by eq 10 if the energy of the e_g orbital is close to that of the a_{1g} orbital and they are much smaller than 2.0023. The hydrated ion in the alum crystal therefore shows small g factors. Although the energy of the a_{1g} orbital is higher, this hydration structure is stable in the crystal because the increase of the orbital energy is compensated by the strong hydrogen bondings between the coordinating water and the surrounding water molecules and ions. The distortion of the hydration structure is concluded to arise from the long-range order of the crystal structure.

Acknowledgment. We thank Professor A. Lund at the Linköping Institute of technology for measuring the ENDOR spectrum of the hydrated Ti^{3+} ion.

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Geometrical Structure and Electronic States of the Hydrated Titanium(III) Ion. An ab Initio CI Study

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Abstract: The geometrical structure and the electronic states of the hydrated Ti^{3+} ion, $[Ti(H_2O)_6]^{3+}$ complex, have been studied by means of ab initio MO calculations including electron correlation. The optimized geometrical structure is in good agreement with the structure that has been experimentally determined by means of an electron spin-echo modulation analysis. The complex possesses D_{3d} symmetry, which is slightly distorted from O_h symmetry by the Jahn–Teller effect. The electronic ground state is the $^2A_{1g}$ state in which the unpaired electron is mainly distributed in the d_{z^2} orbital. The g tensor of $g_\parallel = 2.000$ and $g_\perp = 1.864$ calculated by a second-order perturbation method with the wave functions obtained from the MR-SD-CI calculation is in good agreement with the experimental values. The shoulder of the electronic absorption spectrum appearing at 570 nm is determined to be caused by the Jahn–Teller distortion of the excited $^2E_g'$ state.

Since hydration of metal ions plays an important role in structural chemistry and chemical reactions in aqueous solutions, it has been extensively studied experimentally[1-3] and theoretically.[4-6] The hydrated trivalent titanium ion, $[Ti(H_2O)_6]^{3+}$ complex, is one of the simplest paramagnetic transition-metal complexes that has only one electron in the d orbital. However, the structure of the $[Ti(H_2O)_6]^{3+}$ complex has not been much studied because of its chemical instability. The structure of the $[Ti(H_2O)_6]^{3+}$ complex in the crystal of cesium titanium alum, $CsTi(SO_4)_2 \cdot 12H_2O$, has been studied by using electron spin resonance (ESR),[7] UV, and visible spectroscopies.[8] It has been concluded from these studies that the $[Ti(H_2O)_6]^{3+}$ complex in the alum crystal has C_3 symmetry with the water molecules aligned toward the central Ti^{3+} ion. However, the hydration structure of the Ti^{3+} ion in water is not the same as that in the alum, because the ESR spectrum of the Ti^{3+} ion in glassy water is totally different from that in the alum crystal.

The hydrated Ti^{3+} ion in water shows a characteristic absorption spectrum around 500 nm with the shoulder at 570 nm.[9] Three structural models have been proposed for explaining the absorption spectrum; The first model[10] is based on the crystal field (CF) theory[11] and assumes O_h symmetry as a starting structure. The d orbitals then split into the t_{2g} and e_g orbitals. Owing to electrostatic interactions, the unpaired electron in the d_{xy} orbital pushes the four ligands on the xy plane away from the central metal ion. The symmetry is therefore changed from O_h to D_{2h}, and an absorption band due to the $^2T_{2g}$ to ^2E_g transition emerges in the visible region. The second model[12] was proposed for explaining the shoulder band at 570 nm. The ground state in this model is assumed to have O_h symmetry. The excited ^2E_g state splits into the $^2A_{1g}$ and $^2B_{1g}$ states because of the Jahn–Teller effect. The absorption bands at 500 and 570 nm are therefore assigned to be $^2T_{2g}$ to $^2B_{1g}$ and $^2T_{2g}$ to $^2A_{1g}$ transitions, respectively. The third model[13] assumes the structure to be a distorted octahedron (D_{3d} symmetry) with compression along the C_3 axis. The orbitals generated by mixing of the d orbitals are a_{1g}, e_g, and e_g'. The absorption bands are assigned to be the transition from a_{1g} to e_g (500 nm) and to e_g' (570 nm), respectively.

We have studied the geometrical structure of the $[Ti(D_2O)_6]^{3+}$ complex in the amorphous solid of a 2-propanol/D_2O mixture by means of ESR and electron spin-echo (ESE) techniques and concluded that the complex is in D_{3d} symmetry with the $g_\parallel$ and $g_\perp$ factors of 1.994 and 1.896, respectively.[14] The optical absorption spectrum of the complex in the amorphous solid is the same as that of the hydrated Ti^{3+} ion in the aqueous solution, so that the determined structure is the same as the hydration structure of the Ti^{3+} ion in water.

In the present study, ab initio molecular orbital calculations including electronic correlation have been performed on the $[Ti(H_2O)_6]^{3+}$ complex. The main purposes of this study are (1)

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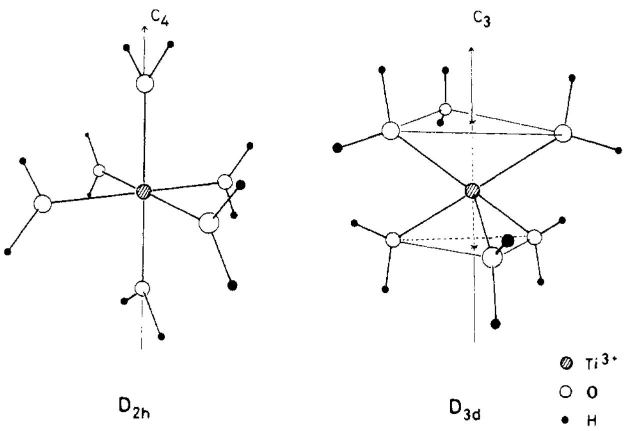

Figure 1. Structural models of the $[Ti(H_2O)_6]^{3+}$ complex under D_{2h} and D_{3d} symmetries. The molecular dipoles of the coordinated water molecules are oriented toward the central Ti^{3+} ion in both models.

to compare the calculated structure with the experimental one for clarifying whether the D_{3d} symmetry of the complex is caused by the Jahn–Teller distortion or by the distortion arising from the matrix molecules around the complex,[15] (2) to assign the optical absorption bands, and (3) to compare the calculated g tensor with the experimental one.

Method of Calculation

Since the state energies of transition-metal ions have been known to be strongly affected by electron correlation and the choice of basis sets,[16,17] we carefully checked the effects of the basis sets and electron correlation on the calculated results. Basis sets used for the Ti atom in the ab initio Hartree–Fock (HF) calculation were the minimal (3333/33/3) basis (basis I) proposed by Huzinaga and Tatewaki,[18] the split valence type (43321/43/31) basis (basis II), and the split valence plus polarization (43321/43/31)+P(0.073) (basis III). For the ligand H_2O molecules, the STO-3G basis[19] was used.

The geometry optimization of the $[Ti(H_2O)_6]^{3+}$ complex was performed with the GAMESS program[20] by using the unrestricted HF (UHF) energy gradient method.[21] The geometries were fully optimized with the (3333/33/3) basis sets under two possible symmetries, D_{2h} and D_{3d}, as shown in Figure 1. Because of the convenience of the calculation, C_s symmetry was actually used in the calculation instead of D_{3d} symmetry. The SCF energies of each state were calculated under the optimized configurations by means of the restricted open-shell HF (ROHF) method[22] with the JAMOL3[23] program. The state energies were also calculated by the ΔSCF method.[24]

In order to calculate electron correlation, we performed the multireference single- and double-excitation CI (MR-SD-CI) calculation.[25] The reference functions were constructed from the HF configuration. The reference functions with the weight larger than 0.95 were used for the calculation. The 1s to 2p orbitals of the Ti atom and the 1s orbital of the oxygen atom were treated with the frozen-core approximation. One- or two-electron excitations within the (3s)(3p)(3d)(4s)(4p) orbitals of the Ti atom were permitted. The CI dimension for the two-electron excitations was about 8200. The final CI dimension was about 2000 after the configuration state functions (CSF) contributing to energy lowering were selected by means of the Rayleight-Schrödinger's second-order perturbation method.[26] The contribution of unlinked quadruple excitations was estimated with Davidson's method.[27] All the CI calculations were carried out by using the MICA3 program[28] developed by Murakami et al.

Table I. Optimized Parameters for $[Ti(H_2O)_6]^{3+}$ Complex Obtained by ab Initio UHF Energy Gradient Method with the (3333/33/3) Basis Sets[a]

symmetry	parameter	
D_{2h}	R(Ti–O), z	1.930
	R(Ti–O), x, y	1.972
	R(O–H)	0.982
D_{3d}	R(Ti–O)	1.966
	R(O–H)	0.993
	∠(C_3–Ti–O)	58.1

[a] Bond lengths and angles are in angstroms and degree.

Since the $[Ti(H_2O)_6]^{3+}$ complex has an unpaired electron in the d orbital, the orbital angular momentum of the electron is not completely quenched. In the present study, we made the theoretical calculation of the g-tensor components by using natural orbitals (NO). The spin Hamiltonian[29] is given by

$$\mathbf{H}_{\text{spin}} = \beta \sum_i \mathbf{H}_i g_{ii} S_i \tag{1}$$

where β is the Bohr magnetron, H is the magnetic field, and **S** is the effective spin vector. Since the spin–orbit coupling is weaker than the electronic energy, the spin–orbit coupling terms were added to NO by a second-order perturbation method. The **g**-tensor components have the following form

$$g_{ij} = g_e + \Delta g_{ij} \tag{2}$$

$$\Delta g_{ij} = g_e \sum \langle \Phi_0 | \mathbf{L}_i / \hbar | \Phi_n \rangle \langle \Phi_n | \xi \mathbf{L}_j / \hbar | \Phi_0 \rangle (E_0 - E_n)^{-1} \tag{3}$$

where $\mathbf{L}_i$ is the i component of the total angular momentum, Φ_n is NO with the energy E_n, and $\xi = 121$ cm^{-1} is the spin–orbit coupling constant for the Ti^{3+} ion.

Results and Discussion

Optimized Geometrical Structure of the $[Ti(H_2O)_6]^{3+}$ Complex. The optimized geometries for the D_{2h} and the D_{3d} complexes obtained by means of the energy gradient method with the minimal (3333/33/3) basis set are given in Table I. As is expected from the CF theory, the Ti–O bond lengths of the D_{2h} complex are slightly longer on the xy plane.

Although the geometrical optimization for the D_{3d} complex was performed by reducing the symmetry to C_s, the optimized structure still retains D_{3d} symmetry, which indicates that the D_{3d} structure is stable even though the symmetry change from D_{3d} is permitted. The UHF method is known to cause a large amount of spin contamination due to independent orbital calculations of α and β spins. However, the calculated spin angular momentum S^2 of the D_{3d} complex is 0.763, which compares well with the exact value of 0.75. The effect of the spin contamination is therefore negligibly small.

The optimized Ti–O bond length of the D_{3d} complex is 1.996 Å. The angle between the Ti–O bond and the C_3 axis is 58.1°, which implies that the complex is slightly distorted from a regular octahedron by a compression along the C_3 axis. The calculated C_3 axis–Ti–O angle of the D_{3d} complex is in good agreement with the experimental one. However, the bond length is a little shorter than the experimental value. The calculated bond length may be slightly underestimated because of the minimal basis set used in the geometry optimization. The preliminary MR-SD-CI calculation with the (43321/43/31)+P basis set showed the energy minimum at the Ti–O distance of 2.05 Å. Since the difference of the bond length between the UHF and the MR-SD-CI calculations is less than 0.1 Å, it is concluded that the optimized structures obtained from the UHF calculation are very close to the real ones. The optimized geometrical parameters given in

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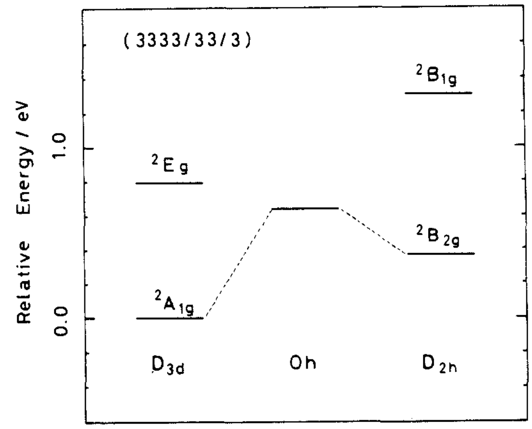


Figure 2. Relative state energies of the $[Ti(H_2O)_6]^{3+}$ complex calculated by the ΔSCF method with minimal (3333/33/3) basis. The zero level corresponds to −1293.90163 au.

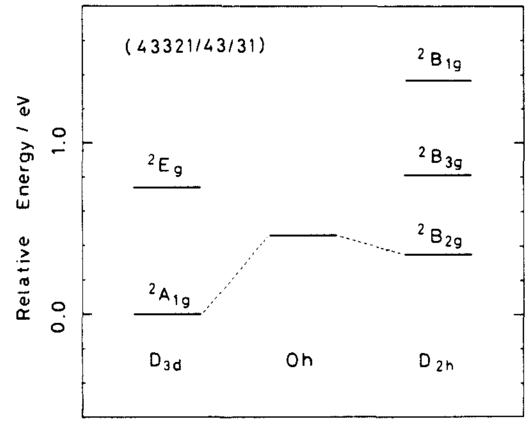


Figure 3. Relative state energies of the $[Ti(H_2O)_6]^{3+}$ complex calculated by the ΔSCF method with the double-ζ type (43321/43/31) basis. The zero level corresponds to −1296.82550 au.

Table I are used in the following calculations.

Electronic States and Jahn–Teller Effect. The reason why the D_{3d} complex is more stable than the D_{2h} complex can be shown by comparing the electronic states of these complexes. The state energies for the optimized structures calculated by the ΔSCF method with basis I and basis II are shown in Figures 2 and 3, respectively. A term O_h in these figures infers the symmetry of the complex with six equivalent oxygens under D_{2h} symmetry. The state energies obtained from the two independent basis sets show a similar tendency with respect to the symmetry change of the complex; the $^2A_{1g}$ state under D_{3d} symmetry is more stable than the $^2B_{2g}$ state under D_{2h} symmetry. The geometrical distortion from O_h to D_{2h} or D_{3d} symmetries arises from the Jahn–Teller effect. The energy difference between the $^2A_{1g}$ and the $^2B_{2g}$ states is 8.5 kcal/mol for basis I and 8.2 kcal/mol for basis II.

Figure 4 shows the state energies of the D_{3d} and D_{2h} complexes at the MR–SD–CI level. The ground states are the same as those obtained by the HF calculations: the $^2B_{2g}$ and $^2A_{1g}$ states for the D_{2h} and D_{3d} complexes, respectively. The energy of the $^2A_{1g}$ state is also lower than that of the $^2B_{2g}$ state. The stabilization energy by the symmetry change from O_h to D_{3d} is 12.5 kcal/mol at the MR–SD–CI level and 12.2 kcal/mol after the Davidson corrections. The low-laying doublet states under O_h symmetry are the $^2T_{2g}$ and ^2E_g states. The symmetry of this complex is reduced to D_{3d} by the Jahn–Teller distortion. The electronic states then split into three components, the $^2A_{1g}$, $^2E_g{}'$, and ^2E_g states. The $^2A_{1g}$ and $^2E_g{}'$ states are stabilized by the distortion whereas the ^2E_g state is slightly destabilized.

Since the lowest state is always the $^2A_{1g}$ state irrespective of the method of calculation, it is concluded that the D_{3d} complex is inherently stable because of the Jahn–Teller effect, and the interaction of the complex with the matrix molecules in the amorphous solid does not change the symmetry of the complex.

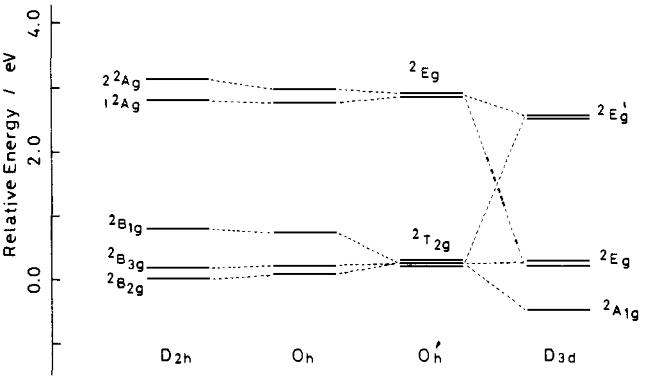


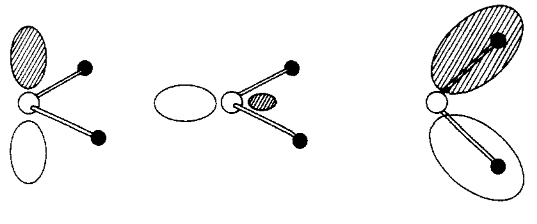
Figure 4. Relative state energies of the $[Ti(H_2O)_6]^{3+}$ complex calculated by the MR–SD–CI method with the double-ζ plus polarization, (43321/43/31)+P, basis. The zero level corresponds to −1297.07442 au.

Table II. Muiliken Atomic Bond Populations and Atomic Charges for the Ti Atom and the H_2O Molecule with D_{2h} Structure Based on MR–SD–CI Calculations

electronic state	Ti–O	O–H	Ti	H_2O
$^2B_{2g}$	0.387	0.569	+0.888	+0.352
$^2B_{3g}$	0.382	0.569	+0.936	+0.344
$^2B_{1g}$	0.379	0.569	+0.948	+0.342
1^2A_g	0.348	0.564	+1.008	+0.332
2^2A_g	0.347	0.563	+1.026	+0.329

The Jahn–Teller splitting energy, $^2T_{2g} \rightarrow {}^2A_{1g} + {}^2E_g$, is calculated to be 5646 cm^{-1} at the MR–SD–CI level. The splitting energy for the Ti(III)–trisacetylacetonate complex is 7500 cm^{-1},[30] which is substantially larger than that for the $[Ti(H_2O)_6]^{3+}$ complex. Since this value is proportional to the covalency of metal–ligand bonds, the Ti–OH_2 bond might be weaker than the bond formed between Ti and the oxygen of the C=O carbonyl group.

The orbitals important for the bond formation between Ti and H_2O are[31]



The ab initio calculations showed that the energies of the orbitals below SOMO (singly occupied MO) are approximately the same for the ground and the excited electronic states, so that the differences of the state energies can be discussed with only SOMO orbital energies.

The contour maps of the molecular orbitals for the unpaired electron in the ground and low-lying excited states under D_{2h} and D_{3d} symmetries are shown in Figures 5 and 6, respectively. As is shown in Figure 5A, SOMO in the ground $^2B_{2g}$ state of the D_{2h} complex is the antibonding $(d_\pi{-}\pi_{OH_2})^*$ orbital, which is composed of one d orbital and six π_{OH_2} orbitals. The metal–ligand interaction in the $^2B_{1g}$ state arises from the n_π orbitals of the H_2O molecule. The $(d_\pi{-}n_\pi)^*$ type orbital overlapping is larger than the $(d_\pi{-}\pi_{OH_2})^*$ type overlapping, so that the energy of the $^2B_{1g}$ state is higher than that of the $^2B_{2g}$ state. SOMO in the $^2B_{3g}$ state is formed as a result of two $(d_\pi{-}n_\pi)^*$ and two $(d_\pi{-}\pi_{OH_2})^*$ interactions. The energy difference between the $^2B_{2g}$ and $^2B_{3g}$ states is large enough to prohibit the rotation of the H_2O molecules toward the *xy* plane. SOMO in the 1^2A_g and the 2^2A_g states are composed of σ-type antibonding orbitals. These results suggest that the stability or

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(30) See the reference on p 178 in ref 29.

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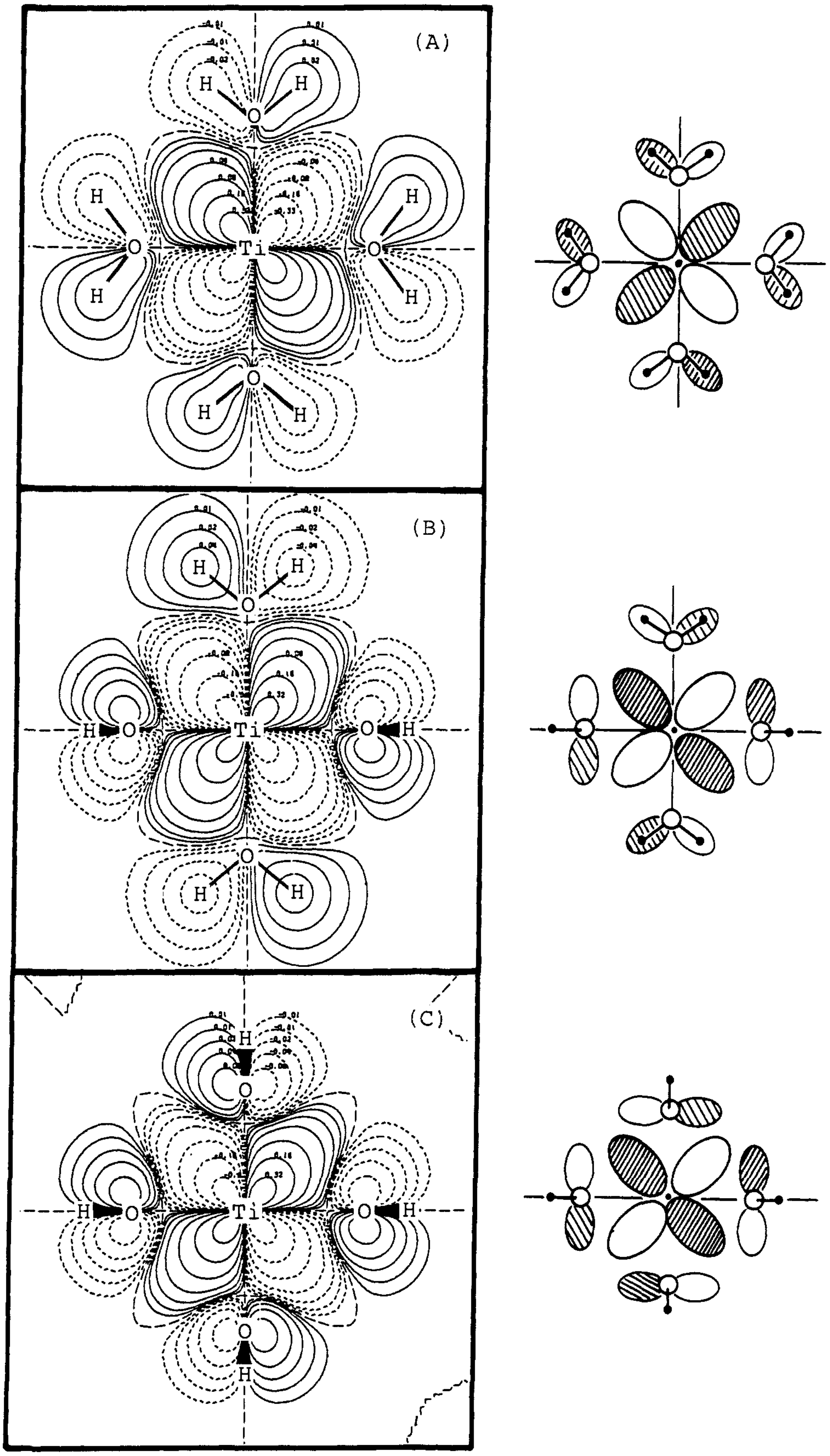

Figure 5. Contour maps of singly occupied molecular orbitals and orbital interaction between the Ti atom and water molecules under D_{2h} symmetry: (A) $^2B_{2g}$ state (d_π–π_{OH_2} interaction); (B) $^2B_{3g}$ state; (C) $^2B_{1g}$ state.

the state energy of the D_{2h} complex is governed by the repulsive interaction between the d orbital of the metal ions and the n_π orbitals of the H_2O molecules.

Table II shows the atomic charges and the Mulliken populations of the D_{2h} complex. The atomic populations on the Ti atom and the H_2O molecules are approximately the same for the ground and the excited states. The Ti–O bond is slightly weaker in the excited states because of the increase of the antibonding $(d_\pi$–$n_\pi)^*$ interaction.

As is shown in Figure 6A, the unpaired electron of the

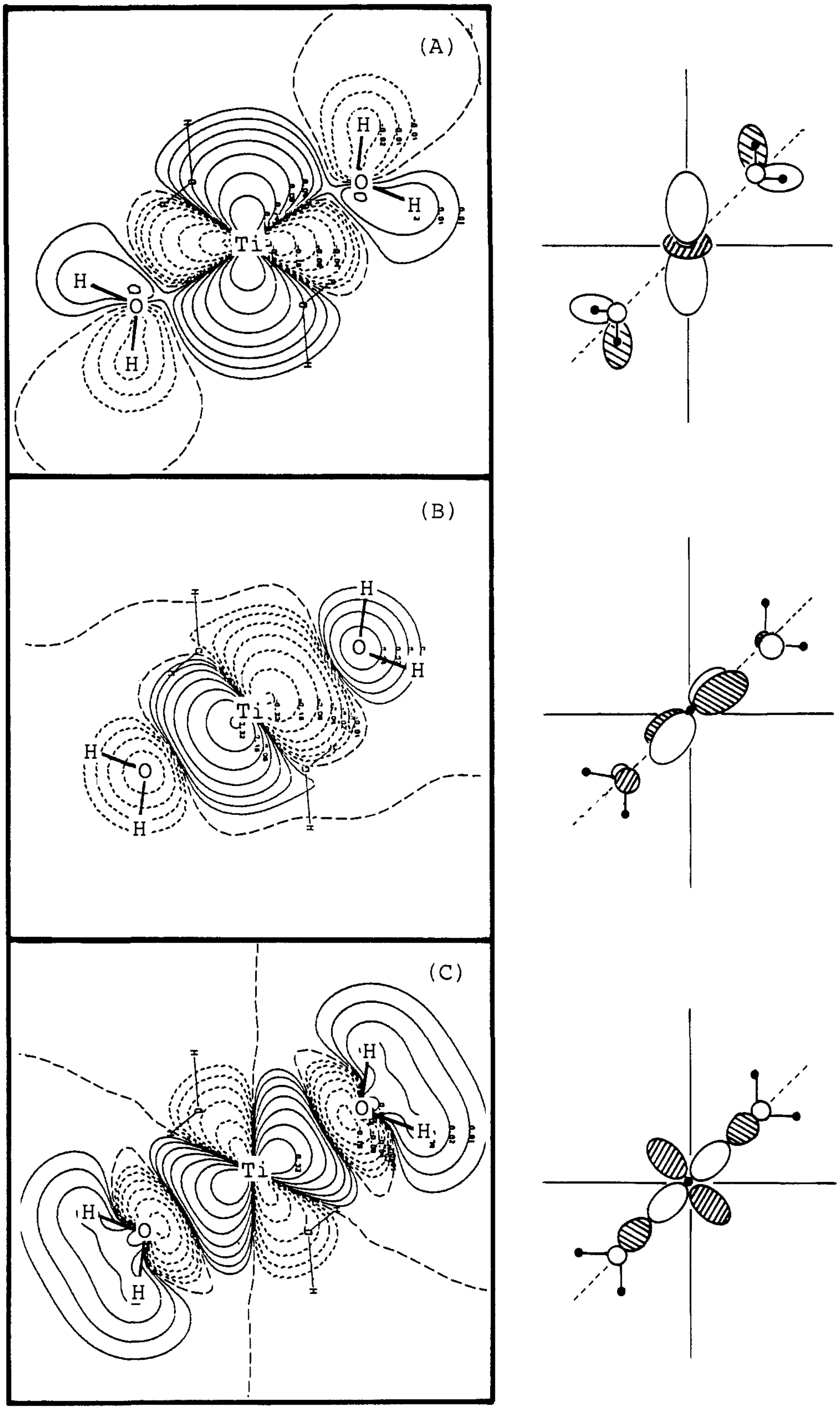

Figure 6. Contour maps of singly occupied molecular orbitals and orbital interaction between the Ti atom and water molecules under D_{3d} symmetry: (A) $^2A_{1g}$ state (d_{z^2}–π_{OH_2} interaction); (B) ^2E_g state (d_π–n_π interaction); (C) $^2E_g{}'$ state (d_σ–n_σ interaction).

ground-state D_{3d} complex is mainly distributed along the C_3 axis. SOMO is composed of a weak antibonding $(d_{z^2}-\pi_{OH_2})^*$ orbital. As is shown in parts B and C of Figure 6, SOMO in the ^2E_g and $^2E_g{}'$ states are composed of strongly repulsive $(d_\pi-n_\pi)^*$ and $(d_\sigma-n_\sigma)^*$ antibonding orbitals, respectively. The Mulliken atomic populations[32] and the atomic charges calculated at the MR–SD–CI level with the natural orbital are given in Table III. A significant amount of charge transfer from the H_2O molecules to the central metal atom takes place. The total amount of the charge transfer is about 2e, which implies that the apparent charge of the Ti ion in the complex is about +1.

Table IV shows the Mulliken populations of SOMO on the Ti–O bond for the D_{3d} complex calculated by using the ROHF method. Since the unpaired electron occupies the antibonding

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(32) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1841.

Table III. Mulliken Atomic Bond Populations and Atomic Charges for the Ti Atom and the H_2O Molecule with D_{3d} Structure Based on MR-SD-CI Calculations

electronic state	Ti-O	O-H	Ti	H_2O
$^2A_{1g}(1^2A')$	0.379	0.568	+0.930	+0.345
$^2E_g(2^2A')$	0.373	0.567	+0.978	+0.337
$2E_g(1^2A'')$	0.373	0.567	+0.978	+0.337
$^2E_g'(3^2A')$	0.342	0.562	+1.044	+0.326
$^2E_g'(2^2A'')$	0.343	0.562	+1.050	+0.325

Table IV. Mulliken Atomic Bond Populations on the Ti-O Bond under D_{3d} Symmetry Calculated with SOMO at the HF Levels

electronic state	Ti-O
$^2A_{1g}$	-0.019
^2E_g	-0.052
$^2E_g'$	-0.241

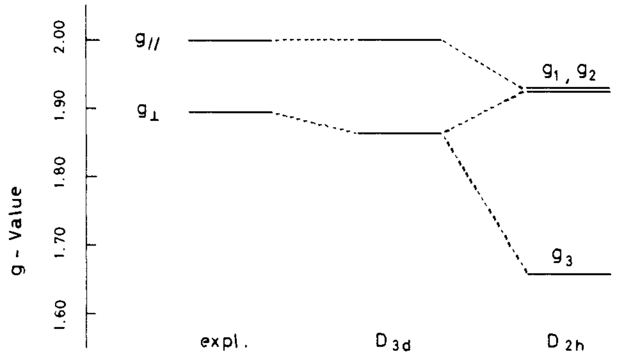

Figure 7. Comparison of the experimental and theoretical g-tensor components for the $[Ti(H_2O)_6]^{3+}$ complex. The calculations were carried out at the MR-SD-CI level by using a second-order perturbation theory.

orbital, the sign of the population is always negative. The repulsion between the metal and the ligands in the $^2E_g'$ state is larger than those in the $^2A_{1g}$ and ^2E_g states. These results indicate that the geometrical distortion might occur in the $^2E_g'$ excited state to lower the energy of the excited state. The absorption spectrum of the $[Ti(H_2O)_6]^{3+}$ complex appearing at 500 nm with the shoulder at 570 nm is therefore explained as due to the excited Jahn-Teller effect or the energy splitting from the $^2E_g'$ state to the $^2A'$ and $^2A''$ states.

g Tensor. In the previous paper,[14] we determined the symmetry of the complex by the analysis of the ESR *g* factors and the ESE nuclear modulation pattern. In this section, we carry out the g-tensor calculation by using NO and the state energies obtained from the MR-SD-CI calculation. Figure 7 shows the calculated g-tensor components of the D_{3d} and the D_{2h} complexes. The g-tensor components for the D_{3d} complex are in good agreement with the experimental values, which also supports the idea that the symmetry of this complex is D_{3d}. The calculation of the g tensor under the configuration that the H-O-H plane is perpendicular to the C_3 axis-Ti-O plane was also performed. The results suggest that the rotation of the H-O-H plane causes the increase of the $^2A_{1g}$ state energy and the increase of the mixing of the ^2E_g and $^2E_g'$ states by spin-orbit coupling and therefore causes the decrease of the $g_\parallel$ and, especially, $g_\perp$ values.

The g-tensor components of the hydrated Ti^{3+} ion in the $CsTi(SO_4)_2 \cdot 12H_2O$ crystal are 1.25 for $g_\parallel$ and 1.14 for $g_\perp$, which are much different from those in the amorphous solid.[33] The coordinated water molecules in the crystal strongly interact with the adjacent water molecules and ions, so that the H-O-H plane cannot to be aligned parallel to the C_3 axis. On the other hand, because of the lack of long-range order and the low concentration of ions, the hydrated Ti^{3+} ion in the amorphous water shows the ESR spectrum close to that of the isolated hydrated ion.

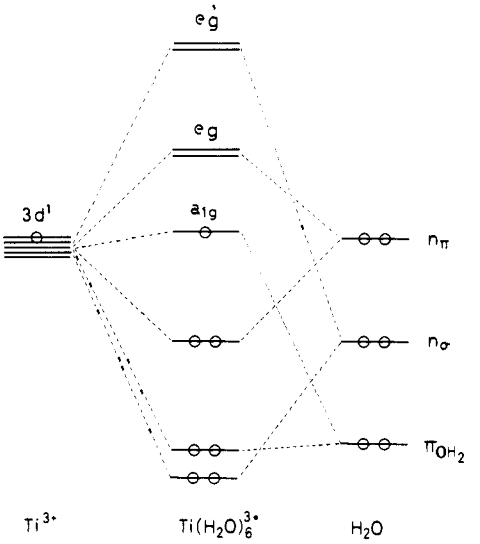

Figure 8. Schematic representation of orbital interactions between the Ti^{3+} ion and a coordinated water molecule.

Conclusion

The ab initio HF and MR-SD-CI calculations for the $[Ti(H_2O)_6]^{3+}$ complex revealed that the ground-state complex possesses D_{3d} symmetry with the H-O-H plane parallel to the C_3 axis. The Ti-O distance and the C_3 axis-Ti-O angle are 1.966 Å and 58°, which are in reasonable agreement with the values derived from the ESE nuclear modulation analysis.

The ground electronic state of the complex is the $^2A_{1g}$ state. Since the unpaired electron in the $^2A_{1g}$ state is mainly distributed in the d_{z^2} orbital of the Ti atom, the repulsion between the central metal ion and the coordinated water molecules is minimized under D_{3d} symmetry. The stability of the complex is governed by the repulsive interaction between the SOMO d orbital and the nonbonding orbitals of the coordinated water molecules. Although the structure of the complex is close to a regular octahedron, because of the presence of the axial field arising from the repulsive interaction, the complex shows the axially symmetric ESR spectrum with the $g_\parallel$ value larger than the $g_\perp$ value. The calculated g tensor is in good agreement with the experimental one. It is noted that the Jahn-Teller stabilization of the ground-state complex is not induced by the change of the Ti-O bond lengths and bond angles but is attained by the rotation of the H_2O molecular planes.

The first excited state of the complex is ^2E_g. However, the excitation energy is not as larger as that predicted by the CF theory. The visible absorption band of the complex is therefore not due to the $^2A_{1g} \rightarrow {}^2E_g$ transition but due to the $^2A_{1g} \rightarrow {}^2E_g'$ transition. The shoulder band appearing at 570 nm is due to the splitting of the $^2E_g'$ state to the $^2A'$ and $^2A''$ states by the excited Jahn-Teller effect.

Finally, the schematic representation of the orbital interactions between the coordinated molecules and the central Ti^{3+} ion is shown in Figure 8. The e_g' and e_g orbitals are made as a result of $(d_\sigma - n_\sigma)$ and $(d_\pi - n_\pi)$ interactions, respectively. The unpaired electron occupies the orbital composed of the d and π_{OH_2} orbitals.

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