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Structure and Singlet–Triplet Separation in Simple Germylenes GeH_2, GeF_2, and $Ge(CH_3)_2$

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Abstract: Ab initio valence-only calculations were performed on the three first states of GeH_2, GeF_2, and $GeMe_2$ with double ζ plus polarization basis sets. The three compounds are predicted to have singlet ground states. SCF singlet-triplet (S-T) energy gaps are 10 kcal/mol for GeH_2, 64 kcal/mol for GeF_2, and 14 kcal/mol for $GeMe_2$. SCF ground state equilibrium geometries correspond to GeH = 1.60 Å, ∠HGeH = 93°, GeF = 1.76 Å, ∠FGeF = 97°, CGe = 2.02 Å, and ∠CGeC = 98°. Extended CI increases the S-T gap to 19 kcal/mol for GeH_2 and to 74 kcal/mol for GeF_2. Full sets of force constants and vibrational frequencies were calculated and compare well with available IR and UV data.

I. Introduction

Divalent species of the group 4B elements are of considerable interest in organic and organometallic chemistry. Mainly this is due to the high reactivity of these unstable intermediates.

Recently, an excellent review describing their electronic structure and reactivity has been published by Nefedov et al.;[2] the evolution of the main features of these carbene-like molecules on going from carbon to lead is discussed in detail from the available experimental data.

In recent years, there have been a large number of theoretical studies to examine the low-lying electronic states of methylene,[3] halogenated carbenes,[4] and unsaturated carbenes.[5] The major aim of these works is to ascertain the nature of the ground state and to calculate the singlet-triplet (${}^1A_1$-${}^3B_1$) separation in comparison with the results of experimental works. Similar studies are also reported on the simplest silylene (SiH_2)[6-8] and silicon difluoride.[9,10] However, despite the important contribution of germylenes as starting products or intermediates in organometallic chemistry,[11] up to now the electronic structure of the simplest germylene (GeH_2) has not been subjected to any theoretical investigations.

The question as to whether the ground state of substituted germylenes is a singlet or a triplet is of interest in this context. The purpose of the present research is to answer this question for some simple germylenes, especially for the organic derivatives which are practically unexplored.

To this end, ab initio valence-only calculations have been carried out for the three lowest states of GeH_2, GeF_2, and $Ge(CH_3)_2$. Moreover, vibrational frequencies are calculated and compared with experimental values, when available, for all the states studied.

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Table I. Pseudopotential Parameters (au)

atom	l	α_l	n_1	C_1	n_2	C_2
carbon	0	0.650 84	2	1.152 10	−2	−0.226 76
	1	7.222 29	0	−2.278 44		
fluorine	0	1.576 75	2	1.227 80	−2	−1.424 91
	1	17.285 18	0	−3.606 19		
germanium	0	0.727 03	2	4.161 83	−2	−0.404 98
	1	0.636 29	2	3.353 87	−2	−0.189 45
	2	0.817 84	2	0.419 56	−2	0.701 23

II. Theoretical Details

All the SCF results contained herein are obtained from the PSIBMOL algorithm[12] using the pseudopotential method proposed by Durand and Barthelat.[13] Recent works[14] have shown that this method is both economical and accurate for studies of molecules containing heavy atoms such as germanium.

For each atom, the core electrons are taken into account through a nonempirical atomic pseudopotential determined from the double ζ atomic Hartree-Fock calculations of Clementi and Roetti.[15] The atomic pseudopotentials have the following analytical form:

$$W(r) = \sum_l W_l(r)P_l - z/r \qquad (1)$$

where z is the number of valence electrons for the neutral atom, P_l is the projector on the lth subspace of the spherical harmonics, and

$$W_l(r) = \left[\sum_i C_i/r^{n_i}\right] \exp(-\alpha_l r^2) \qquad (2)$$

The values of the parameters are given in Table I. The s and p components of the C and Ge pseudopotentials were obtained from their ($ns^2\,np^2$) ^3P ground state, and the Ge d component was obtained from the ($4s^3\,4p\,4d$) ^3D atomic state. For fluorine, the s and p components were obtained from the ($2s^2\,2p^5$) ^2P ground state of this atom.

For each atom, a valence basis set was optimized in a pseudopotential SCF calculation of the atomic ground state using a quadruple ζ Gaussian basis set. These four Gaussian functions were contracted to the double ζ level by means of a 3 + 1 procedure (except for the p basis set of Ge, where a 2 + 2 procedure has been used). For germanium, a 4d Gaussian function was added as a polarization function. For fluorine and germanium, the basis sets used here are listed in Table II. For hydrogen and carbon, valence basis sets are already reported in a previous paper.[16] For calculations on GeH_2, a set of p functions (exponent 0.8) was added to the basis set of each hydrogen atom.

The SCF wave functions for the $^1B_1$ and $^3B_1$ states were obtained using Roothaan's restricted open-shell procedure.[17]

Extended configuration interaction (CI) calculations have been performed for the various states of germylene and difluorogermylene according to the CIPSI algorithm.[18] For each state a zeroth-order wave function was built from an iterative selection of the most important determinants (up to triply excited) involved in it (about 25 determinants for GeH_2 and 19 for GeF_2). The resulting variational wave functions have been perturbed to the second order in energy, involving up to 2×10^4 and 2×10^5 determinants for GeH_2 and GeF_2, respectively. The Möller-Plesset definition[19] was used for the description of the nonperturbed Hamiltonian. The valence correlation energies obtained under these conditions are of the order of 50 kcal/mol for the different states of GeH_2 and 200 kcal/mol for those of GeF_2.

Table II. Atomic Gaussian Basis Sets for Fluorine and Germanium

atom	orbital	exponent	contraction coefficients
fluorine	2s	122.444	−0.008 656
		16.3399	−0.056 326
		1.104 43	0.573 625
		0.356 988	1.0
	2p	20.5867	0.047 544
		4.848 16	0.238 076
		1.332 29	0.504 225
		0.346 740	1.0
germanium	4s	5.045 10	−0.000 067
		1.232 08	−0.253 770
		0.215 152	0.735 067
		0.081 433	1.0
	4p	2.051 96	−0.038 008
		0.272 679	0.446 696
		0.097 935	0.552 370
		0.035 594	0.122 167
	4d	0.25	1.0

Precise equilibrium geometries were predicted by minimization of the total valence energy with respect to both bond distance and bond angle from a set of points suitably chosen on the two-dimensional potential surface. This procedure was extensively used except for dimethylgermylene, where the geometrical parameters were optimized independently for the sake of convenience.

Harmonic force constants and vibrational frequencies were determined for germylene GeX_2 by means of the **F** and **G** matrix method of Wilson, Decius, and Cross.[20] Using internal coordinates, the potential energy of the molecule may be written

$$2\Delta E = f_r(\Delta r_1{}^2 + \Delta r_2{}^2) + f_\alpha \Delta\alpha^2 + 2f_{rr}\Delta r_1 \Delta r_2 + 2f_{r\alpha}\Delta\alpha(\Delta r_1 + \Delta r_2) \qquad (3)$$

where r_1 and r_2 are the two GeX bond lengths and α is the XGeX angle. For each state, the force constants have been calculated at the optimized geometry from a set of calculated energy points corresponding to various atomic displacements.

III. Results

A. Germylene (GeH_2). Although GeH_2 generated by the vacuum-ultraviolet photolysis of germane has been studied by matrix isolation techniques,[21] its molecular structure and the spin multiplicity of its ground state are not definitely established.

The total valence energies and the optimized geometries for the $^1A_1$, $^3B_1$, and $^1B_1$ states of GeH_2 at two levels of calculation are presented in Table III.

All our calculations predict germylene to have a singlet ground state. The adiabatic $^1A_1$–$^3B_1$ energy splitting is computed to be 10.2 kcal/mol at the SCF level while the CI results produce a much larger value (19.1 kcal/mol). It is well known that the triplet state is approximately described by a single determinant SCF wave function, whereas a two-configuration SCF treatment would be required for a reliable description of the singlet state. Consequently, the CI treatment lowers the total valence energy of the singlet state by 58.9 kcal/mol while for the triplet state the lowering is only 50.0 kcal/mol. The result is an increase of the $^1A_1$–$^3B_1$ separation by about 9 kcal/mol. Note that for the same reason the inclusion of electron correlation produces a reverse effect on the singlet-triplet separation of methylene, which has a triplet ground state.[3]

The $^1B_1$ state is predicted to lie above the $^1A_1$ ground state by 43.7 kcal/mol at the SCF level. A very close value (46.7

Table III. Equilibrium Geometries, Total Valence Energies, and Adiabatic Energy Separations for the Low-Lying Electronic States of GeH_2 at Two Levels of Theory

state	theoretical description	bond distance, Å	bond angle, deg	total valence energy, au	adiabatic energy separation ΔE, kcal/mol
$^1A_1$	SCF	1.599	92.9	−4.741 962	
	CI	1.607	92.6	−4.835 773 (−4.835 756)[a]	
$^3B_1$	SCF	1.545	118.4	−4.725 724	10.2
	CI	1.555	118.6	−4.805 393 (−4.805 320)[a]	19.1
$^1B_1$	SCF	1.544	123.4	−4.672 308	43.7
	CI	1.566	123.2	−4.761 302 (−4.761 051)[a]	46.7

[a] The total valence energy value in parentheses is obtained from CI calculation carried out at the SCF optimized geometry.

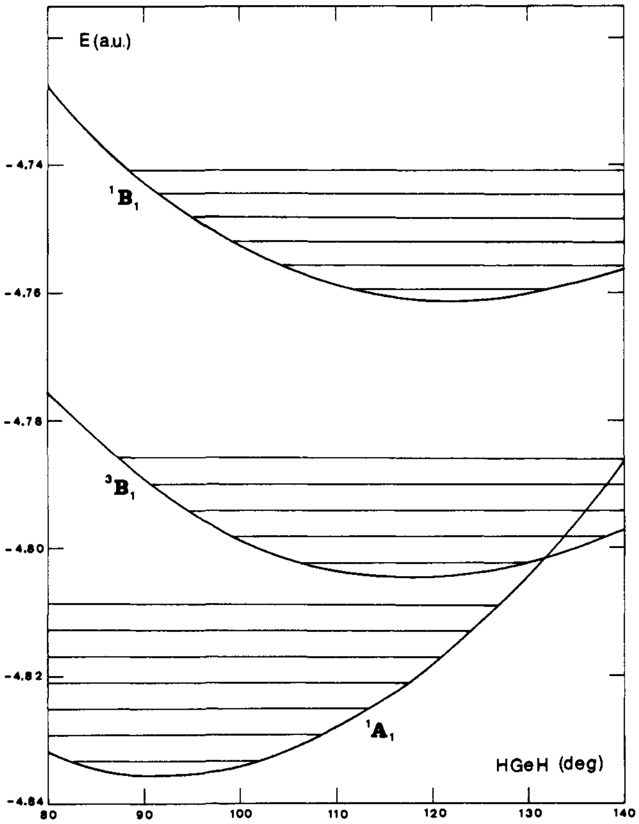


Figure 1. CI energy of the three first states of GeH_2 vs. HGeH angle for a GeH distance of 1.588 Å, with corresponding harmonic levels.

kcal/mol) is obtained at the CI level. Vertical energy splittings have also been computed at the CI level. The values are 27.6 kcal/mol for the $^1A_1$-$^3B_1$ splitting and 56.7 kcal/mol for the $^1A_1$-$^1B_1$ splitting.

The structure of singlet $^1A_1$ germylene has been estimated from matrix isolation spectroscopy.[21] Our predicted CI values (see Table III) perfectly agree with these estimated values, namely, a bond length of 1.6 Å and a bond angle of the order of magnitude of 92°. The structures of $^3B_1$ and $^1B_1$ GeH_2 are not known, and we predict GeH = 1.555 Å and HGeH = 118.6° for the $^3B_1$ state, and GeH = 1.566 Å and HGeH = 123.2° for the $^1B_1$ state. In Figure 1 are shown the energy vs. bond angle CI curves for the GeH_2 states at an intermediate bond length of 3 au.

It is interesting to note that the effect of CI on predicted geometries is not very important. As expected,[22] the inclusion of electron correlation lengthens the bond distances and does not alter significantly the bond angles relative to their SCF values. In order to avoid geometry optimizations at the CI level for reason of economy, we have calculated again the adiabatic energy separations from CI calculations carried out at the SCF optimized geometries. It is encouraging that the errors involved in using CI calculations at SCF geometries to determine energy splittings do not exceed 0.3%. Therefore this procedure does not change significantly the results and can be reasonably employed to solve our problem.

At both SCF and CI levels of theory, full sets of harmonic force constants and vibrational frequencies have been calculated at the optimized geometries for the three states studied. The results are reported in Table IV. The most noticeable differences between the SCF and CI values of the force constants are first a decrease of the GeH stretching force constant and second a change of the sign of f_{rr}. The comparison between our CI values and those deduced from experiment by Smith and Guillory[21] using a three-constant potential function leads to errors of 9.7% for the stretching force constant and 8% for the bending force constant. Considering the vibrational frequencies determined from the calculated force constants, the CI values seem to lead to a reverse order of the ν_1 and ν_3 frequencies with regard to experiment.

However, the agreement is satisfactory enough for purposes of calculating the change in zero-point vibrational energies in going from one electronic state to another. For the $^1A_1$ ground state, the zero-point vibrational energy determined from the three calculated vibrational frequencies is 7.0 kcal/mol, which may be compared with the value of 6.7 kcal/mol obtained from the experimental frequencies.

For the $^3B_1$ and $^1B_1$ states, the zero-point vibrational energies are calculated to be 6.9 and 6.8 kcal/mol, respectively. Thus the contributions to the energy separations are only 0.1 kcal/mol for the $^1A_1$-$^3B_1$ splitting and 0.2 kcal/mol for the $^1A_1$-$^1B_1$ splitting. Including vibrational corrections, the value of the $^1A_1$-$^3B_1$ energy difference is predicted to be 19.0 kcal/mol and the value of the $^1A_1$-$^1B_1$ energy difference 46.5 kcal/mol.

As concerns charge repartition in the singlet ground state of GeH_2, the population analysis gives a net charge of +0.31 on the germanium atom, reflecting a fairly weak dipole moment of 0.05 D.

B. Difluorogermylene (GeF_2). As mentioned in the preceding section, full geometry optimizations of GeF_2 have been carried out at the SCF level. A CI was performed on these SCF equilibrium geometries for $^1A_1$, $^3B_1$, and $^1B_1$ states. The results are reported in Table V. Difluorogermylene is predicted to have a singlet ground state. The $^1A_1$-$^3B_1$ gap is larger than for GeH_2, 74.1 kcal/mol at the CI level. As concerns the ground-state geometry a comparison with most relevant microwave experimental data of Takeo et al.[23] is made in Table V. Our calculated bond angle perfectly agrees with the ex-

Table IV. Calculated Force Constants and Vibrational Frequencies for the Low-Lying Electronic States of GeH_2

state	theoretical description	force constants[a]				vibrational frequencies[b]		
		f_r	f_{rr}	$f_{r\alpha}$	f_α	ν_1	ν_2	ν_3
$^1A_1$	SCF	2.37	0.11	0.02	0.28	2056	969	1964
	CI	2.36	−0.17	0.03	0.27	1887	958	2036
	exptl[c]	2.06	0.02		0.25	1887	920	1864
$^3B_1$	SCF	2.62	0.14	0.03	0.24	2166	901	2065
	CI	2.25	−0.23	0.07	0.25	1855	924	2063
$^1B_1$	SCF	2.70	0.16	0.04	0.18	2204	773	2091
	CI	2.21	−0.20	0.01	0.22	1864	860	2011

[a] Units are mdyn/Å for stretching-stretching, mdyn/rad for bending-stretching, and mdyn Å/rad^2 for bending force constants. [b] Frequencies are in cm^{-1}. [c] Experimental values are from ref 21.

Table V. Equilibrium Geometries, Total Valence Energies E, and Adiabatic Energy Separations ΔE for the Low-Lying Electronic States of GeF_2[a]

state	bond distance, Å	bond angle, deg	SCF calculations		CI calculations	
			E, au	ΔE, kcal/mol	E, au	ΔE, kcal/mol
$^1A_1$	1.761 (1.732)	97.5 (97.2)	−51.637 43		−51.956 81	
$^3B_1$	1.749	112.1	−51.535 74	63.8	−51.838 70	74.1
$^1B_1$	1.765	114.6	−51.433 72	127.8	−51.771 42	116.3

[a] Experimental values are given in parentheses.[23]

Table VI. Calculated Force Constants and Vibrational Frequencies for the Low-Lying Electronic States of GeF_2 at the SCF Level[c]

state	force constants[a]				vibrational frequencies[b]		
	f_r	f_{rr}	$f_{r\alpha}$	f_α	ν_1	ν_2	ν_3
$^1A_1$	4.58 (4.08)	0.33 (0.26)	0.01 (−0.01)	0.37 (0.32)	736 (692)	284 (263)	702 (663)
$^3B_1$	4.85	0.15	0.02	0.23	721	233	756
$^1B_1$	4.37	0.20	0.04	0.21	685	222 (164)	715

[a,b] Same units as in Table IV. [c] Experimental values are given in parentheses.[23,24]

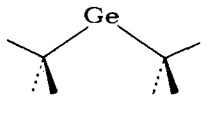
perimental value while the calculated GeF distance is overestimated by 0.03 Å. This can be attributed to the lack of d polarization AOs on the fluorine atom in our calculation. As in the carbene series, for which CF_2 is also singlet in its ground state,[4] when going from hydrogen to fluorine the bond angle increases for the $^1A_1$ singlet state and decreases for the $^3B_1$ triplet state (see Tables III and V).

In Table VI are given the force constants and vibrational frequencies for the three states studied, calculated at the SCF level. The spectroscopic properties of GeF_2 have been extensively studied.[24-29] Our calculated values are in good agreement with experimental data[23,24] for the $^1A_1$ ground state. One can notice that, if considering Margrave's assignments,[24] it is confirmed that $\nu_3 < \nu_1$.

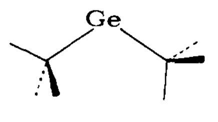
The experimental $^1A_1$-$^1B_1$, 0,0,0-0,0,0 transition is known from the ultraviolet absorption spectrum of GeF_2[25] to be 125.5 kcal/mol. This value compares very well with our SCF calculated adiabatic energy separation (see Table V), 127.8 kcal/mol, while at the CI level this value is underestimated, 116.3 kcal/mol. Our calculated ν_2 frequency in the $^1B_1$ excited state is in rather good agreement with the experimental value deduced from vibrational progression.[25]

As expected the charge separation is very strong in monomer GeF_2. The Mulliken net atomic charges are +1.03 e on Ge and −0.52 e on each fluorine atom. The calculated dipole moment, 3.24 D, compares rather well with the experimental value of 2.61 D.[23] These strong net charges on such elements, the most electronegative one with a very electropositive one, are not surprising and are certainly responsible for the propensity of this molecule to arrange as a dimer.

C. **Dimethylgermylene ($GeMe_2$).** Dimethylgermylene was investigated as the prototype of symmetrical alkylgermylenes. Because of the size of this molecule, calculations were performed only at the SCF level. A conformational problem arises with the respective positions of the two methyl groups which can star each other in a C_{2v} symmetry or stagger each other in a C_s symmetry. These two more relevant conformations were both investigated but are nearly degenerate anyway ($\Delta E \simeq 0.5$ kcal/mol).



C_{2v}



C_s

Assuming tetrahedral methyl groups with a CH bond length fixed at 1.09 Å, the geometry optimization on GeC bond length and CGeC bond angle led to the structures and relative energies for the three first states reported in Table VII. The ground state is again singlet ($^1A'$ since the C_s conformation is preferred). The first triplet state takes the C_{2v} form (the CGeC

Table VII. Equilibrium Geometries,[a] Total Valence Energies E, and Adiabatic Separation Energies ΔE for the Low-Lying Electronic States of $Ge(CH_3)_2$ at the SCF Level

symmetry group and state		Ge-C, Å	∠CGeC, deg	E, au	ΔE, kcal/mol
C_s	$^1A'$	2.024	97.8	−18.085 23	
C_{2v}	$^3B_1$	1.999	117.5	−18.063 43	13.7
	$^1B_1$	2.021	122.0	−18.004 11	50.9

[a] Methyl groups are assumed tetrahedral with C-H = 1.09 Å.

Table VIII. Calculated Force Constants and Vibrational Frequencies for the Low-Lying Electronic States of Dimethylgermylene

	force constants[a]				vibrational frequencies[b]		
state	f_r	f_{rr}	$f_{r\alpha}$	f_α	ν_1	ν_2	ν_3
$^1A'$	2.05	0.28	0.003	0.31	560	288	497
$^3B_1$	2.59	0.05	0.01	0.14	576	203	611
$^1B_1$	2.48	0.001	0.01	0.13	554	194	607

[a,b] Same units as in Table IV. [c] Assumed joint methyl groups and C_{2v} symmetry.

angle being larger in this state, as in the first singlet excited state) and stands 13.7 kcal/mol above the ground state, at the SCF level. One can notice that a CI would only increase this gap, bringing more correlation energy to the singlet ground state. The first singlet excited state $^1B_1$ lies 50.9 kcal/mol above the ground state. The substitution of hydrogen atoms by methyl groups has increased the singlet-triplet gap by about 4 kcal/mol at the SCF level. According to the SCF calculations of Baird and Taylor[4b] the same relative singlet stabilization occurs from CH_2 to CMe_2, which are both triplet in their ground state, however.

Assuming point methyl groups, a set of force constants and vibrational frequencies calculated at the SCF level is given in Table VIII. As concerns charge separation in the singlet ground state, the net charge on the germanium atom in $Ge(CH_3)_2$, +0.41 e, is close to that in GeH_2; the dipole moment was calculated to be 0.97 D.

IV. Discussion and Conclusion

The presently studied simple germylenes all have a singlet ground state. From the knowledge on carbene series[4] it is very likely that all germylenes have a singlet ground state; the only doubt might concern unsaturated substituted germylenes since unsaturated substituents such as C=O, C≡N, and C=C are known to stabilize triplet states.[4,5] So methylene (CH_2) seems to be the only group 4B dihydride to possess a triplet ground state; the singlet-triplet gap should increase down to the heavier group 4B elements but our calculated S-T gap for germylene (GeH_2) (19.1 kcal/mol) is quite similar to the S-T gap for silylene (SiH_2) calculated with a comparable basis set (18.6 kcal/mol).[7]

In Table IX the SCF calculated equilibrium geometries of the three first states of GeH_2 are compared with analogous SCF calculations on CH_2 and SiH_2.[7] A great difference appears from CH_2 to SiH_2 while minor geometrical changes appear from SiH_2 to GeH_2.

Our valence MO's energy pattern is numerically very close to that of ref 7 for SiH_2. The separation between the highest a_1 and b_1 orbitals can be related to the tendency to a singlet ground state (large gap) or triplet (small gap) ground state. The a_1-b_1 separations were calculated in ref 7 to be 0.0733 au for CH_2 and 0.1089 au for SiH_2. Our calculated value for GeH_2, 0.1054 au, is close to the SiH_2 value, reflecting here also the same singlet-triplet separation.

Table IX. SCF Calculated Trends in Bond Distances (Å) and Bond Angles (deg) for the Lowest Electronic States of Carbene-Like Molecules

		state		
molecule		$^1A_1$	$^3B_1$	$^1B_1$
CH_2[a]	r_e	1.095	1.070	1.065
	θ_e	103.7	129.5	141.2
SiH_2[a]	r_e	1.509	1.471	1.468
	θ_e	93.5	117.6	123.5
GeH_2	r_e	1.599	1.545	1.544
	θ_e	92.9	118.4	123.4

[a] One-configuration SCF results of Meadows and Schaefer.[7]

The SCF energies of the HOMO of singlet ground states are the ionization potentials according to Koopmans' theorem and can measure for these singlet states the nonbonding σ orbital as noticed in ref 2. Our calculated values are 9.05 eV for GeH_2, 11.78 eV for GeF_2, and 8.12 eV for $GeMe_2$. The only experimental data concern GeF_2 (11.6[30] and 11.8 eV[31]) and are in perfect agreement with our value.

This work, which appeared reliable as shown by comparison with available experimental data, has shown a strong propensity for germylenes to have a singlet ground state; the S-T gaps are much higher than for carbenes but are not very much higher than silylene ones. Moreover, the higher S-T gap of GeF_2 with respect to $GeMe_2$ or GeH_2 is consistent with the stronger electrophilic activity of GeF_2 as compared to dialkylgermylene in several types of reactions such as complexation or addition reactions.[11,33-35] With respect to ground-state multiplicity of group 4B divalent compounds, the main change seems to occur from line two (C) to line three (Si). This similarity must not hide, however, structural differences between silylenes and germylenes. A subtle and interesting difference occurs, for instance, in the structure of the difluoride dimer which is bridged for GeF_2[27] and rather π bonded for SiF_2.[32]

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Spectroscopic Studies of Photochemically Important Transition Metal Excited States. 2. The $^1T_{1g}$, $^3T_{1g}$, and $^5T_{2g}$ Excited States of Hexaamminecobalt(III)

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Abstract: Low-temperature, high-resolution, polarized single crystal absorption studies of the $^1T_{1g} \rightarrow {}^1A_{1g}$, $^3T_{1g} \rightarrow {}^1A_{1g}$ electronic transitions in hexaamminecobalt(III) are reported. Analysis of the structure in the electronic origin regions of these transitions combined with Franck–Condon analysis of the absorption band shapes demonstrates that the photochemically active $^3T_{1g}$ state (and $^1T_{1g}$ state) undergoes a large e_g Jahn–Teller effect. This produces a D_{4h} excited state geometry with an expansion of ~0.12 Å in the Co–NH_3 bond length along two axes and a contraction of ~0.02 Å along the third axis. In addition, an analysis of the multiplet splitting pattern of the $^3T_{1g}$ pure electronic origins allows an approximate determination of the energetic position of the $^5T_{2g}$ state which interacts with the triplet through spin–orbit coupling. An experimentally derived potential surface diagram of the above states is presented which indicates an efficient radiationless deactivation pathway for the $^3T_{1g}$ state. The photochemical implications of these results and their relation to other photochemically active d^3 and d^6 complexes are also discussed.

I. Introduction

In a previous study[1] we were able to experimentally determine a reasonable picture of the equilibrium geometry of the photoactive $^4T_2$ excited state of the d^3 octahedral hexaamminechromium(III) complex. These results were made possible through detailed spectroscopic study of a new molecular crystal lattice system, $Cr(NH_3)_6(ClO_4)_2Cl \cdot KCl$, which exhibits a great deal of vibronic structure on the broad band ligand field $^4T_{2g} \leftarrow {}^4A_{2g}$ transition at low temperature. From a theoretical analysis of the origin region and of the overall band shape, it was found that the $Cr(NH_3)_6^{3+}$ complex undergoes reasonably large distortions in both the totally symmetric a_{1g} and Jahn–Teller e_g normal modes upon excitation into the $^4T_{2g}$ excited state. These distortions combine to produce an excited-state molecule with D_{4h} symmetry which is expanded in the equatorial plane, a distortion which is consistent with the observed ligand photodissociation product in the substituted complexes.

In the low-spin d^6 octahedral complexes, particularly $Co(NH_3)_6^{3+}$ and $Co(CN)_6^{3-}$, photochemical studies[2] have implicated the spin-forbidden $^3T_{1g}$ excited state as being responsible for the observed photoreactivity. However, more recent investigations[3] suggest that in $Co(NH_3)_6^{3+}$ the $^3T_{2g}$ and $^1T_{1g}$ states may also play a significant role. These transitions are indicated in the overall $Co(NH_3)_6^{3+}$ absorption spectrum presented in Figure 1.

One particularly striking difference between these two complexes is in their photoaquation quantum yields ($\phi(Co(NH_3)_6^{3+}) = 3.1 \times 10^{-4}$; $\phi(Co(CN)_6^{3-}) = 0.31$).[4a] Possible rationales for these differences involve significant variations[4a,b] in the potential surfaces of the $^3T_{1g}$ state in the hexaammine as compared to the hexacyanide and the effects[4c,d] of the strongly D_q dependent, highly spin forbidden $^5T_{2g}$ state on the $^3T_{1g}$ state in the hexaammine, which has a lower ligand field strength and therefore a lower lying quintet. Although it was possible to determine[5] an average excited state distortion for $Co(CN)_6^{3-}$ by simultaneously fitting the weakly structured emission spectrum and the unstructured absorption spectrum, not enough structure is exhibited by this complex to experimentally distinguish between the different distorting modes and obtain an excited-state geometry. This is in contrast to $Co(NH_3)_6^{3+}$, which does not appear to emit, but which we find to exhibit in its absorption spectrum (like its chromium counterpart) a great deal of excited-state structure in the $Co(NH_3)_3(ClO_4)_2Cl \cdot KCl$ lattice. This has permitted us to obtain reasonable pictures of the $^1T_{1g}$ and $^3T_{1g}$ excited state geometries. Furthermore, the highly structured $^3T_{1g}$ electronic origin region permits us to obtain experimental evidence for a strong $^3T_{1g}$–$^5T_{2g}$ interaction via spin-orbit coupling for this complex and to derive an approximate picture of the potential surfaces and energetic position of the $^5T_{2g}$ state with respect to the $^3T_{1g}$ state. The photochemical implications of these results are considered in the Discussion section.

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