start to appear and they soon become dense in energy. It is thus clear that the PE spectrum above 10 eV cannot be explained without the consideration of satellite lines. A detailed discussion is however not meaningful as only the qualitative aspects are amenable to a calculation for this molecule and because the calculation is only strictly applicable in the limit of high-energy exciting radiation. Above about 17 eV the density of lines becomes very large, and we observe the effect of the breakdown of the molecular orbital model of ionization. There are thus no more simple hole states.

Conclusions

The extensive CI calculations we have described have identified the importance of correlation of the metal–ligand bonding electrons in bis(π-allyl)nickel, leading to an increase in the Ni 3d population compared to that given by an RHF description. Whereas differential relaxation effects lead to a larger *decrease* in the Ni 3d ionization energies than those of the ligand π-electrons, differential correlation effects are found to lead to a significant *increase* in the metal 3d ionization energies, but to a small decrease in ligand π-ionization energies. Thus, both relaxation and correlation effects need to be considered to discuss the PE spectrum of bis(π-allyl)nickel. It is probable that the ΔSCF–CI calculations underestimate this differential correlation, by predicting the ground ionic state to be ^2A_g compared with the more likely ^2A_u contender. We have described the first calculation of the valence ionization energies of a transition-metal complex using an ab initio Green's function formalism. We find that the extended 2ph–Tamm–Dancoff approximation leads to an extremely satisfactory assignment of the PE spectrum.

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Infrared Matrix-Isolation Study of the 1/1 Molecular Complexes of Chlorine Monofluoride with Oxygen-Containing Bases

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The matrix-isolation technique has been successfully employed for the isolation and characterization of the complexes formed between chlorine monofluoride, ClF, and a variety of oxygen-containing bases. Twin-jet deposition of reactants was employed throughout, with either argon or nitrogen as the matrix material. All of the complexes isolated were characterized by the stretching vibration of the perturbed ClF subunit in the complex, shifted to lower energies by 50–100 cm^{-1}. For many of the complexes, a 3/1 doublet was observed, indicative of ^{35}Cl–^{37}Cl splitting in natural abundance. For each base, one or more perturbed vibrational modes were observed; typically, these were modes that involved motion of the oxygen atom in the base, suggesting that the interaction in the complex is through the chlorine of the ClF subunit to the oxygen atom of the base. Comparison of the spectra of the complexes observed here with those of previous studies suggests that ClF is a medium-strength Lewis acid, falling roughly between SiF_4 and GeF_4 in terms of acidity.

Introduction

The study of molecular complexes has increased in importance to chemists in all fields in the past 30 years.[1] An understanding of the nature of the interaction may be gained, trends in reactivities may be formulated, and intermediates in chemical reactions may be characterized. The discovery and interpretation of the charge-transfer spectrum of the I_2/C_6H_6 system led to a revival of interest in this area.[2] Mulliken and others who followed were able to extend Lewis acid–base theory in quantum-mechanical terms.[3-5] A number of other halogen-containing systems have been studied experimentally since this early work,[6-8] but little is known about the molecular complexes of chlorine monofluoride, ClF, in large measure due to the high reactivity of ClF at room temperature. The matrix-isolation technique was developed for the study of such highly reactive species.[9,10] and their reaction products. Twin-jet deposition, in which each reagent is deposited from a separate vacuum line, allows for a very brief mixing period directly in front of the cryogenic surface, before the initial reaction products are trapped in an inert matrix. In this manner, complexes of ClF with avariety of Lewis bases might be isolated, prior to further reaction.

While little is known experimentally about the complexes of ClF, considerable theoretical attention has been given these species.[11-13] For example, workers have calculated that the $ClF{\cdot}NH_3$ complex should be quite strongly bound, by roughly 8 kcal/mol, which is considerably more than the interaction energy in typical charge-transfer complexes. This, in turn, has led to the suggestion that a number of contributions to the binding energy are important, including an electrostatic interaction, a charge-transfer term, polarization effects, and exchange repulsion. Examination of the infrared spectra of molecular complexes of ClF may provide qualitative information about the binding in the product species, and the spectral properties of the complexes can be correlated with selected molecular parameters of the Lewis bases in question. Consequently, a study was undertaken to examine a range of molecular complexes of ClF with oxygen-containing bases in low-temperature, inert matrices.

Experimental Section

The experiments described herein were carried out on a conventional matrix-isolation apparatus, which has been described previously.[14] Acetone (Fisher), methanol (MCB), diethyl ether (Fisher), and furan (Fisher) were introduced into the vacuum system as the vapor above the liquid, after being degassed through repeated freeze–thaw cycles. ClF (Pennwalt), ethylene oxide (C_2H_4O, Matheson), dimethyl ether (Math-

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