

that is not present for the proton (20.8 kcal/mol).

**Fragmentation of the Cations.** In the Introduction we pointed out that Busch et al.<sup>1</sup> observed that CID of  $\text{Ag}_2\text{CH}_3^+$  produced a significant fraction of  $\text{Ag}_2^+$  daughter ions but that none were observed from  $\text{Ag}_2\text{H}^+$ . We have calculated the various fragmentation energies of the title cations, and these are shown in Table II. (For completeness' sake, we list the various dissociation energies and ionization energies that are relevant to this study in Table III.)<sup>26</sup> The resultant values show that there is not a distinct difference between the fragmentation energies of  $\text{Ag}_2\text{H}^+$  and  $\text{Ag}_2\text{CH}_3^+$ . Also, recall from our earlier discussion that there is little difference between the ground-state structures of the two ions. Both Holmes<sup>27</sup> and Lorquet<sup>28</sup> have discussed the relationship between CID and structure specificity. The CID experiment involved a 20-eV collisions between argon atoms and the parent silver ion in the mass spectrometer chamber.<sup>1</sup> Most of the imparted translational energy will be converted into internal vibrational and rotational energy, which is then assumed to be rapidly randomized among the various vibrational modes of the

molecule. The relative abundance of daughter ions is usually independent of the amount of internal energy imparted to the parent ion.

On purely statistical grounds, since the fragmentation energies of  $\text{Ag}_2\text{H}^+$  to produce  $\text{AgH}^+$  and  $\text{Ag}_2^+$  are nearly identical, one might expect equal amounts of these daughter ions in the CID. The fact that no  $\text{Ag}_2^+$  is observed indicates that one or more of the following is true: (1) Our calculated results are not trustworthy. (2) The fragmenting ion with varying degrees of vibrational and rotational excitation does not retain the structure of the ground state. This could occur if the barrier for interconversion between two isomers (e.g., in our case triangular  $\text{Ag}_2\text{H}^+$  and linear  $\text{AgHAg}^+$ ) is considerably lower than that for decomposition. As discussed above, this interconversion barrier is indeed much lower for  $\text{Ag}_2\text{H}^+$  than for  $\text{Ag}_2\text{CH}_3^+$ . (3) There is a kinematic effect whereby the relatively large argon atom is presented with a small collisional cross section by the H atom in  $\text{Ag}_2\text{H}^+$ . Consequently, the vibrational energy might not be randomized among the various vibrational modes of the fragmenting ion. Preferential Ag-Ag bond breaking could occur rather than that of Ag-H.

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- (26) It is evident from Table III that some of the calculated values are in error by 10-18 kcal/mol compared to experiment. Since several values in Table III have no experimental counterpart, it is difficult to know whether or not we are introducing a systematic error into the fragmentation energies presented in Table II. In each of the five cases where a comparison can be made with experiment, we underestimate the experimental quantity. Since we are really only interested in relative fragmentation energies, it may well be that these errors are tending to cancel each other.
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## Assignment of the Valence Ionization Spectrum of $\text{TiCl}_4$

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The ionization energies and relative intensities in the valence region of  $\text{TiCl}_4$  are calculated by an ab initio many-body Green's function formalism that takes the effects of electron correlation and relaxation into account. The calculations are based on a SCF wave function obtained with a double- $\zeta$  basis set. The ordering of the ionic states in the outer valence region is  $1t_1 < 3t_2 < 1e \approx 2t_2 < 2a_1$ . In the inner valence region, i.e. for the orbitals  $1t_2$  and  $1a_1$ , we observe the typical breakdown of the molecular orbital model of ionization. The intensity becomes distributed over many states.

### Introduction

Among the molecules involving a transition-metal atom, the  $\text{TiCl}_4$  molecule is a very simple and fundamental one. The understanding of the electronic structure of this molecule is thus of considerable importance. In spite of a fairly large number of investigations, however, several aspects of the electronic structure could not be clarified unambiguously. Among these is the assignment of the valence photoelectron spectrum (PES). This is due to the large number of states crowded in a narrow energy interval. The He I and also the He II photoelectron spectra of  $\text{TiCl}_4$  have been reported and discussed repeatedly.<sup>1-6</sup> However, some points in the interpretation of the spectrum are still not settled<sup>6</sup> (see also ref 7). A large number of calculations of

semiempirical, discrete variational  $X\alpha$  (DVM- $X\alpha$ ), SCF- $X\alpha$ , and ab initio type have been performed,<sup>4,6,8-17</sup> but the sequence of orbital energies disagreed among the different calculations. Essentially two different assignments are at present proposed for the valence bands named A, B, (C + D), and E by Egde et al.<sup>1</sup> As the bands C and D are very closely spaced and overlap, the ordering of the states assigned to these bands has generally not been specified. The first assignment is  $1t_1$  (A),  $3t_2$  (B),  $(1e + 2t_2)$  ((C + D)), and  $2a_1$  (E). This ordering of states is supported by the experimental results of ref 1-5 and the investigation using synchrotron radiation by Lübcke et al.,<sup>40</sup> who derived this result from the energy dependence of the partial photoionization cross sections, and it is obtained by the calculations with DVM- $X\alpha$ .<sup>13,14</sup>

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**Table I.** Comparison of Valence Ionization Energies of  $\text{TiCl}_4$  (eV) and Their Assignments As Obtained by Different Methods

exptl <sup>5</sup>		exptl <sup>6</sup>		exptl <sup>40</sup>		CNDO <sup>8-10</sup>		INDO <sup>11</sup>		Fenske-Radtke <sup>12</sup>	
1t <sub>1</sub>	11.76	1t <sub>1</sub>	11.69	1t <sub>1</sub>	11.80	1t <sub>1</sub>	14.38	1t <sub>1</sub>	12.54	1t <sub>1</sub>	13.65
3t <sub>2</sub>	12.77	3t <sub>2</sub>	12.67	3t <sub>2</sub>	12.79	3t <sub>2</sub>	15.02	3t <sub>2</sub>	12.83	3t <sub>2</sub>	14.34
1e	13.25	1e	13.17	1e	13.29	2t <sub>2</sub>	15.84	1e	13.31	1e	14.62
2t <sub>2</sub>	(13.25)	2a <sub>1</sub>	13.46	2t <sub>2</sub>	13.54	1e	16.52	2a <sub>1</sub>	13.77	2a <sub>1</sub>	15.90
2a <sub>1</sub>	13.96	2t <sub>2</sub>	13.91	2a <sub>1</sub>	13.98	2a <sub>1</sub>	16.80	2t <sub>2</sub>	17.74	2t <sub>2</sub>	16.42

DVM-X $\alpha$ <sup>13,14</sup>		SCF-X $\alpha$ <sup>15</sup>		SCF-X $\alpha$ <sup>16</sup>		ab initio <sup>17</sup>		OVGF (this work)		extended 2ph-TDA (this work)	
1t <sub>1</sub>	12.2	1t <sub>1</sub>	11.9	1t <sub>1</sub>	11.08	1t <sub>1</sub>	13.4	1t <sub>1</sub>	11.58	1t <sub>1</sub>	11.70
3t <sub>2</sub>	12.7	3t <sub>2</sub>	12.5	3t <sub>2</sub>	11.76	3t <sub>2</sub>	14.6	3t <sub>2</sub>	12.60	3t <sub>2</sub>	12.98
1e	13.0	1e	12.8	1e	12.15	1e	15.2	1e	12.94	1e	13.44
2t <sub>2</sub>	13.8	2a <sub>1</sub>	13.0	2a <sub>1</sub>	13.20	2t <sub>2</sub>	15.5	2t <sub>2</sub>	13.00	2t <sub>2</sub>	13.69
2a <sub>1</sub>	14.1	2t <sub>2</sub>	13.2	2t <sub>2</sub>	13.36	2a <sub>1</sub>	15.7	2a <sub>1</sub>	13.50	2a <sub>1</sub>	13.91

ab initio,<sup>17</sup> and the present Green's function methods. The experimental and theoretical investigation of Bancroft et al.<sup>6</sup> leads to the ordering 1t<sub>1</sub> (A), 3t<sub>2</sub> (B), (1e + 2a<sub>1</sub>) ((C + D)) and 2t<sub>2</sub> (E). These authors reviewed the problem and used in addition to their calculations data on the intensities of the bands and their vibrational structure. However, they still could not arrive at an unambiguous assignment. This latter ordering of states is supported also by INDO,<sup>11</sup> Fenske-Radtke,<sup>12</sup> and SCF-X $\alpha$ <sup>15,16</sup> calculations. The CNDO method leads to yet another assignment.<sup>8-10</sup> The different assignments of the valence PES of  $\text{TiCl}_4$  are presented in Table I.

The calculations performed so far are of semiempirical, X $\alpha$ , or ab initio type, but except for an INDO calculation combined with a Green's function method,<sup>6</sup> they do not account for the correlation energy changes upon ionization and sometimes not for the relaxation energy changes. It thus appears desirable to perform a calculation, preferably in an ab initio framework, that accounts for relaxation and correlation energy changes in the ionization process. In this way more reliable theoretical data could be obtained. This is done in the present work. An ab initio Green's function method is employed to calculate the ionization energies and their relative intensities, which are also referred to as pole strengths. Two different versions of the Green's function method are used. The first method is called the outer-valence Green's function method (OVGF).<sup>18-20</sup> It can only be used if a one-particle picture of ionization applies, i.e. if the ionic states can be described essentially by a (Koopmans) configuration having a simple hole in the orbital in question and if no intense satellite line structure is found. This satellite line structure arises from the mixing of simple hole (1h) with two-hole-one-particle (2h1p) configurations; i.e., ionization couples with ionization plus excitation processes. This can lead to the appearance of satellite lines, which accompany the main line, and to the disappearance of the main line, the intensity being distributed over many lines. In this case the extended two-particle-hole Tamm-Dancoff Green's function method (extended 2ph-TDA) should be used, which applies in the entire valence region.<sup>21,22</sup> Both the OVGF and the extended 2ph-TDA method are accurate to third order in the electron-electron interaction and should thus yield reliable ionization energies provided the basis set is of sufficient quality. In the inner-valence region with the strong splitting of the lines the results of the extended 2ph-TDA method are only correct to first order and we obtain a semiquantitative picture at best. The accuracy and the computational aspects of these Green's function methods are reviewed in ref 23 and 24, and the correlation effects in the inner-valence region are reviewed in ref 25. The present

Green's function methods have also been applied to a transition-metal complex in ref 26.

### Computational Details

The calculations were performed for  $\text{TiCl}_4$  in its ground-state equilibrium structure with  $T_d$  symmetry and an internuclear separation of 218.5 pm.<sup>27</sup> For the Ti atom we used the [14s9p6d]/(8s6p3d) basis set, which consists of the basis set of Huzinaga<sup>28</sup> enlarged with a sixth d-type function according to the suggestion of Hay.<sup>29</sup> The two most diffuse s-type functions are replaced by s-type functions with exponential parameters  $\alpha_s(\text{Ti}) = 0.17, 0.05$  to account for the charge contraction in the formation of the molecule. For the Cl atoms we used the [12s9p]/(6s4p) basis set of Veillard.<sup>30</sup> The entire basis is thus approximately of double- $\zeta$  quality and leads to 116 contracted functions. The integral and SCF calculations were performed with the program system MUNICH.<sup>31</sup>

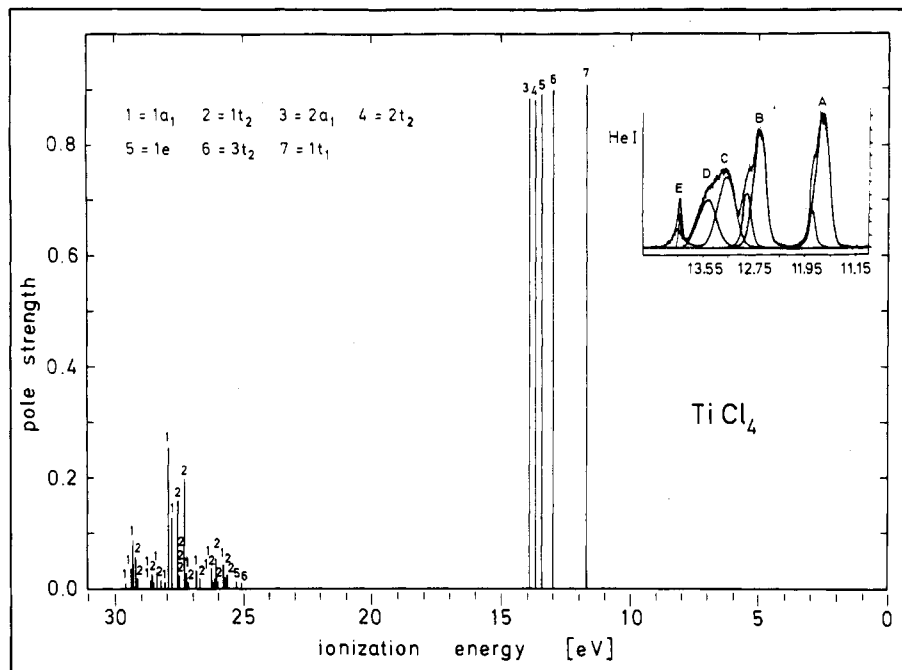
In the OVGF calculation the 16 occupied valence orbitals and the lowest 40 virtual orbitals out of a total of 43 virtual valence orbitals were included. Thus in this calculation the basis set was essentially exhausted. In the extended 2ph-TDA calculation the 16 occupied valence orbitals and the lowest 25 virtual valence orbitals were taken into account. The large number of electrons to be correlated and the consequently large dimension of the matrices that have to be completely diagonalized in this method put a limit to the number of orbitals that can be included in the calculation.<sup>24</sup> The canonical virtual orbitals were used in the calculations, as the Green's function calculations are most easily performed in this basis. However, experience with valence ionization processes has shown that they are probably the best basis for expansion. Because of the incomplete basis set exhaustion in the extended 2ph-TDA method compared to that in the OVGF calculation we cannot expect a perfect numerical agreement between the two sets of results in the outer-valence region, a fact that is found in general if the basis sets are nearly exhausted.<sup>24</sup>

### Results and Discussion

The total SCF energy, the valence orbital energies, and the OVGF and extended 2ph-TDA results for  $\text{TiCl}_4$  are listed together with the experimental results in Table II. Only those ionization energies in the inner-valence region that have a pole strength larger than 0.01 are listed. We have also given the energies of the two lowest virtual orbitals. These orbital energies are negative. As the basis set does not contain diffuse Rydberg functions, these virtual orbitals have to be of valencelike character. It is a very general experience that in molecules containing low-lying virtual valencelike orbitals we experience large and nonuniform many-body effects.<sup>25</sup> These may be of two types. The ordering of the ionic main states may be changed by including correlation and

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**Figure 1.** Valence ionization spectrum of  $\text{TiCl}_4$  calculated with the extended 2ph-TDA method. Only states with a pole strength larger than 0.01 are shown. The experimental spectrum (inset) is from ref 6.

relaxation effects. The ordering of the states deduced in Koopmans' approximation<sup>32</sup> may thus be incorrect. Whether an interchange does occur or whether only the spacing of the ionization energies is changed depends on the matrix elements and their magnitude. Second, we expect that the excitation of an electron from an occupied orbital to one of the low-lying virtual orbitals in addition to the ionization process occurs at relatively low energy and that mixing of 1h and 2h1p configurations leads to a breakdown of the molecular orbital picture of ionization, i.e. to the splitting of lines into many components.

Looking at the detailed results of the OVGf method in second and third order and the renormalized final results, which approximately account for the higher order terms, we find appreciable differences in the correlation effects upon ionization from the  $1t_1$  and  $3t_2$  orbitals on the one hand and the  $1e$ ,  $2t_2$ , and  $2a_1$  orbitals on the other hand. It follows from the extended 2ph-TDA calculation that the one-particle picture of ionization applies to these orbitals, whereas it is not applicable to the  $1t_2$  and  $1a_1$  ionization processes. It is in general found that the Koopmans value is larger than the second-order value, which is smaller than the third-order one; the second- and third-order values bracket the final renormalized value. This is found to be the case for  $1t_1$  and  $3t_2$  ionizations. These orbitals have either zero or only a very small d participation.<sup>17</sup> But this situation is not found in the case of the  $1e$ ,  $2t_2$ , and  $2a_1$  orbitals, which have a substantial participation of the d orbitals on the Ti atom ranging from 9 to 21%.<sup>17</sup> Here the third-order value is smaller than the second-order one. In spite of this different behavior we do not obtain a change of ordering in the ionic states from Koopmans' approximation. From both the OVGf and the extended 2ph-TDA calculation we conclude that the assignment of Egdell et al.<sup>1</sup> is the correct one.  $1t_1$  ionization is assigned to band A,  $3t_2$  to band B, the pair  $1e$  and  $2t_2$  ionization to the close-lying and overlapping bands C and D, and  $2a_1$  ionization to band E. The OVGf results are in satisfactory agreement with the experimental data, having a maximum error of about 0.5 eV. A better agreement cannot be expected because of the lack of polarization functions in the basis. The extended 2ph-TDA results for the first five ionic states are in nearly perfect agreement with experiment, but this is accidental. Since the molecular orbital model of ionization applies to these ionization processes, both the OVGf and the extended 2ph-TDA

**Table II.** Theoretical and Experimental Ionization Energies of  $\text{TiCl}_4$  (eV) together with the Calculated Pole Strengths<sup>a</sup>

MO	$-\epsilon_i$	OVGF		extended 2ph-TDA		exptl <sup>b</sup>
		$E_i$	$P_i$	$E_i$	$P_i$	
$4t_2$	0.17					
$2e$	0.45					
$1t_1$	13.15	11.58	0.92	11.70	0.91	11.69
$3t_2$	14.47	12.60	0.91	12.98	0.90	12.67
				25.11	0.010	
$1e$	14.85	12.94	0.91	13.44	0.89	13.17
				25.31	0.012	
$2t_2$	15.26	13.00	0.90	13.69	0.88	13.46
$2a_1$	15.60	13.50	0.91	13.91	0.89	13.91
$1t_2$	30.24			25.66	0.024	
				25.74	0.020	
				26.05	0.014	
				26.10	0.053	
				26.14	0.018	
				26.73	0.017	
				27.21	0.012	
				27.34	0.20	
				27.54	0.011	
				27.56	0.024	
				27.58	0.048	
				27.59	0.16	
				28.08	0.011	
				28.55	0.012	
				29.16	0.020	
				29.23	0.056	
$1a_1$	30.71			25.80	0.042	
				26.26	0.013	
				26.26	0.037	
				26.87	0.032	
				27.22	0.027	
				27.83	0.13	
				27.95	0.26	
				27.96	0.017	
				28.23	0.014	
				28.40	0.030	
				28.59	0.027	
				28.64	0.015	
				29.33	0.088	
				29.36	0.035	
				29.60	0.010	

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<sup>a</sup> The total SCF energy is  $-2685.8922$  au. <sup>b</sup> Reference 6.

methods would give very similar results if the basis set were exhausted, but this is not done in the latter calculation here. The additional relaxation due to the inclusion of the higher energy virtual orbitals in the extended 2ph-TDA calculation would move the ionization energies down and put them into closer agreement with the OVG results. The nearly perfect agreement with experiment thus results from the limited number of virtual orbitals that were taken into account.

Electron ejection from the  $1t_2$  and  $1a_1$  orbitals, which are essentially combinations of the Cl 3s atomic orbitals, cannot be described within a one-particle picture. Here a strong mixing of ionization with ionization plus excitation processes occurs, leading to the strong splitting of the lines. The extended 2ph-TDA results are given in Table I and are graphically represented in Figure 1, which contains as an insert also the He I photoelectron spectrum from ref 6. For  $1t_2$  ionization the maximum pole strength of a component is obtained as 0.2, and for  $1a_1$  ionization it is obtained as 0.26. The 2h1p configurations, which couple strongly with the simple hole configurations, involve as particle states the 2e,  $3a_1$ , and most important, the  $4t_2$ ,  $5t_2$ , and  $6t_2$  orbitals. The 2e orbital is built up from Cl p and Ti d functions, and the other ones are built from Cl s and p and Ti p and d functions. In many cases the Ti d participation is strong. To a certain degree this can be interpreted as a repopulation of the d orbitals on Ti, but this should not be overemphasized as the splitting of the Cl 3s lines is a general phenomenon (see references in ref 24) and is independent of the presence or absence of a transition-metal atom. The results obtained in this energy range are only qualitative or semiquantitative for several reasons. One of them has been mentioned above. In this case the ionic states are dominated by 2h1p configurations and the extended 2ph-TDA method gives only results that are accurate to first order of perturbation theory.<sup>22</sup> To improve this, one has to include the 3h2p and 3p2h configurations (i.e. the double excitations on top of the simple hole and simple particle states) in addition to the 2h1p and 2p1h configurations, which are included in the present calculation. Such a theory has been developed,<sup>22</sup> and a simplified version is being applied to some small molecules.<sup>33</sup> However, the  $\text{TiCl}_4$  molecule is just slightly too large for the application of this high-order and demanding theory. A second reason is the following one. In the inner-valence region, where we find this splitting of lines, we also find the

double-ionization threshold, which for  $\text{TiCl}_4$  probably lies between 30 and 40 eV. An infinite number of Rydberg states of the ion converge to this threshold. To describe them properly would require an extremely large basis set. Since this cannot be done, one does not calculate true eigenstates but pseudostates, which give only a rough idea of the spectral distribution. It has also been found for the  $\text{Cl}_2$  and the HCl molecules<sup>34,35</sup> that d-type functions are necessary to describe this part of the spectrum. Experimental information on this energy range is scarce or unavailable for  $\text{TiCl}_4$ , but more and more information is being obtained by (e,2e) spectroscopy<sup>36,37</sup> and synchrotron radiation,<sup>38,39</sup> which together with theoretical calculations help to develop an understanding of the process in this interesting energy range.

### Summary

The ionization energies of  $\text{TiCl}_4$  are calculated in the outer- and inner-valence regions by ab initio many-body Green's function methods, which include the effect of electron correlation and relaxation. The first five ionization processes can be well-described in the molecular orbital model of ionization. The calculated ionization energies lead to the assignment of the photoelectron spectral bands A, B, (C + D), and E as  $1t_1$ ,  $3t_2$ , ( $1e + 2t_2$ ), and  $2a_1$ . For  $1t_2$  and  $1a_1$  ionization we observe the breakdown of the molecular orbital model of ionization and the intensity becomes distributed over many lines, which carry only a small fraction of the intensity associated with these ionizations.

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## Electrochemistry and Spectroelectrochemistry of Mononuclear and Binuclear Cobalt Phthalocyanines

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The electrochemistry of (2,9,16,23-tetraneopentoxophthalocyanato)cobalt, and some binuclear analogues, has been studied in dichlorobenzene and in dimethylformamide. The redox mechanisms and species on the electrode are discussed. With the use of an optically thin electrode, the electronic spectra of seven different oxidation states of the mononuclear derivative are reported. Data for a selection of oxidation states of several binuclear species are also presented.

### Introduction

The electrochemistry and spectroelectrochemistry of metalloporphyrins have been extensively studied.<sup>2-16</sup> However, relatively

little spectroelectrochemistry has been carried out on phthalocyanines<sup>17-25</sup> due to their low solubilities in suitable solvents for

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