106. The Photoelectron Spectra of Ni, Pd, Pt-Diallyl[1])

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Summary

The He(I) photoelectron (PE.) spectra of bis(π-allyl)palladium (**2a**), bis(π-allyl)platinum (**3a**), bis(π-methallyl)palladium (**2b**) and bis(π-methallyl)-platinum (**3b**) have been recorded and compared with the PE. spectra of bis(π-allyl)nickel (**1a**) and bis(π-methallyl)nickel (**1b**). By use of the He(II) PE. spectra **2a**, **2b** and **3b** and correlations between the PE. spectra of **1**-**3** it is possible to assign the first seven to eight transitions in the PE. spectra of **1**-**3**. In contrast to previous assignments it is shown that the first band in the PE. spectrum of **1a** corresponds to the ejection of an electron from $7a_u$, a pure ligand orbital. The assignment proposed is supported by semiempirical calculations of the INDO-type by considering the relaxation effects explicitly using the ΔSCF and transition operator method.

The vast and growing amount of transition metal complexes has led to various theoretical approaches and concepts to rationalize their structure and reactivity. In case of nonmetal compounds low energy photoelectron spectroscopy [2] [3] was of great help in unraveling their electronic structure.

Based on the validity of *Koopmans'* theorem ($-\varepsilon_J = I_{V,J}$) [4] it is possible to obtain information regarding the electronic structure of a molecule in the ground state from measuring its vertical ionization potentials. In the case of transition metal complexes, however, there is ample evidence that *Koopmans'* theorem is no longer valid. The relaxation contributions to ionization events from electrons predominantly localized at the metal site are so important that the measured ionization potentials cannot be identified with one-electron energies (orbital energies) of the ground state. Typical examples for transition metal compounds which show marked *Koopmans'* defects due to relaxation are metallocenes like ferrocene [5], dibenzene-chromium [6] or cyclopentadienylnitrosylnickel [7] various tricarbonyliron-com-

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[1]) Part 6 of the series: 'Electronic Structure of Metalorganic Compounds. For Part 5 see [1]. Part of the dissertation by *M.C. Böhm*, T.H. Darmstadt 1980.

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plexes [8] and different other carbonylmetal compounds [9]. The most popular example for the non validity of *Koopmans'* theorem, however, is bis(π-allyl)nickel (**1a**).

MO-Model and Previous PE. Assignments of 1a. - In *Figure 1* we have shown the highest occupied MO's of **1a** assuming C_{2h} symmetry. The energy levels and wave functions are obtained from a recently developed semiempirical INDO-method which includes 3d-transition metals [10]. The 3d-levels of the central atom are split in this figure due to their different interaction with the σ-frame of the diallyl units. The $3d_{xz}$, and to some extent $3d_{yz}$, interact with the σ frame of the allylic part and thus are destabilized with respect to $3d_{z^2}$, $3d_{xy}$ and $3d_{x^2-y^2}$.

The main outcome of this diagram is in line with results obtained from calculations of the *Wolfsberg-Helmholtz* type [11] and *ab initio* calculations [12].

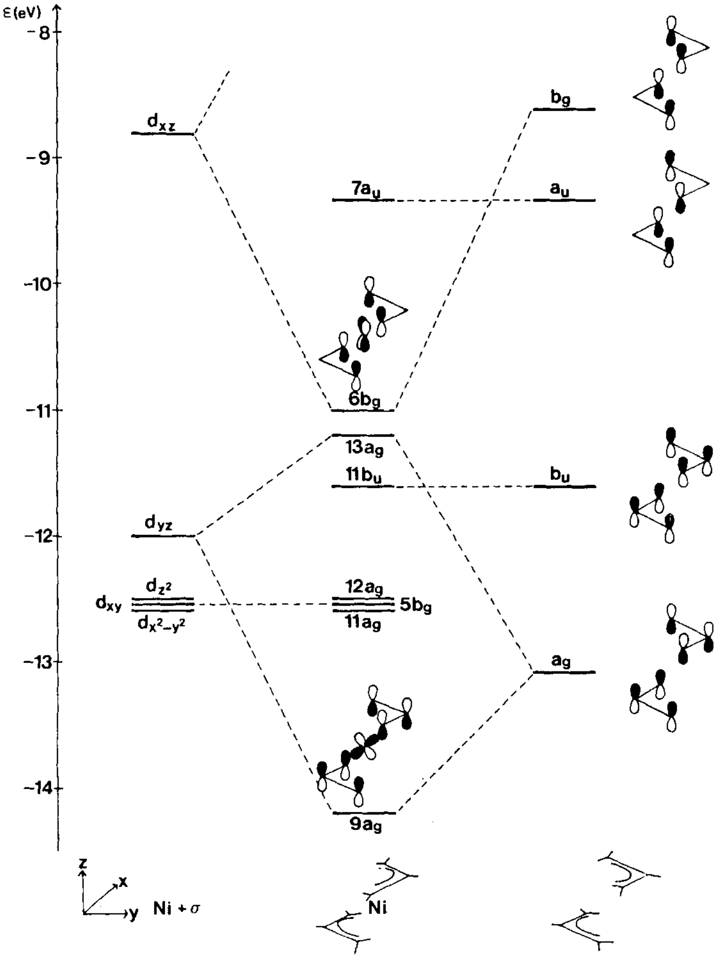


Fig. 1. *Interaction diagram between the 3d-orbitals of Ni and the π-orbitals of the allylic moieties of* **1a**. The 3d orbitals of Ni are split due to the interaction with the σ-orbitals of the ligands.

Table 1. *Orbital energies, ε_i, MO type and the contribution of Ni, π and σ to each MO for bis(π-allyl)nickel* **(1a)**

MO number	Orbital	MO-type	$-\varepsilon_i$(eV)	% Ni 3d	% diallyl π	% allyl σ
22	$7a_u$	π	9.12		99.04	
21	$6b_g$	$3d_{xz}+\pi$	11.04	46.34	41.63	12.03
20	$13a_g$	$3d_{yz}-\pi$	11.15	66.60	21.67	11.73
19	$11b_u$	π	11.42		92.94	7.06
18	$12a_g$	$3d_{z2}$	12.44	96.05	1.50	2.45
17	$5b_g$	$3d_{xy}$	12.48	95.71	0.72	3.57
16	$11a_g$	$3d_{x2-y2}$	12.51	92.90	4.15	2.95
15	$6a_u$	σ	13.92			100.00
14	$10b_u$	σ	14.09		5.33	94.67
13	$10a_g$	σ	14.27	5.84	8.31	85.85
12	$4b_g$	σ	14.41	12.54	1.20	86.26
11	$9a_g$	$\pi+3d_{yz}$	14.44	26.18	63.36	5.46
10	$5a_u$	σ	16.76			100.00
9	$3b_g$	σ	16.87	4.38		95.62
8	$9b_u$	σ	18.43			100.00
7	$8a_g$	σ	19.06	3.76		96.24

In *Table 1* the calculated ground state MO's are characterized by their irreducible representations, their type (*e.g.* π, 3 d) and their energy.

The highest occupied molecular orbital (HOMO) is predicted to be the in phase linear combination of the two nonbonding allylic π-orbitals. Due to its symmetry *(A_u)* interaction with 3 d-orbitals is not possible. It is found that the HOMO ($7a_u$) is localized to 99% at the four terminal p_z-AO's of the allylic part. Next in energy are predicted two MO's, $6b_g$ and $13a_g$, with considerable 3 d-participation followed by an orbital ($11b_u$) which is a pure π-orbital centered at the allylic moieties. The next three orbitals, almost degenerate in energy, are predominantly localized at the Ni-center of **1a**. The interaction between Ni-3d_{z2}, $-3d_{x2-y2}$ and $-3d_{xy}$ with the wave functions centered at the allylic part is negligible. Between these pure metal orbitals and $9a_g$ four σ-levels ($6a_u$, $10b_u$, $10a_g$ and $4b_g$) are predicted. The Ni-3 d contribution to $10a_g$ and $4b_g$ is small compared to the 3 d-intermingling in $9a_g$. As can be seen from *Figure 1* considerable interaction arises only between $b_g(\pi^*)$ and Ni-3d_{xz} and $a_g(\pi)$ and Ni-3d_{yz}. The interaction between $b_g(\pi^*)$ and Ni-3d_{xz} leads to a stabilization of the occupied metal orbital while the latter interaction ($a_g(\pi)-3d_{yz}$) leads to a net destabilization. Our MO-analysis just presented is confirmed by the population analysis given in *Table 2.* It clearly displays the donor-acceptor interaction between Ni-3d_{xz} and $b_g(\pi^*)$. For Ni-3d_{xz} the calculated occupation number is 1.3692, for all other Ni-3 d orbitals the values obtained are close to 2. Due to the metal-π^*-interaction charge is transferred to the p_z-functions of the terminal C-atoms. As a result of this charge transfer the net charge of -0.51 is predicted at the terminal C-atoms while the central C-atoms of the allylic units are nearly neutral (-0.06). The MO-sequence and the calculated populations with the INDO-procedure are very close to values obtained by double zeta *ab initio* calculations [12].

The assignment of the low energy PE. spectrum of **1a** has been the subject of controversy since its publication [13]. Ligand-field considerations [13] as well as

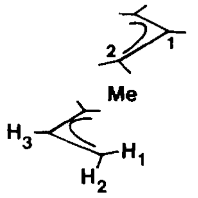
Table 2. *Population analysis for bis(π-allyl)nickel* (**1a**) *(ground state).* For the choice of axis see *Figure 1.* For the numbering see formulas in text

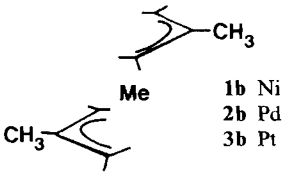
	Ni	C_1	C_2	H_1	H_2	H_3
s	0.0478	1.0463	1.1285	0.8793	0.8444	0.8695
p_x	0.0217	1.0392	1.0555			
p_y	0.0151	1.0549	1.0485			
p_z	0.0267	0.9199	1.2747			
d_{z^2}	1.9978					
d_{xz}	1.3692					
d_{yz}	1.9821					
$d_{x^2-y^2}$	1.9359					
d_{xy}	1.8207					
Net charge	0.7833	– 0.0603	– 0.5073	0.1207	0.1556	0.1305

ab initio calculations of different levels of sophistication [12] led to quite different assignments. Recently a comparison between the He(I) PE. spectra of **1a** and its various methyl substituted derivatives bis(π-methallyl)nickel (**1b**), bis(π-crotyl)-nickel (**1c**) and bis(π-1,3-dimethallyl)nickel (**1d**) has been published [14]. An analysis of the methyl induced shifts of the PE. bands together with intensity arguments and a comparison between the He(I)/He(II) PE. spectra of **1b** led to the following assignment of the PE. spectrum of **1a**: The first, third and fourth band is due to ionization from 3d-orbitals localized at the Ni-atom. The second in part, the fifth and the sixth band is due to ionization from ligand π-orbitals.

Current Investigations. – *PE. Spectra of Ni-, Pd-, and Pt-Bisallylderivatives.* – *Qualitative Assignment.* The new assignment for **1a** [14] substantially reduces the continuing disagreement between experiment and theoretical *Koopmans'* type calculations. It rests, however, mainly on qualitative arguments concerning methyl substituent effects. To check the given assignment we have extended the experimental investigations to the bis(π-allyl) derivatives of Pd and Pt on one side and improved the methods of semiempirical calculations on the other. In the following we compare the PE. spectra of **1a** and **1b** with the corresponding Pd- and Pt-compounds listed below.

1a Ni
2a Pd
3a Pt





1b Ni
2b Pd
3b Pt

The He(I) spectra of **2a**, **2b** and **3a**, **3b** are compared in *Figure 2* with those of **1a** and **1b** and the vertical ionization potentials, $I_{V,J}$, are collected in *Table 3.* To aid the assignment of the spectra we also recorded the He(II) spectra of **2a**, **2b** and **3b** *(Fig. 3).* Furthermore we make use of the observation that the PE. cross sections of metal 3d-orbitals and ligand MO's differ significantly. In nickelocene [15] and ferrocene [16] [17] it was found that the intensity ratio between a ligand-

MO and a metal 3d-orbital amounts to 1.60:1.00, *i.e.* the π-cross section is found to be greater by almost 60% than the metal 3d-cross section. By increasing the energy of the light source (He(I) to He(II)) the intensity of the bands due to ejection of metal electrons increases when compared with bands which are mainly due to ligand ionizations [8] [9]. Within the series 3d-4d-5d the cross section for the d-orbitals steadily is enhanced relative to the cross section of the ligand. This effect has been demonstrated for carbonyl compounds of Cr, W[2], Mn, Re[18] as well as for ferrocene and ruthenocene [16]. In a large variety of organometallic systems it was found that in 4d-complexes the cross section between ligand-π and metal-4d ionization is about the same [19].

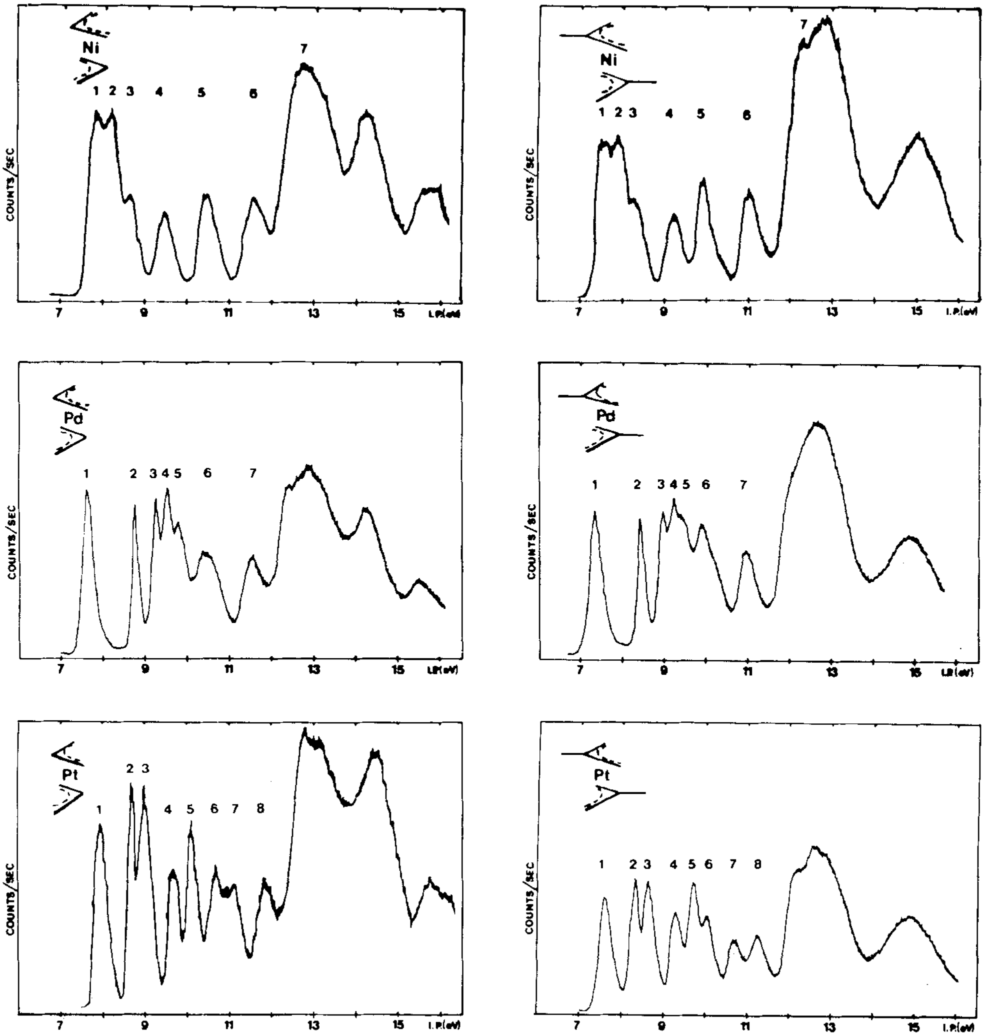


Fig. 2. *He(I) spectra of* **1a**, **1b**, **2a**, **2b** *and* **3a**, **3b**

To start with our qualitative assignment we look for bands that remain nearly constant in energy within the series **1a**-**3a** and **1b**-**3b** respectively. These peaks must correspond to ionizations from ligands since they are not influenced by metal exchange. The two most important reference peaks correspond to ionizations from $7a_u$ and $11b_u$ (we assume the same symmetry (C_{2h}) for all complexes for reasons of simplicity and in case of the Pd- and Pt-complexes the additional core electrons were neglected in order to retain the same orbital numbering scheme as for **1a**). In the bis(π-allyl) series we find three ionization potentials showing only small variations under exchange of the central atom. It is the first peak in **1a**, **2a** and **3a** at 7.76 eV (Ni), 7.56 eV (Pd) and 7.91 eV (Pt). The next correspondence is found between band ⑤ of **1a** at 10.38 eV, band ⑥ of **2a** at 10.45 eV and band ⑥ of **3a** at 10.73 eV. A

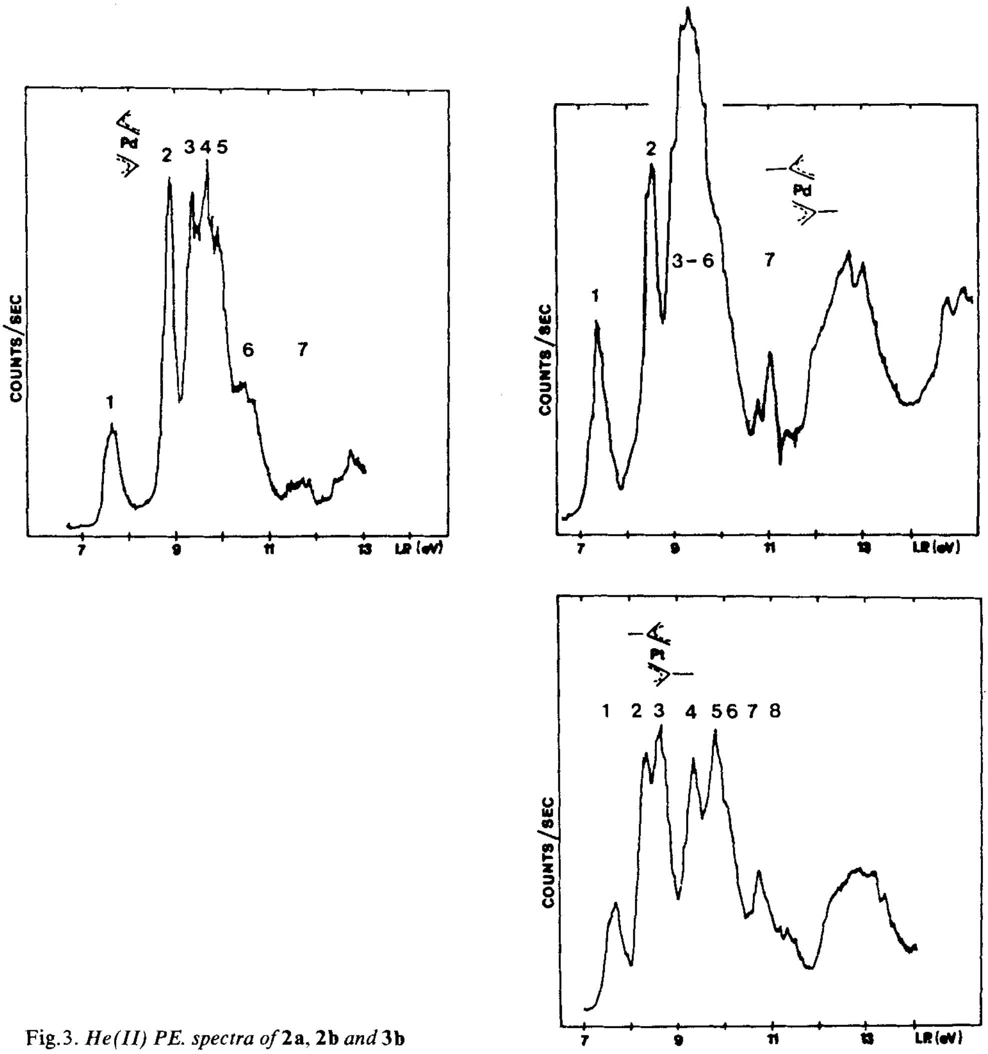


Fig. 3. *He(II) PE. spectra of* **2a**, **2b** *and* **3b**

Table 3. *Vertical ionization potentials* $I_{V,J}$ *for the bis(π-allyl) complexes* **1a**-**3a** *and the bis(π-methallyl) compounds* **1b**-**3b**. All values in eV

Peak	**1a**	**2a**	**3a**	**1b**	**2b**	**3b**
①	7.76	7.56	7.91	7.53	7.33	7.65
②	8.19	8.72	8.64	7.91	8.45	8.37
③	8.58	9.25	8.95	8.32	8.97	8.68
④	9.40	9.51	9.65	9.22	9.25	9.37
⑤	10.38	9.78	10.14	9.86	9.45	9.81
⑥	11.55	10.45	10.73	10.93	9.93	10.12
⑦	12.70	11.57	11.15	12.20	11.01	10.80
⑧			11.90			11.35

third series correlates band ⑥ of **1a** at 11.55 eV with band ⑦ of **2a** and band ⑧ of **3a** at 11.57 eV and 11.90 eV respectively. A similar correlation pattern is found in the bis(π-methallyl) series **1b**-**3b**. The corresponding vertical ionization potentials together with the series of constant ionization potentials in the bis(π-allyl) compounds are listed in *Table 4*.

A very reasonable assignment for this correlation is $7a_u$ for the first, $11b_u$ for the second and $9a_g$ for the third series (see also *Fig. 1*). This assignment for the first band is in case of **1a** in contrast to all previous ones.

A further substantiation of the assignment of the first band can be found by considering the first ionization potential of the allyl radical. The first peak in the PE. spectrum of this species is found at 8.13 eV [20]. In the bis(π-allyl) complexes **1a**, **2a** and **3a** each allylic moiety is partially negative charged (~ −0.4 e for each allyl fragment in **1a**). As a result of this charge the ionization potential corresponding to $7a_u(\pi)$ in the bis(π-allyl)complexes of Ni, Pd, Pt should be lower than 8.13 eV. Inspection of *Table 3* shows that only the first band meets this demand. Additional support is found if we assume that the orbital relaxation for the ionization out of $7a_u$ and $9a_g$ is of comparable size. A simple *Hückel* model predicts a splitting between both allyl MO's of 1.414 β. With a β-parameter of 2.70 eV [21] one calculates an energy difference of 3.8 eV between both MO's. This value is close to the observed differences of 3.79 eV, 4.01 eV and 3.99 eV for **1a**, **2a** and **3a** respectively.

If we adopt the assignment just discussed the bands of **1a** and **1b** at lower energy than 10 eV have to be assigned to ionization events from orbitals with dominant 3d-character. The integrated intensity of peak ② and ③ compared with peak ⑤ or

Table 4. *Assignment of the bands belonging to ionizations from ligand orbitals.* All values in eV

	1a	**2a**	**3a**	**1b**	**2b**	**3b**
Band	①	①	①	①	①	①
I_V	7.76	7.56	7.91	7.53	7.33	7.65
Band	⑤	⑥	⑥	⑤	⑥	⑥
I_V	10.38	10.45	10.73	9.86	9.93	10.12
Band	⑥	⑦	⑧	⑥	⑦	⑧
I_V	11.55	11.57	11.90	10.93	11.01	11.35

⑥ is 2.30:1.00. This ratio is compatible with four ionization events with dominant Ni-3d contribution. A value of 0.58 (2.30:4) for the ratio Ni-3d/ligand-π is in close agreement with the already mentioned ratio of 0.6 found in other cases [15-17]. This leads us to assign peak ② and ③ to ionizations arising from $13a_g$-, $12a_g$-, $5b_u$- and $11a_g$-orbitals with 67, 96, 96 and 93% Ni-3d character.

The remaining peak in the PE. spectrum of **1a** below 10 eV is band ④ at 9.40 eV. The intensity ratio between band ④ and ⑤ or ⑥ is found to be 0.80:1. This means that the ionization must arise from a molecular orbital with an amount of 3d-participation intermediate between the four metal orbitals and the ligand MO's. There is only one orbital left which meets this demand, namely $6b_g$, the bonding combination between Ni-3 d_{xz} and -b_g (π^*) with 46% metal contribution (see *Fig. 1*). Inspection of *Table 3* and *Table 1* completes the qualitative assignment of the remaining bands in the PE. spectrum of **1a**. The band with its maximum at 12.70 eV corresponds to ionizations from the C,C-σ-orbitals $6a_u$, $10b_u$, $10a_g$ and $4b_g$. Band ⑧ at 14.20 eV and band ⑨ at 15.50 eV arise from the C,H-σ-orbitals $5a_u$, $3b_g$, $9b_u$ and $8a_g$ respectively.

Molecular Orbital Scheme of Bis(π-allyl)palladium and -platinum. With the aid of arguments based on overlap criteria we extrapolate the INDO-results obtained for **1a** to the Pd- and Pt-derivatives **2a** and **3a**. The geometrical changes in replacing Ni by Pd are obtained by comparing the results of the X-ray data of **1b** [22] with those of similar Pd-allyl complexes [23]. The mean Ni-C distance is found to be 2.0 Å, that of Pd-C is found to be 2.1 Å. A comparison between the structures of equivalent Pd- and Pt-complexes shows that the exchange of the two metal atoms does not change the bond lengths or bond angles in the molecules. Therefore we assume the same geometry for **2a** and **3a**. The overlap integrals between metal d-orbitals and allyl π-levels for Ni, Pd and Pt as central atom with a mean metal-carbon distance of 2.0 Å (Ni) and 2.1 Å (Pd, Pt) are given in *Table 5*. The 3d-, 4d-, 5d-single-zeta exponents used were taken from the work of *Burns* [24].

A rationalization of the results given in *Table 5* shows that the value for the overlap integrals between metal-d_{z^2} and the ligand π-orbitals is smallest. Thus the d_{z^2}-orbital should essentially be unaffected by the ligands. The $d_{x^2-y^2}$ and d_{xy}-orbitals, however, show a remarkable interaction with the allylic ligands. One expects that $d_{x^2-y^2}$ is destabilized by interaction with the $a_g(\pi)$-combination of the ligands which is predicted to increase in the series Ni-Pd-Pt. The d_{xy}-orbital on the other hand should be stabilized due to the bonding interaction with $b_g(\pi^*)$. Both

Table 5. *Metal-d-carbon overlap in bis(π-allyl)nickel, bis(π-allyl)palladium and bis(π-allyl)platinum* (*Burns*-single-zeta exponents were used for 3d, 4d and 5d functions)

Metal-d-component	p_zC_1			p_zC_2/C_2'		
	Ni	Pd	Pt	Ni	Pd	Pt
d_{z^2}	0.0086	0.0305	0.0786	0.0087	0.0294	0.0778
d_{xz}	0.0000	0.0000	0.0000	0.0318	0.0829	0.1273
d_{yz}	0.0370	0.0936	0.1455	0.0179	0.0533	0.0819
$d_{x^2-y^2}$	0.0295	0.0800	0.1424	0.0152	0.0338	0.0594
d_{xy}	0.0000	0.0000	0.0000	0.0251	0.0742	0.1305

trends, together with the increasing electronegativity [25] lead to the split of the three metal levels as indicated in *Figure 4.*

PE. spectra of Bis(π-allyl)palladium and Bis(π-allyl)platinum. In the Pd-allyl systems **2a** and **2b** the π-orbitals have already been tentatively assigned (see *Table 4*). The next task is to identify the ionization potentials from orbitals with dominant metal character. In **2a** the bands which remain to be assigned are those at 8.72 eV and the three overlapping peaks at 9.25 eV, 9.51 eV and 9.78 eV. The corresponding bands of the bis(π-methallyl) complexe **2b** arise at 8.45 eV and 8.97 eV, 9.25 eV and 9.45 eV respectively (see *Fig. 2* and *3* and *Table 3*). From the orbital correlation diagram shown in *Figure 4* the interpretation of these bands is straightforward since we expect similar reorganization effects for the corresponding ionization events.

What remains is an assignment of the band corresponding to the $6b_g$-orbital, the bonding combination between $b_g(\pi^*)$ of the allylic moieties and $4d_{xz}$ of Pd. To locate this band we have measured the He(II) spectra of **2a** and **2b** shown in *Figure 3.* Comparison of the bands ②, ③, ④ and ⑤ in the He(I) and He(II) PE. spectra of both compounds show a comparable enhancement of the intensity compared with the ligand peaks ①, ⑥ and ⑦. From this we estimate that the band corresponding to $6b_g$ must be situated in the range 9.25 to 9.78 eV in **2a** and 8.97 eV to 9.45 eV in **2b**. The corresponding bands in case of the related Ni-complexes **1a** and **1b** are found at 9.40 eV and 9.22 eV respectively.

Finally we have to discuss the remaining bands in the PE. spectra of **3a** and **3b**. (The bands corresponding to ejection from ligand orbitals have been assigned as

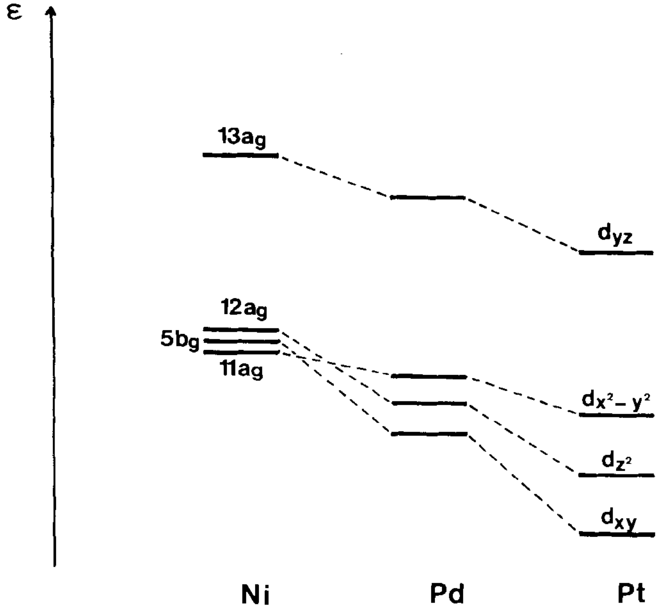


Fig. 4. *Estimated behaviour of the metal AO's* d_{yz}, $d_{x^2-y^2}$, d_{z^2}, *and* d_{xy} *in the series* **1a–3a** *by considering the overlap integrals with the ligand π-orbitals and the electronegativity of the central atom*

listed in *Table 4*.) In *Figure 5* we have compared the first bands in the series **1a**–**3a** with the corresponding bis(π-methallyl) complexes **1b**–**3b**.

We notice a shift of 0.2–0.3 eV for those bands which correspond to MO's mainly localized at the metal center or at the terminal allyl centers but a shift of 0.5–0.6 eV for bands which correspond to the ligand MO's $9a_g$ and $11b_u$. In **1a**–**1b** and **2a**–**2b** the bands $9a_g$, $11b_u$ follow each other; in case of **3a**–**3b**, however, another band appears inbetween. The assignment of bands ②, ③, ④ and band ⑤ in the Pt compounds **3a**–**3b** seems to be straightforward on the basis of the correlation diagram shown in *Figure 4*. A further confirmation of the assignments for band ② to ⑤ is found by comparing the He(I) and He(II) PE. spectra of **3b**. This shows a considerable increase of intensity of bands ② to ⑤ compared to band ①. The relative intensity ratios are:

Band	②	③	④	⑤
He(II)/He(I)	1.40	1.58	1.80	1.60

These ratios are in line with the diagram given in *Figure 4*. It suggests the strongest interaction between a 5d-orbital and a ligand orbital for the MO leading to the second band and the weakest interaction ($5d_{z^2}$) for the fourth level. The interactions for peak 3 ($5d_{x^2-y^2}$) and 5 ($5d_{xy}$) in *Figure 4* are predicted to be comparable.

The remaining peak in the PE. spectrum of **3a** at 11.15 eV (**3b**, 10.80 eV) is assigned to the ionization from $6b_g$. The comparison between He(I) and He(II) PE. spectra shows considerable metal character for the corresponding band in the spectra of **3b**.

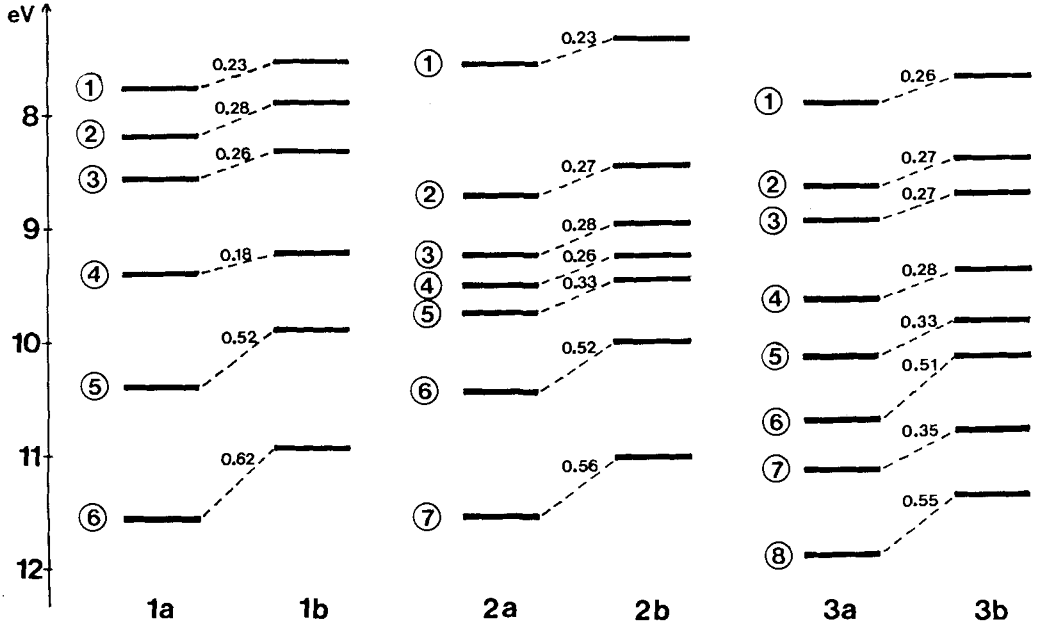


Fig. 5. *Comparison of the first PE. bands in the series* **1a**–**1b**, **2a**–**2b** *and* **3a**–**3b**

In *Figure 6* we have summarized the correlations discussed in the PE. spectra of **1a**, **2a** and **3a**. A similar correlation diagram is found for **1b**, **2b** and **3b**.

Calculations. In order to check our qualitative assignments and to estimate the relaxations involved by generating the various ionic states we have carried out detailed calculations based on our recently developed semiempirical INDO-method [10]. Under the assumption of the validity of *Koopmans'* theorem [4] the Jth vertical ionization potential $I^K_{V,J}$ is given by:

$$I^K_{V,J} = -\varepsilon_J = E^{\text{unrelaxed}}_{+,J} - E \quad (1)$$

In (1) E is the total energy of the electronic ground state, $E^{\text{unrelaxed}}_{+,J}$ the total energy of the Jth cationic hole state without consideration of relaxation effects. This implies that both expectation values are determined with the same wave functions

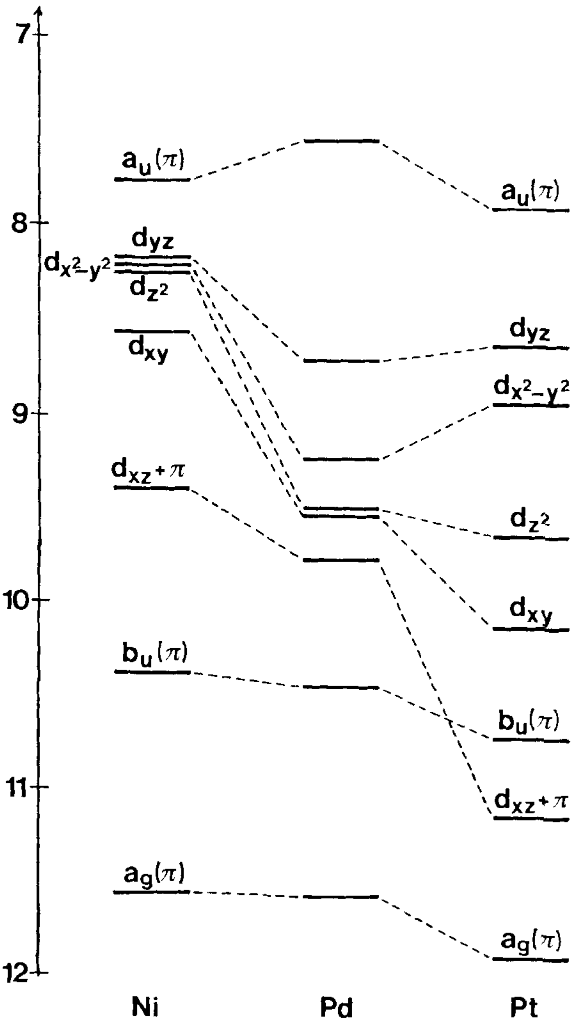


Fig. 6. *Correlation of the first bands in the PE. spectra of the bis-π-allyl complexes of Ni, Pd and Pt.* The correlation is based on qualitative arguments discussed in the text.

(of the ground state). Using the ΔSCF method [26] [27] which has been applied successfully for the interpretation of transition metal PE. spectra [5–8], separate SCF-calculations are performed for the various ionic states. In contrast to the *Koopmans'* value $I^{K}_{V,J}$, the Jth ionization potential within the ΔSCF formalism is determined by:

$$I^{\Delta SCF}_{V,J} = E^{\mathrm{relaxed}}_{+,J} - E \qquad (2)$$

The total energies for the hole states $E^{\mathrm{relaxed}}_{+,J}$ must be determined for each cationic state separately.

An alternative to the ΔSCF approach is a model which makes use of fractional occupation numbers within the SCF *Hartree-Fock*-scheme [28]. It is the 'transition-operator method' (TOM) developed by *Goscinski, Pickup & Purvis* [29] as an operator analogue (*Fock* Operator) to *Slater's* transition state model in the statistical X_α approximation [30]. In this approach the J^{th} ionization potential $I^{TOM}_{V,J}$ is given by minus the J^{th} eigenvalue ε^{TOM}_{J} of a 'transition *(Fock)* operator' F^{TOM}_{J}

$$\begin{aligned} F^{TOM}_{J}(1) &= h_1 + \sum_{i \neq j} \langle i^{TOM}(2) | \, | i^{TOM}(2) \rangle + \frac{1}{2} \langle j^{TOM}(2) | \, | j^{TOM}(2) \rangle \\ &= F(1) - \frac{1}{2} \langle j^{TOM}(2) | \, | j^{TOM}(2) \rangle \\ F^{TOM}_{J}(1)\, i^{TOM}(1) &= \varepsilon^{TOM}_{J}(1) \cdot i^{TOM}(1) \\ I^{TOM}_{V,J} &= -\varepsilon^{TOM}_{J} \end{aligned} \qquad (3)$$

F(1) is the *Fock* operator associated to the set of spin orbitals $[i^{TOM}][j^{TOM}] \ldots i,j = 1,2 \ldots N$. h_1 is the one-electron part of the *Hamiltonian* while $\langle i^{TOM}(2) | \, | i^{TOM}(2) \rangle$ symbolizes the *Coulomb*-exchange-operator of spin orbital $[i^{TOM}]$. The equations given in (3) show that the J^{th} spin orbital has the occupation number 1/2 which corresponds to a 'transition state' for the J^{th} cationic hole-state. The latter is characterized by the occupation number 0. Within the TO method, $-\varepsilon^{TOM}_{J}$ represents an approximation for the J^{th} ionization potential; all other N-1 eigenvalues are without physical significance. Because an aufbauprinciple is unreliable in the open shell SCF procedures for the calculation of the various ionic states we make use of a maximum overlap criterion of the iterated MO's with the previous set of orbitals in both methods used (ΔSCF and TOM).

The open-shell calculations were performed within the unrestricted *Hartree-Fock* (UHF) framework leading to different orbitals for different spins [31]. In all semiempirical MO calculations the application of a single annihilator to the open shell orbitals did not improve any of the results [32]. Therefore we performed the ΔSCF calculations without spin projection, so the ΔSCF open shell wave function is not an exact eigenfunction of S^2. In the TOM scheme the total spin is not conserved, therefore the question of projection is immaterial.

Results. – *ΔSCF and TOM Calculations on Bis(π-allyl)nickel.* In *Table 6* and *Figure 7* we have compared the calculated ionization potentials for the various approximations (*Koopmans'* theorem, ΔSCF and TOM) with the experimental values for **1a**. By inspection of *Table 6* and *Figure 7* it is evident that *Koopmans'*

Table 6. *Calculated vertical ionization potentials for bis(π-allyl)nickel* (**1a**) *according to Koopmans' theorem* $I^{K}_{V,J}$, *the ΔSCF-formalism* $I^{\Delta SCF}_{V,J}$ *and the transition-operator method* $I^{TOM}_{V,J}$. All values in eV

Peak	Assignment	$I^{exp}_{V,J}$	$I^{K}_{V,J}$ $(=-\varepsilon_J)$	$I^{\Delta SCF}_{V,J}$	$\Delta I_1 = I^{K}_{V,J} - I^{\Delta SCF}_{V,J}$	$I^{TOM}_{V,J}$	$\Delta I_2 = I^{K}_{V,J} - I^{TOM}_{V,J}$
1	$7a_u$	7.76	9.12	7.55	1.57	7.50	1.62
2+3	$13a_g$		11.15	8.81	2.34	7.55	3.60
	$12a_g$	8.19	12.44	9.19	3.25	7.70	4.74
	$5b_g$	8.58	12.48	9.25	3.23	7.89	4.59
	$11a_g$		12.51	9.35	3.16	7.91	4.60
4	$6b_g$	9.40	11.04	9.63	1.41	9.54	1.48
5	$11b_u$	10.38	11.42	11.16	0.26	10.96	0.46
6	$9a_g$	11.55	14.44	12.68	1.76	12.55	1.89
7	$6a_u$		13.92	13.82	0.10	13.77	0.15
	$10b_u$	12.70	14.09	13.95	0.14	13.88	0.21
	$10a_g$		14.22	14.06	0.21	13.88	0.39
	$4b_g$		14.41	14.15	0.26	14.20	0.21

theorem is not valid. The relaxation effects calculated for ionization from Ni 3d-orbitals are considerably larger than for ionization from ligand orbitals.

The sequence of calculated ionization potentials is in agreement with our qualitative assignment discussed in the previous chapters: The first ionization potential corresponds to the ejection from $7a_u$. The next four calculated IP's are due to the removal of electrons from strongly localized Ni 3d-orbitals $13a_g$, $12a_g$, $5b_g$ and $11a_g$. The computed *Koopmans'* defects ΔI_1 and ΔI_2 reach their maximum for those three orbitals that are localized at the metal by more than 90%. The calculated relaxation energies are about 3.20 eV by applying the ΔSCF procedure and 4.60 eV using the TO-method. In case of $13a_g$ (67% Ni-3d-participation) the deviation from $I^{K}_{V,J}$ is found to be smaller (2.34 eV for ΔSCF and 3.60 for TO method). For most of the ligand orbitals relaxation energies in the order of 0.5 eV or less are calculated. In the cases $6b_g$ and $9a_g$ where exceptions are found a significant Ni-3d-participation is the reason.

Table 7. *Population analysis for* ^2A_u*-state at bis(π-allyl)nickel cation* $(\mathbf{1a})^+$. For the choice of axis see *Figure 1*. For the numbering see formulas in text

	Ni	C_1	C_2	H_1	H_2	H_3
s	0.0477	1.0610	1.1329	0.8848	0.8196	0.8136
p_x	0.0201	1.0336	1.0734			
p_y	0.0149	1.0885	1.0567			
p_z	0.0265	0.9774	0.9978			
d_{z^2}	1.9982					
d_{xz}	1.3171					
d_{yz}	1.9842					
$d_{x^2-y^2}$	1.9556					
d_{xy}	1.8269					
Net charge	0.8088	−0.1604	−0.2608	0.1152	0.1804	0.1864

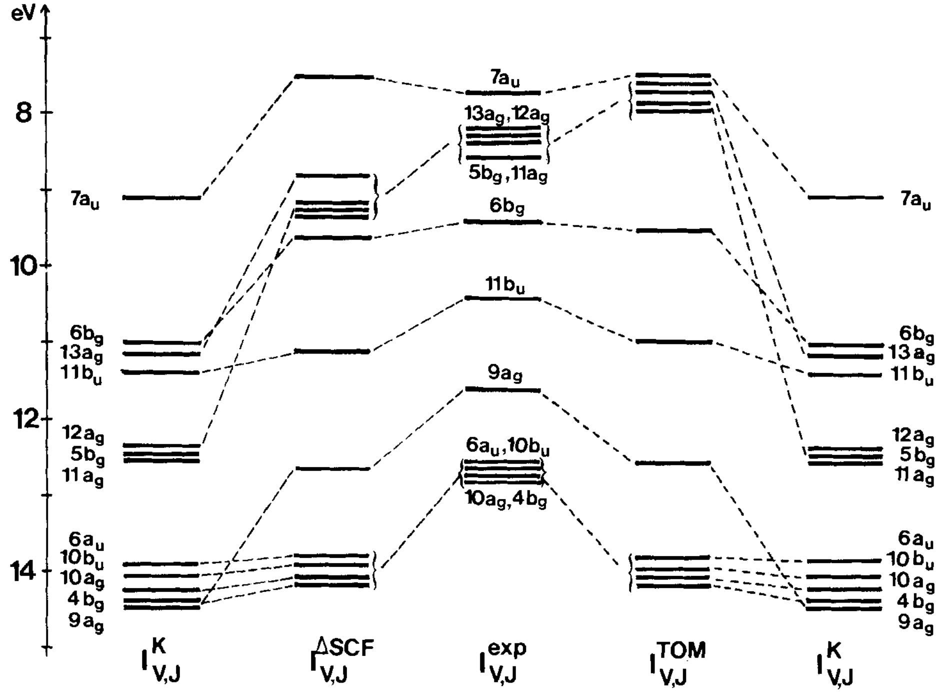


Fig. 7. *Comparison between the measured* ($I^{exp}_{V,J}$) *and calculated ionization potentials of bis(π-allyl)nickel.* In the first and fifth column the values according to *Koopmans'* theorem are listed ($I^{K}_{V,J}$). In the second and fourth column the calculated values according to the ΔSCF method ($I^{\Delta SCF}_{V,J}$) and transition operator method ($I^{TOM}_{V,J}$) respectively are shown.

Both procedures agree with our assignment that band ⑥ should arise from the ionization of $9a_g$ and band ⑦ is due to several ionization processes from σ-orbitals This sequence is the result of a stronger relaxation in $9a_g$ (see *Table 6*) since in the ground state the σ-orbitals $6a_u$, $10b_u$, $10a_g$ und $4b_g$ are predicted to be at lower energy than $9a_g$.

In case of the HOMO ($7a_u$) the calculated *Koopmans'* defect is in the order of 1.5 eV although no Ni-3d-participation is present. This strong defect has its origin in the localization of the wave function at the p_z-AO's of the terminal carbon centers. The calculated relaxation energies can only be the result of a significant charge reorganization in the σ-frame of the radical cation. To get insight into it, we performed a population analysis for the ^2A_u-state of **1a**$^+$ *(Table 7)* and compared the result with the population scheme obtained for ^1A_g of **1a** *(Table 2)*. This comparison shows that a strong decrease of π-charge at the four terminal C-atoms of the allylic moieties and a drift of negative charge from the H-atoms to the adjacent C-atoms. This drift is especially strong in case of the central C–H unit. This observed effect similar to that observed in fulvenes [33], has to be considered when substituent effects are used to discuss shift of PE. bands in case of methyl-substitution.

Conclusion. - The PE. spectrum of Ni-diallyl is most often taken as the example to demonstrate the non-validity of *Koopmans'* theorem in case of transition metal compounds. Therefore a very detailed discussion of our assignment has been given. The comparison between the calculated *Koopmans'* states of **1a** and the experimental results in *Figure 7* clearly demonstrates large *Koopmans'* defects for strongly localized orbitals. These orbitals are the 3d-orbitals of Ni and with some extend $a_u(\pi)$. From this *Figure* it can be extrapolated that the MO-sequence according to *Koopmans'* theorem may only be used in those cases where the 3d-orbitals are predicted on top of the ligand orbitals in the ground state.

Our assignment given rests strongly on the comparison of intensities between He(I)/He(II) spectra (see *Fig. 2* and *3*), methyl shifts *(Fig. 5)* and the comparison between Ni-, Pd- and Pt-compounds *(Fig. 6)*: This latter comparison allows to separate the ligand bands (which should stay constant in the series **1a**-**3a** or **1b**-**3b**) from the metal bands (which should change according to *Fig. 4*).

Our assignment summarized in *Figures 6* and *7* confirms a previous assignment given for **1a** [14] with the exception of the assignment of the first band. A final settlement of this issue we postpone until more accurate calculations are available.

Experimental Part. - The preparation of the allyl complexes has been described in [34]. The He(I) spectra have been recorded on a modified PS-16 spectrometer (*Perkin-Elmer,* Beaconsfield) based on the design of *Turner* [35]. The spectra were calibrated with Xenon and Argon. A resolution of about 20 meV on the Argon-Line was obtained. The He(II) spectra were measured on an instrument constructed in the physical chemistry laboratory in Basel. A modified heated inlet and lamp from *Perkin-Elmer* was used.

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