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Investigation of the Electronic Structure of TiCl_4

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The electronic absorption spectrum of gaseous TiCl_4 over the range 4000–1100 Å is presented and discussed in light of extensive CNDO-MO calculations. From calculated transition energies and the variation of these energies with respect to small changes in Ti–Cl bond length a tentative assignment of the six-band spectrum is offered.

Das Absorptionsspektrum von gasförmigen TiCl_4 wurde im Bereich 4000–11 000 Å untersucht. Die mit der CNDO-MO-Methode berechneten Übergangsenergien und die Variation dieser Energien mit kleinen Änderungen der Ti–Cl-Bindungslänge erlauben eine Zuordnung der sechs Banden des Spektrums.

Le spectre d'absorption électronique de TiCl_4 gazeux dans la zone 4000–1100 Å a été obtenu et discuté à la lumière de calculs CNDO MO. A partir des énergies de transition calculées et des variations de ces énergies par rapport à de faibles modifications dans la longueur de la liaison Ti–Cl, on propose une attribution possible des six bandes du spectre.

1. Introduction

The experimental electronic absorption spectrum of the tetrahedral molecule TiCl_4 and the theoretical discussion of this spectrum have already been the object of numerous investigations [1–6]. In the work reported here the ultraviolet absorption spectrum has been extended to include the vacuum UV region of 2000 to 1100 Å and attempt has been made to explain the total six-band electronic spectrum in terms of extensive CNDO-MO calculations.

While a previous CNDO-MO treatment of the TiCl_4 molecule [6] was concerned primarily with an optimization of the component valence atomic orbitals by the minimization of the total energy, and was therefore a purely theoretical consideration, this treatment is directed at the attempted spectral assignments for the experimentally observed electronic transitions in TiCl_4 . First let us look at the experimental spectrum.

2. Experimental Spectra of TiCl_4

The 35,000 to 90,000 cm^{-1} spectral range of gaseous TiCl_4 was scanned with a 2 m McPherson Model 240 vacuum u.v. spectrograph (grating: 1200 lines/mm) using as light source a McPherson Model 630 Hinteregger-type discharge lamp with argon or hydrogen, and modified to give a continuous spectrum. The TiCl_4 was circulated through a 10 cm stainless steel cell with LiF windows by purified He carrier gas; no attempt was made to determine the absolute concentration of TiCl_4 in the cell. The separately amplified double-beam signals (off sodium salicylate, 10 mg/cm^2 , scintillators) were

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feed through a $\log I_1/I_2$ amplifier and then through an *XY*-recorder, the *x*-input controlled by wavelength. The McPherson spectrum of TiCl_4 , representing the averaging of a great many runs, is reproduced in Fig. 1.

Since the absolute concentration of TiCl_4 was not known, the extinction coefficients of the absorption bands have been approximated by assuming that the maximum intensity of the band at $36,000\text{ cm}^{-1}$ is approximately the same

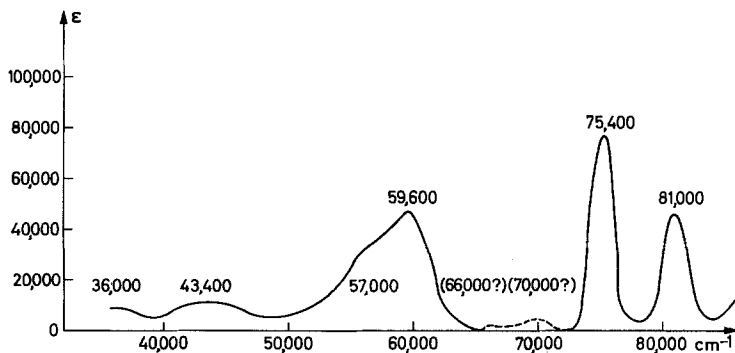


Fig. 1. The vacuum ultraviolet absorption spectrum of gaseous TiCl_4 measured with a McPherson Model 240 spectrograph

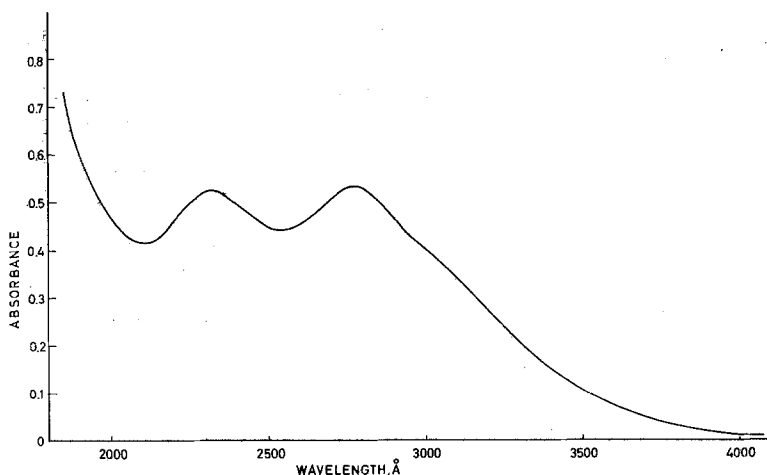


Fig. 2. The visible and near ultraviolet absorption spectrum of gaseous TiCl_4 measured with a Cary Model 14 spectrophotometer

intensity as was measured in cyclohexane [2], in *n*-hexane [3] and in the gas phase [9]. The other absorption bands are known relative to this band. While this "normalization procedure" is not entirely valid, of course, for precise values, it is certainly valid to the right order of magnitude and does enable us to recognize these bands as being most probably electric dipole allowed one-electron transitions. In the spectral region around $70,000\text{ cm}^{-1}$ faint absorption was detected for very concentrated TiCl_4 flow, but if this does represent electronic absorption(s) the intensity is of such orders of magnitude less than the other bands that the

one or two bands here cannot be considered as representing electric dipole allowed transitions. The longer wavelength electronic spectrum of gaseous TiCl_4 was obtained on a Cary Model 14 spectrophotometer and is reproduced in Fig. 2. The maxima of the first two absorption bands are identical in the two spectra. The experimental ionization potential of TiCl_4 was not observed.

3. Comparison of Experimental and Theoretical Transition Energies

The electric dipole allowed one-electron transition energies for TiCl_4 obtained from a CNDO-MO calculation using the previously determined apparently-optimum valence atomic orbitals, *i. e.* $3d(d^4)$, $4s(\zeta_4 = 1.14)$, $4p(d^2 p^2)$ and $\text{Cl}(-0.5)$ (see Ref. [6]), are listed in Table 1, where these values may be compared with the

Table 1. *Electronic spectrum for TiCl_4*

Theoretical [$3\text{Cl}(-0.5)$, $3d(d^4)$]		Experimental
Transition	$\Delta E_{i \rightarrow k}$ (eV)	Band maximum (eV)
$t_1 \rightarrow 3a_1$	(1.39)	$\sim 4.0^a$
$3t_2 \rightarrow 3a_1$	2.49	4.43
$t_1 \rightarrow 4t_2$	4.39	5.38
$3t_2 \rightarrow 4t_2$	5.41	7.07
$1e \rightarrow 4t_2$	6.56	7.39
$2a_1 \rightarrow 4t_2$	8.18	9.35
$2t_2 \rightarrow 3a_1$	10.67	10.04
$t_1 \rightarrow 2e$	11.02	
$3t_2 \rightarrow 2e$	11.72	
$2t_2 \rightarrow 4t_2$	13.18	

^a Poorly defined shoulder at longer wavelength.

experimentally obtained spectrum. The lowest energy transition, $t_1 \rightarrow 3a_1$ (an electric dipole forbidden transition), has also been included for comparison with the apparent, unresolved absorption band at lower energy than the first resolved band at 2800 \AA (4.43 eV), as indicated in the Cary 14 spectrum of Fig. 2. It is rather doubtful that this low energy, weak intensity shoulder, which can be crudely resolved to show its maximum at 3150 \AA (4.0 eV) or even slightly longer wavelength, should be assigned to the $t_1 \rightarrow 3a_1$ transition, however, since other transitions we have not calculated, such as to triplet excited states, may also occur at this energy.

The first electric dipole allowed transition for TiCl_4 seems to occur then at 4.43 eV, and from our calculations this should be the $3t_2 \rightarrow 3a_1$ transition, even if the calculated transition energy is too low. Indeed, allowing that the energies are subject to configuration-interaction displacements, one is almost tempted to initially suggest spectral assignments listed in the order of Table 1, in which the calculated transition energies are 1–2 eV lower than the experimental and only one of the four closely-lying, highest-energy transitions is observed. While there is not sufficient data to justify such a complete spectral assignment and, as will be seen shortly, additional theoretical data suggests a slightly different assignment,

one must nevertheless acknowledge the good qualitative agreement between experiment and parameterless theory at this point. We also feel able to conclude from the extensive variations of the valence atomic orbitals in the CNDO-MO calculations [6] that electric dipole allowed transitions other than the nine predicted are not expected to be observed experimentally; so the observed spectrum must be interpreted within the framework of these nine electronic transitions.

4. MO Calculations with Variable Bond Length

New CNDO-MO calculations in which the Ti-Cl bond distance has been contracted and expanded 0.05 Å and 0.10 Å about the equilibrium value 2.170 Å [7] have been performed using the optimum valence atomic orbitals. The variations of the one-electron MO levels and of the electric dipole allowed transitions with respect to these small changes in bond length are shown in Figs. 3 and 4, respectively. The dependency in these graphs of energy vs bond length is linear, or nearly so,

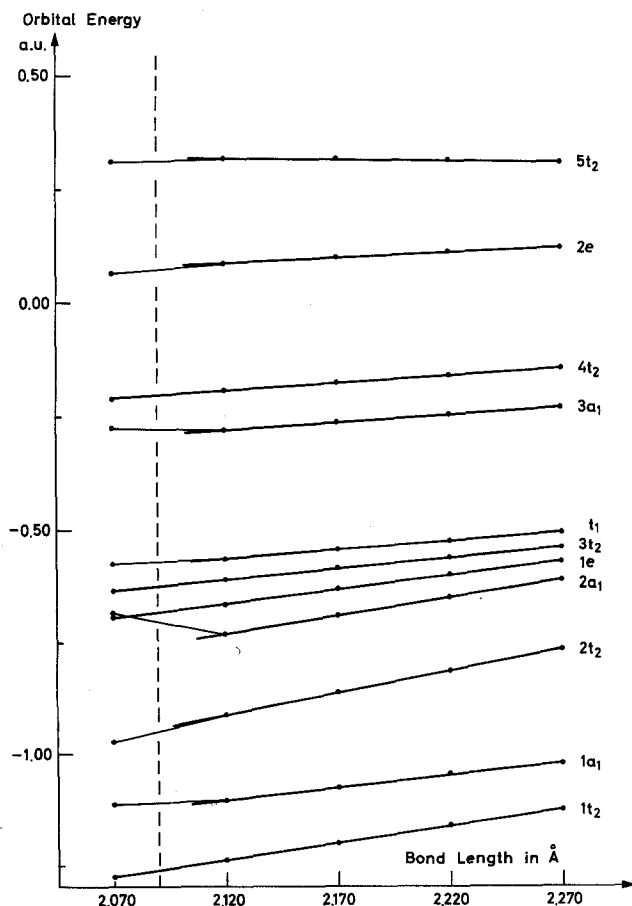


Fig. 3. Variation of the one-electron MO levels of TiCl_4 with small changes in the Ti-Cl bond distance calculated for $3d(d^4)$, $4s(\zeta_4 = 1.14)$, $4p(d^2 p^2)$ and $\text{Cl}(-0.5)$ valence orbitals

for Ti-Cl bond length of 2.120 Å or greater, but apparent discontinuity is observed for bond length of 2.070 Å. Suffice to say these anomalous values are undoubtedly indicative of an unrealistic shortening of the Ti-Cl bond, so only the energy values resulting for bond lengths of 2.120, 2.170, 2.220 and 2.270 Å will be used in the following discussion.

The well-known but rather crude principle, observed from a consideration of the potential energy surfaces, that electronic transitions showing large variation with small changes in bond length should be associated with broad absorption bands may now help us tentatively assign the electronic transitions. Speaking qualitatively then the absorption spectrum for TiCl_4 should consist of relatively sharp bands since most of the transitions can be seen to vary rather slightly with small changes in bond length.

Numerical values from Figs. 3 and 4 have been summarized in Table 2. The second column lists the graphical slopes for the one-electron transition energies themselves (from Fig. 4), and in the third column is tabulated the differences

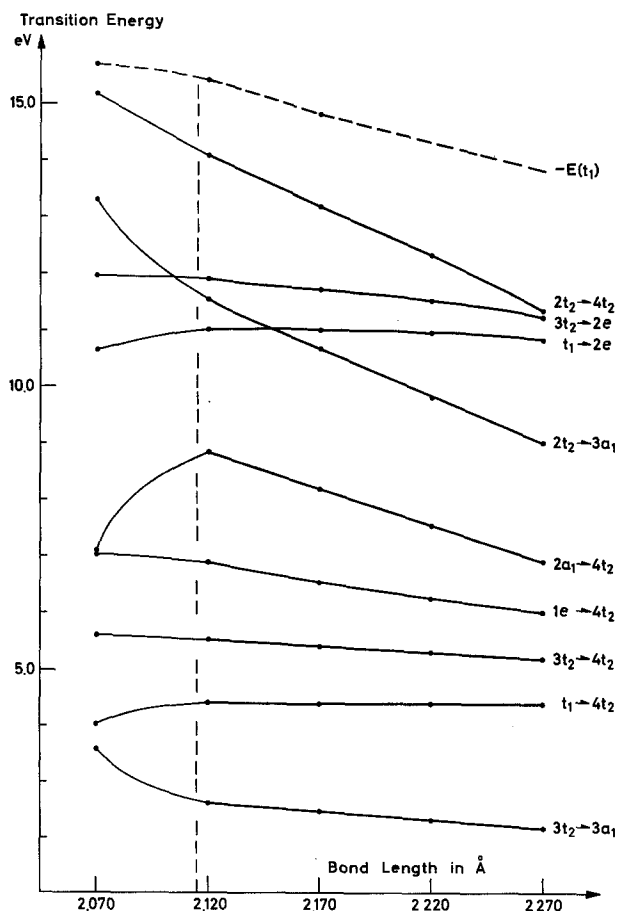


Fig. 4. Variation of the electric dipole allowed one-electron transitions of TiCl_4 with small changes in the Ti-Cl bond distance calculated for $3d(d^4)$, $4s(\zeta_4 = 1.14)$, $4p(d^2 p^2)$, and Cl (-0.5) valence orbitals

between the graphical slopes of the one-electron MO levels representing the excited states and the ground states of the one-electron transitions (from Fig. 3). Although the values in the two columns are not directly proportional, they do exhibit the same qualitative trends, but for our present considerations, the values in the second column are more valid, of course, since they include the Coulomb integrals between the excited and ground states. In the experimental section of Table 2 is tabulated the half-band widths – taken as the width of the absorption band at one-half its maximum intensity – for the six electronic absorption bands of interest, the values for the third and fourth bands being necessarily obtained through a resolution of these overlapping bands. Relative intensities, normalized to the band at $43,400\text{ cm}^{-1}$, have also been included for convenience.

Table 2. Consideration of expected and observed widths of electronic absorption bands in TiCl_4 .

Theoretical $[3d(d^4), 3\text{Cl}(-0.5)]$			Experimental		
Transition	$\delta(\Delta E_{i \rightarrow k})^a$	$(\delta_k - \delta_i)^b$	Band maximum (cm^{-1})	Relative intensity	Half-band width ^c (cm^{-1})
$3t_2 \rightarrow 3a_1$	0.433	0.022	36,000	0.9	5200
$t_1 \rightarrow 4t_2$	0.018	0.009	43,400	1.00	7700
$3t_2 \rightarrow 4t_2$	0.341	0.020	56,000	2.2	3050
$1e \rightarrow 4t_2$	0.894	0.043	59,600	4.2	4300
$2a_1 \rightarrow 4t_2$	1.952	0.070	75,400	6.9	2300
$2t_2 \rightarrow 3a_1$	2.580	0.097	81,000	4.1	2600
$t_1 \rightarrow 2e$	0.262	0.023			
$3t_2 \rightarrow 2e$	0.686	0.034			
$2t_2 \rightarrow 4t_2$	2.538	0.094			

^a Graphical slope of one-electron transition energies plotted against change in Ti–Cl bond length.

^b Difference of the graphical slopes for the one-electron MO levels involved in the predicted transitions ($i \rightarrow k$) as plotted against change in Ti–Cl bond length.

^c Calculated as the width of the absorption band at one-half its maximum intensity.

Since complete agreement is highly improbable and these crude numerical values are at best only qualitatively correct, the suggested spectral assignments should be made on the best agreement of this band-width data and the calculated values for the transition energies considered in context of their variation with changes in the valence atomic orbitals. Upon initial inspection this agreement is not complete, but some interesting possibilities readily emerge. Since the $3t_2 \rightarrow 3a_1$ transition is always of lowest energy in all variations of the $\text{Ti}(3d)$ and $\text{Cl}(-\delta)$ valence orbitals [6], it seems necessary to at least tentatively assign this transition to the absorption peak at $36,000\text{ cm}^{-1}$. Now the only other predicted transition to the $3a_1$ virtual orbital is the $2t_2 \rightarrow 3a_1$ transition, calculated to occur at high energy and to be a relatively wide absorption band with respect to the $3t_2 \rightarrow 3a_1$ transition. Such an absorption band is not observed experimentally, and we conclude that the $2t_2 \rightarrow 3a_1$ transition has not been seen. Completely analogous argument may also be used to exclude the $2t_2 \rightarrow 4t_2$ transition from further consideration. The calculated energies for both these transitions, it must also be remembered, are near and therefore possibly beyond the high energy limit of our experimental spectrum.

The next lowest energy transitions should all be from different filled orbitals to the same virtual orbital, the $4t_2$, and here the band-width data is in apparent disagreement with the calculated energy values. The best overall agreement would appear to be the tentative assignments of $3t_2 \rightarrow 4t_2$, $t_1 \rightarrow 4t_2$ and $1e \rightarrow 4t_2$ to the absorption bands at 43,400; 56,000; and 59,600 cm^{-1} respectively, for which the most narrow band has been associated with $t_1 \rightarrow 4t_2$, thereby establishing the right band-width relationship between $t_1 \rightarrow 4t_2$ and $3t_2 \rightarrow 4t_2$, but the $1e \rightarrow 4t_2$ transition has been retained as the fourth band purely on energetic considerations. In variations of the $\text{Ti}(3d)$ orbitals the $3t_2 \rightarrow 4t_2$ transition was observed to drop to slightly lower energy than the $t_1 \rightarrow 4t_2$ for very contracted $3d$ -orbitals [6], but the $1e \rightarrow 4t_2$ transition was always observed to remain at higher energy than either the $t_1 \rightarrow 4t_2$ or the $3t_2 \rightarrow 4t_2$.

The remainder of the experimental spectrum is the pair of intense, narrow absorption bands at 75,400 and 81,000 cm^{-1} , and the remaining unassigned transitions are $2a_1 \rightarrow 4t_2$, $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$. On the grounds that the close similarity of the two absorption peaks strongly suggests transitions to the same virtual orbital, that the transitions to the $2e$ orbital are predicted to be relatively narrow bands of comparable half-width but the $2a_1 \rightarrow 4t_2$ transition should be very broad, and that the calculated energies of the three transitions approach similar values for contracted $3d$ -orbitals, it is suggested that the 75,400 and 81,000 cm^{-1} absorption bands be associated with the $t_1, 3t_2 \rightarrow 2e$ transitions and that the $2a_1 \rightarrow 4t_2$ transition is not observed. The calculated (optimum) energy for the $2a_1 \rightarrow 4t_2$ transition, indeed, is in the region of 70,000 cm^{-1} , but we have previously concluded that the possible absorption here cannot be attributed to electric dipole allowed transitions. It may be well now to investigate in more detail the changes in the ordering of one-electron transitions, as suggested here in contrast to the order predicted from using the optimum valence orbitals.

5. Additional Variation of $\text{Ti}(3d)$ and $\text{Cl}(-\delta)$ Orbitals

In this final series of CNDO-MO calculations in which both the $\text{Ti}(3d)$ and $\text{Cl}(-\delta)$ valence orbitals are varied beyond their previously determined "optimum" values, the $3d(d^m)$ orbitals have been extended to include $3d(d^0)$, the hypothetical $\text{Ti}(3d)$ orbital which would be appropriate for $\text{Ti}(\text{IV})$ or for a d^0 electronic configuration. While a d^0 -configurational orbital cannot be calculated directly, of course, it has been extrapolated from tables of existing double-zeta form $\text{Ti}(d^m)$ orbitals [8] and should validly approximate a $3d$ radial function that would exist for a $\text{Ti}(d^0)$ configuration.

In Fig. 5 the one-electron transition energies are shown under variation of the $\text{Ti}(3d)$ orbitals, with constant $\text{Cl}(-1.0)$, $4s(\zeta_4 = 1.14)$ and $4p(d^2 p^2)$ valence orbitals. In an even more pronounced manner than for the similar variation with the $\text{Cl}(0)$ valence orbital [6] the re-arrangement of the ordering for transition energies into greater conformity with that postulated in the preceding section can be seen for more contracted $\text{Ti}(3d)$ orbitals, specifically for $3d(d^0)$. The $3t_2 \rightarrow 3a_1$ transition remains unchallengedly lowest in energy, but the $3t_2 \rightarrow 4t_2$ does indeed drop below the $t_1 \rightarrow 4t_2$ for the $3d(d^0)$ orbital, and in fact the $1e \rightarrow 4t_2$ is also in very close proximity for this choice of $\text{Ti}(3d)$ orbital. These three transitions (*i.e.*,

$t_1, 3t_2, 1e \rightarrow 4t_2$) may actually be similar enough in energy to be easily exchanged by even slight configuration interaction, and therefore perhaps their relative order cannot be predicted. The $3t_2 \rightarrow 2e$ transition is seen to be very sensitive to choice of Ti($3d$) orbital, but for $3d(d^0)$ it drops below the questioned $2a_1 \rightarrow 4t_2$ transition and is in precisely the right energy range to be one of the two high-energy absorp-

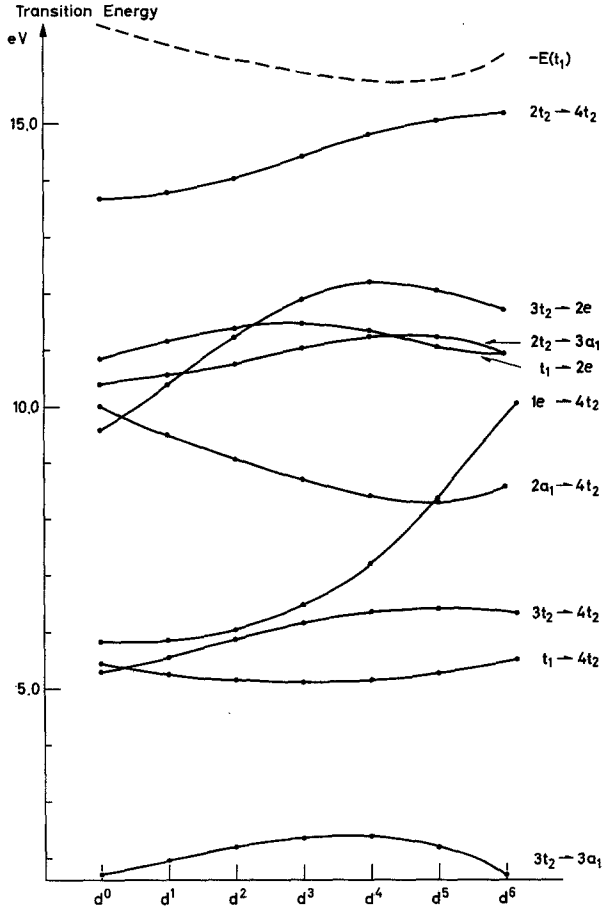


Fig. 5. Dependency of the electric dipole allowed one-electron transitions of TiCl_4 on the $\text{Ti}(3d)$ orbitals, with $4s(\zeta_4 = 1.14)$, $4p(d^2 p^2)$, and $\text{Cl}(-1.0)$ other valence orbitals

tion peaks. The $t_1 \rightarrow 2e$ transition does not drop below the $2a_1 \rightarrow 4t_2$, however, and is therefore above the $3t_2 \rightarrow 2e$ for part of the range of $3d(d^m)$ variation. Throughout most of the $3d(d^m)$ variation the $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$ transitions remain separated by about 1 eV or less, however, so as a pair these two transitions can still be associated with the two high-energy bands, even if their relative ordering is now under question. The $2t_2 \rightarrow 4t_2$ transition is at high enough energy to be safely ignored, and quite possibly the $2t_2 \rightarrow 3a_1$ and $2a_1 \rightarrow 4t_2$ transitions may also be pushed out of visibility range by even slight configuration interaction.

Table 3, which offers an even more extensive choice of appropriate $\text{Ti}(3d)$ and $\text{Cl}(-\delta)$ valence orbitals, only further confirms our observations from Fig. 5. Here the energies of the six tentatively assigned transitions, as well as that of $2a_1 \rightarrow 4t_2$ which we have suggested is not observed, grouped as they are expected to occur experimentally, are listed for selected $\text{Ti}(3d)$ and $\text{Cl}(-\delta)$ orbitals. The new ordering of the transition energies observed with the $3d(d^0)$ orbital is maintained for full variation of the $\text{Cl}(-\delta)$ orbitals, but the order previously observed for the "optimum" orbitals [6] is quickly established for the $3d(d^2)$ and $3d(d^4)$ orbitals except that the $t_1, 3t_2 \rightarrow 2e$ transitions remain inverted for the $3d(d^2)$ orbitals as well as the $3d(d^0)$.

Table 3. Variation of the expected one-electron transition energies with respect to the $\text{Ti}(3d)$ and $\text{Cl}(-\delta)$ valence orbitals and constant $4s(\zeta_4 = 1.14)$ and $4p(d^2 p^2)$ orbitals

$3d(d^n)$	$\text{Cl}(0.0)$	$\text{Cl}(-0.5)$	$\text{Cl}(-1.0)$		
$3d(d^0)$	2.610	2.112	1.701	$3t_2 \rightarrow 3a_1$	
	4.337 } 3.724 }	4.863 } 4.494 }	5.433 } 5.304 }	{ $t_1 \rightarrow 4t_2$ $3t_2 \rightarrow 4t_2$	
	4.710	5.249	5.830	$1e \rightarrow 4t_2$	
	(9.405)	(9.779)	(9.991)	$(2a_1 \rightarrow 4t_2)$	
	9.795 } 8.116 }	10.371 } 8.894 }	10.852 } 9.584 }	{ $t_1 \rightarrow 2e$ $3t_2 \rightarrow 2e$	
	$3d(d^2)$	2.668	2.412	2.196	$3t_2 \rightarrow 3a_1$
		3.723 } 4.162 }	4.447 } 4.998 }	5.155 } 5.878 }	{ $t_1 \rightarrow 4t_2$ $3t_2 \rightarrow 4t_2$
		4.684	5.371	6.052	$1e \rightarrow 4t_2$
(8.508)		(8.855)	(9.061)	$(2a_1 \rightarrow 4t_2)$	
10.477 } 10.093 }		10.972 } 10.689 }	11.392 } 11.251 }	{ $t_1 \rightarrow 2e$ $3t_2 \rightarrow 2e$	
$3d(d^4)$		2.624	2.485	2.391	$3t_2 \rightarrow 3a_1$
		3.561 } 4.522 }	4.385 } 5.408 }	5.153 } 6.346 }	{ $t_1 \rightarrow 4t_2$ $3t_2 \rightarrow 4t_2$
		5.886	6.557	7.193	$1e \rightarrow 4t_2$
	(7.813)	(8.180)	(8.402)	$(2a_1 \rightarrow 4t_2)$	
	10.594 } 11.243 }	11.021 } 11.722 }	11.355 } 12.201 }	{ $t_1 \rightarrow 2e$ $3t_2 \rightarrow 2e$	

In one sense Table 3 may be regarded as a re-evaluation of the valence $\text{Ti}(3d)$ and $\text{Cl}(-\delta)$ orbitals. Minimization of the total energy clearly favors expanded valence orbitals [6], so the "optimum" energy values in this sense are those at the bottom or lower-right of the table [*i.e.*, for $3d(d^4)$ and $\text{Cl}(-0.5) - \text{Cl}(-1.0)$]. The "free-atom" valence orbitals for TiCl_4 , on the other hand, would be more closely approximated by $3d(d^2)$ (*i.e.*, assuming the electronic configuration $[\text{Ar}] 3d^2 4s^2$ for Ti) and $\text{Cl}(0)$. Finally, the selection of $3d(d^0)$ and $\text{Cl}(-1.0)$ as valence orbitals could possibly be looked upon as a crude attempt to achieve the conventional but rather unrealistic ionic model of TiCl_4 as $\text{Ti}^{4+} \text{Cl}_4^{1-}$. Quite ironically this last selection of valence orbitals yields the apparently best agreement with experimental data and simultaneously offers spectral assignments very different from those extrapolated from crystal field theory, based also on an ionic model.

6. Conclusion

While a complete assignment of the six-band electronic absorption spectrum of TiCl_4 in terms of the calculated electric dipole allowed one-electron transitions has been suggested in the preceding text (*i. e.*, associating the transitions $3t_2 \rightarrow 3a_1$; $3t_2 \rightarrow 4t_2$, $t_1 \rightarrow 4t_2$; $1e \rightarrow 4t_2$; $t_1 \rightarrow 2e$, $3t_2 \rightarrow 2e$ with the absorption peaks at 4.43, 5.38, 7.07, 7.39, 9.35 and 10.04 eV, respectively) and argument given for these tentative assignments, perhaps this is far too ambitious as a conclusion. From our extensive CNDO-MO calculations we would seem to be led to conclude, however, that the lower energy electronic absorption bands in TiCl_4 (*i. e.*, certainly the absorption bands at 4.43 and 5.38 eV, and most probably also the bands at 7.07 and 7.39 eV) represent transitions from the higher energy filled levels to either the $3a_1$ or the $4t_2$ virtual orbitals, and that if the t_1 , $3t_2 \rightarrow 2e$ transitions are observed at all, they must be associated with higher energy absorption bands, suggested here as the 9.35 and 10.04 eV bands.

As noted previously [6] this conclusion is in disagreement with other spectral investigations of TiCl_4 , of several different theoretical approaches, which assign or imply the assignment of the transitions $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$ to the first pair of absorption bands, at 4.43 and 5.38 eV; but seems to be in at least partial agreement with paramagnetic Faraday rotation calculations for the first electronic band of TiCl_4 [10], which suggest that the $t_1 \rightarrow 2e$ transition must be at higher energy than the $t_1 \rightarrow 3t_2$ transition. Thus instead of closing the question of the electronic structure of TiCl_4 , this work may only prompt further investigation by posing a serious doubt, if not actual challenge, to the previously anticipated electronic structure along the ideas of crystal field theory. The doubt posed is really how far to the left-hand side of the transition series and to how large a formal oxidation state should a crystal field-type behavior be expected to extend.

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