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# Correlation between the Vibrational Frequencies of the Carboxylate Group and the Types of Its Coordination to a Metal Ion: An *ab Initio* Molecular Orbital Study

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The structures and vibrational frequencies of the acetate ion interacting with a metal ion ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) in the unidentate, bidentate, bridging, and pseudobridging forms are studied by *ab initio* molecular orbital calculations. Effects of a water molecule coordinating to either the acetate ion or the metal ion are also examined. The calculations are carried out by using the self-consistent reaction field method at the Hartree–Fock level with the 6-31+G\*\* basis set. For the species interacting with a divalent metal cation, the lengths of the two CO bonds of the acetate ion are nearly equal in the bidentate form but are significantly different in the unidentate form. The frequency of the  $\text{COO}^-$  antisymmetric stretch of the unidentate species is higher than that of the ionic species, which is in turn higher than that of the bidentate species. The reverse is the case for the  $\text{COO}^-$  symmetric stretch. As a result, the frequency separations ( $\Delta\nu_{\text{a-s}}$ ) between the  $\text{COO}^-$  antisymmetric and symmetric stretches for the unidentate, bidentate, and ionic species are in the following order:  $\Delta\nu_{\text{a-s}}$  (unidentate) >  $\Delta\nu_{\text{a-s}}$  (ionic) >  $\Delta\nu_{\text{a-s}}$  (bidentate). It is demonstrated that such a correlation between the vibrational frequencies of the  $\text{COO}^-$  group and the types of its coordination to a divalent metal cation is related to changes in the CO bond lengths and the OCO angle. The results of the present study clarify the physical basis of the empirical structure–frequency correlation, which has been used in the analysis of the infrared spectra of  $\text{Ca}^{2+}$ -binding proteins.

## 1. Introduction

There are three representative types of coordination of the carboxylate ( $\text{COO}^-$ ) group to metal ion(s):<sup>1,2</sup> unidentate, bidentate, and bridging. A metal ion interacts equally with the two oxygen atoms of the  $\text{COO}^-$  group in the bidentate form, whereas it interacts with only one of those oxygen atoms in the unidentate form. In the bridging form, a metal ion interacts with one of those oxygen atoms, and another metal ion interacts with the other oxygen atom. When one of these metal ions is replaced by a hydrogen atom of a water molecule, the system is in the pseudobridging form.

Correlation between the  $\text{COO}^-$  stretching frequencies and the types of  $\text{COO}^-$  coordination has been investigated in several studies.<sup>1–8</sup> Deacon and Phillips<sup>1</sup> have examined the structures and vibrational frequencies observed for a number of acetate salts in the solid state and have found an empirical rule for the correlation between  $\Delta\nu_{\text{a-s}}$  (frequency separation between the  $\text{COO}^-$  antisymmetric and symmetric stretches) and the types of coordination of the  $\text{COO}^-$  group to divalent metal cations, which is expressed as  $\Delta\nu_{\text{a-s}}$  (unidentate) >  $\Delta\nu_{\text{a-s}}$  (ionic)  $\sim$   $\Delta\nu_{\text{a-s}}$  (bridging) >  $\Delta\nu_{\text{a-s}}$  (bidentate). However, the theoretical basis for this correlation has not been fully clarified.

Interactions between the  $\text{COO}^-$  group and divalent metal cations play important roles in some biologically active molecules, such as calmodulin and parvalbumin which are known as  $\text{Ca}^{2+}$ -binding proteins. We (M.N. and M.T.) have recently shown<sup>9,10</sup> that the existence of the  $\text{COO}^-$  antisymmetric stretching band at  $1553\text{ cm}^{-1}$  and the  $\text{COO}^-$  symmetric stretching band at  $\sim 1424\text{ cm}^{-1}$  is a feature characteristic of  $\text{Ca}^{2+}$ -bound calmodulin and parvalbumin. In order to derive information on the metal–ligand interactions in such metal-ion-binding sites from vibrational spectra, it is important to

understand the factors giving rise to the correlation between the  $\text{COO}^-$  stretching frequencies and the types of coordination of the  $\text{COO}^-$  group to  $\text{Ca}^{2+}$ .

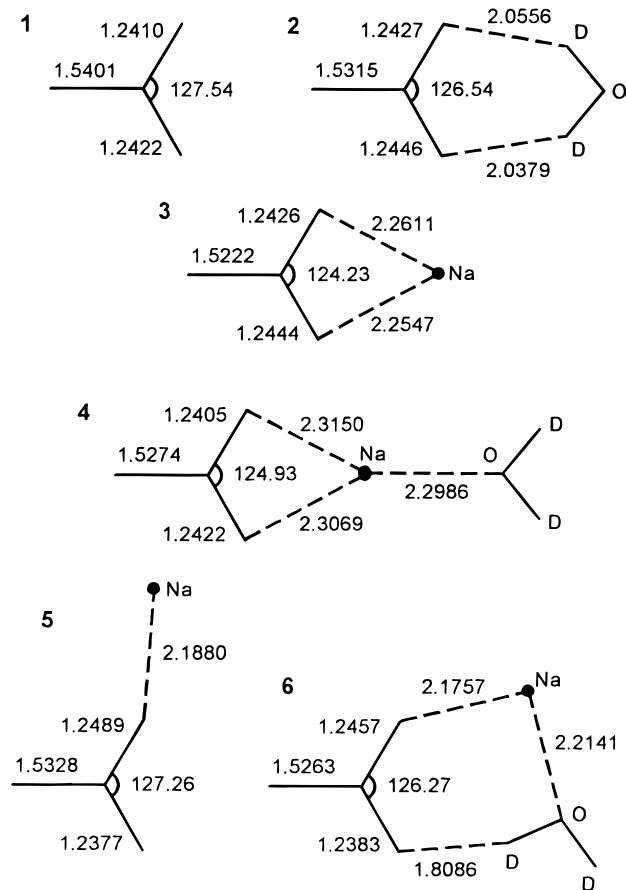
In the present study, the structures and vibrational frequencies of the acetate ion interacting with a metal ion ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) in the unidentate, bidentate, bridging, and pseudobridging forms are studied by *ab initio* molecular orbital (MO) calculations. Since the infrared spectra of these systems are measurable only in the condensed phases, *ab initio* MO calculations for isolated species in vacuum may not be appropriate to obtain vibrational frequencies that can be compared with experimental results. Since the acetate ion has a large dipole moment ( $\sim 5\text{ D}$ ), interaction with surrounding molecules is expected to be significant. Wong et al.<sup>11–14</sup> have shown that the self-consistent reaction field (SCRF) method is useful for studying molecular properties of dipolar species in the condensed phases. This method is based on Onsager's reaction field theory<sup>15</sup> of electrostatic solute–solvent interactions. We use the results (structures and vibrational frequencies) calculated by this method for discussing the correlation between the  $\text{COO}^-$  stretching frequencies and the types of coordination of the  $\text{COO}^-$  group to a metal ion.

## 2. Computational Procedure

*Ab initio* MO calculations have been performed by using the Gaussian 92 program<sup>16</sup> on a Hewlett-Packard workstation (Apollo 9000 series model 735) at the Research Center for Spectrochemistry of the University of Tokyo. The SCRF method has been employed to take into account the effects of surrounding dielectric media. In some calculations, a strongly interacting water molecule has been explicitly included. All the calculations have been carried out at the Hartree–Fock (HF) level. For the atoms in the acetate ion and the water molecule as well as for  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , the 6-31+G\*\* basis set has been used. For  $\text{Ca}^{2+}$ , we have used the SVD basis set developed by Schäfer et al.<sup>17</sup>

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**Figure 1.** Optimized structures of the “free” acetate ion (**1**), the acetate ion hydrogen bonded with a water molecule (**2**), and the acetate ion interacting with  $\text{Na}^+$  (**3–6**).

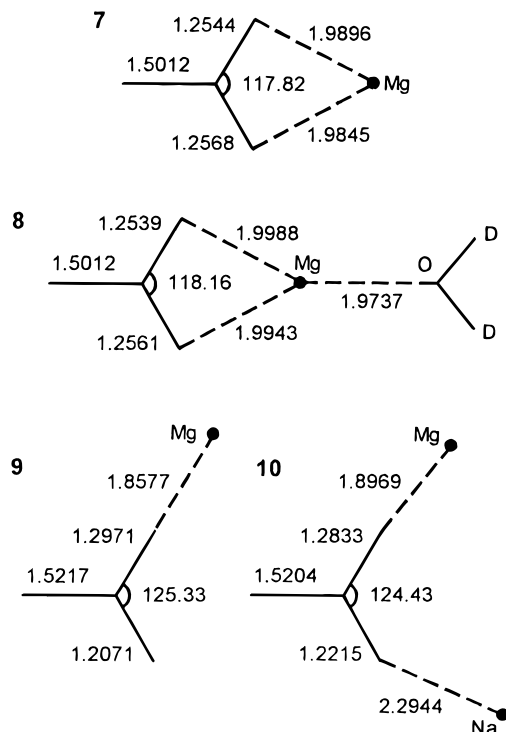
The cavity radii employed in the SCRF calculations have been determined by using the VOLUME keyword in the Gaussian 92 program, so that they are consistent with the molecular volumes of the structures obtained by geometry optimization. The dielectric constant of the surrounding medium in the SCRF calculations has been assumed to be 78.5.

The optimized structures have been obtained on the assumption that one of the hydrogen atoms of the methyl group is on the plane of the  $\text{COO}^-$  group. In the calculations of vibrational frequencies, the hydrogen atoms of the methyl group are deuterated in order to remove the mixing between the  $\text{COO}^-$  symmetric stretch and the methyl deformations, which does not exist in the side chains of proteins. The hydrogen atoms of the explicitly considered water molecule are also deuterated, because infrared spectra of proteins are often measured in  $\text{D}_2\text{O}$  instead of  $\text{H}_2\text{O}$ . All the calculated frequencies are multiplied by 0.89 to obtain better fits to the observed values.

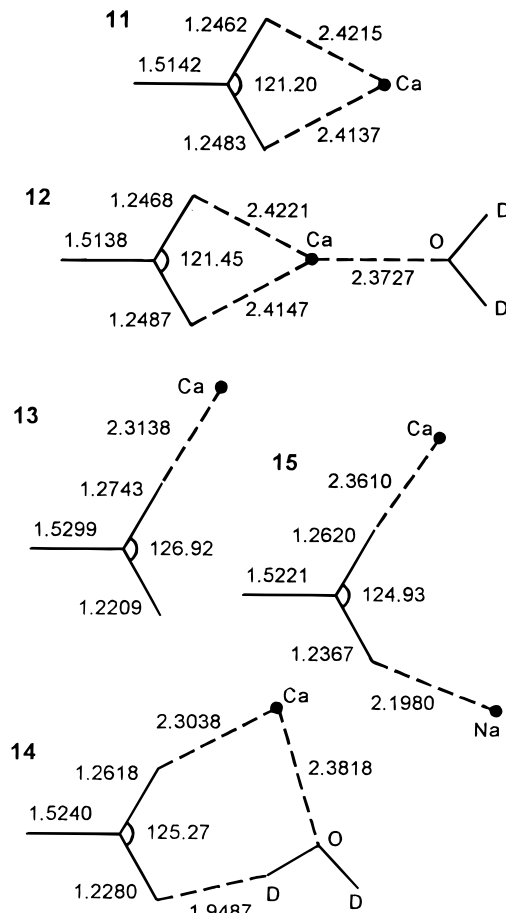
### 3. Results and Discussion

**3.1. Structures.** The optimized structures of all the species calculated in the present study are shown in Figures 1–3. The hydrogen atoms of the methyl groups are not shown in these figures.

The structures of the free acetate ion (**1**) and the acetate ion hydrogen bonded to a water molecule (**2**) are very similar to each other. In each of these two species, the lengths of the two  $\text{CO}$  bonds are nearly equal to each other and are in the range 1.241–1.245 Å, indicating that the  $\text{COO}^-$  group is nearly symmetric. The effect of hydrogen bonding on the  $\text{CO}$  bond lengths is small. The  $\text{OCO}$  angle in these two species is about 127°.



**Figure 2.** Optimized structures of the acetate ion interacting with  $\text{Mg}^{2+}$  (**7–10**).



**Figure 3.** Optimized structures of the acetate ion interacting with  $\text{Ca}^{2+}$  (**11–15**).

In the following, we discuss the structures of the acetate–metal systems in comparison with those of the above two species.

*Acetate Ion Interacting with  $\text{Na}^+$ .* The acetate ion interacting

with  $\text{Na}^+$  in the bidentate form (**3**) has a nearly symmetric  $\text{COO}^-$  group. Its CO bond lengths are nearly equal to those of **1** and **2**. However, its OCO angle is smaller by  $2-3^\circ$  than those of **1** and **2**. These structure parameters do not change appreciably upon coordination of a water molecule to  $\text{Na}^+$  (**4**). The distances between  $\text{Na}^+$  and the two oxygen atoms of the  $\text{COO}^-$  group are different by about  $0.05 \text{ \AA}$  between **3** and **4**.

The acetate ion interacting with  $\text{Na}^+$  in the unidentate form (**5**) has a slightly asymmetric  $\text{COO}^-$  group. The CO bond interacting with  $\text{Na}^+$  is longer than the free CO bond by about  $0.011 \text{ \AA}$ . The OCO angle is nearly equal to that of **1**. When a water molecule interacts with both the  $\text{COO}^-$  group and  $\text{Na}^+$  in the pseudobridging form (**6**), the difference between the two CO bond lengths is about  $0.007 \text{ \AA}$  and is smaller than that in **5**. The OCO angle of **6** is nearly equal to that of **2**.

The above results indicate that the interaction between  $\text{COO}^-$  and  $\text{Na}^+$  is very small, so that the structure of the acetate ion does not change substantially. We therefore regard the acetate ion shown in Figure 1 (species **1–6**) as being in the ionic state.

**Acetate Ion Interacting with  $\text{Mg}^{2+}$ .** The  $\text{COO}^-$  group of the acetate ion interacting with  $\text{Mg}^{2+}$  in the bidentate form (**7**) is nearly symmetric as in the cases of **1** and **2**. However, the CO bonds of **7** ( $1.2544$  and  $1.2568 \text{ \AA}$ ) are noticeably longer than those of **1** and **2** ( $1.241-1.245 \text{ \AA}$ ). The OCO angle of **7** is smaller than those of **1** and **2** by about  $8^\circ$ . These results indicate that the interaction between  $\text{COO}^-$  and  $\text{Mg}^{2+}$  is stronger than that between  $\text{COO}^-$  and  $\text{Na}^+$ .

The structure parameters of the  $\text{COO}^-$  group in **7** do not change substantially upon coordination of a water molecule to  $\text{Mg}^{2+}$  (**8**). However, the distances between  $\text{Mg}^{2+}$  and the oxygen atoms of the  $\text{COO}^-$  group become longer by about  $0.01 \text{ \AA}$ .

The acetate ion interacting with  $\text{Mg}^{2+}$  in the unidentate form (**9**) has a significantly asymmetric  $\text{COO}^-$  group. The CO bond interacting with  $\text{Mg}^{2+}$  is longer by  $0.09 \text{ \AA}$  than the other CO bond. The OCO angle of this species is smaller than those of **1** and **5** by about  $2^\circ$ . The interaction between  $\text{COO}^-$  and  $\text{Mg}^{2+}$  is stronger than that between  $\text{COO}^-$  and  $\text{Na}^+$  in the unidentate form (**9** compared with **5**) as well as in the bidentate form (**7** compared with **3**).

We have not been able to obtain an optimized structure for the acetate ion interacting with  $\text{Mg}^{2+}$  and a water molecule in the pseudobridging form. The acetate ion interacting with both  $\text{Mg}^{2+}$  and  $\text{Na}^+$  in the bridging form (**10**) is shown in Figure 2. The difference between the two CO bond lengths of this species is about  $0.06 \text{ \AA}$  and is smaller than that of **9**. The asymmetry of the  $\text{COO}^-$  group of **10** is therefore smaller than that of **9**. The OCO angle of **10** ( $124.43^\circ$ ) is smaller than that of **9** (in the unidentate form) but is larger than that of **7** (in the bidentate form).

**Acetate Ion Interacting with  $\text{Ca}^{2+}$ .** The acetate ion interacting with  $\text{Ca}^{2+}$  in the bidentate form (**11**) has a nearly symmetric  $\text{COO}^-$  group. Its CO bonds are longer than those of **1** and **2** by about  $0.005 \text{ \AA}$  but are shorter than those of **7** by  $0.008 \text{ \AA}$ . The OCO angle of **11** is smaller than that of **1** by about  $6^\circ$  and is larger than that of **7** by about  $3^\circ$ . These results indicate that the interaction between  $\text{COO}^-$  and  $\text{Ca}^{2+}$  is weaker than that between  $\text{COO}^-$  and  $\text{Mg}^{2+}$ . The structure parameters of the  $\text{COO}^-$  group in **11** do not change appreciably upon coordination of a water molecule to  $\text{Ca}^{2+}$  (**12**).

When the acetate ion interacts with  $\text{Ca}^{2+}$  in the unidentate form (**13**), the  $\text{COO}^-$  group becomes asymmetric. However, the difference between the two CO bond lengths in **13** ( $0.05 \text{ \AA}$ ) is smaller than that in **9** ( $0.09 \text{ \AA}$ ), indicating that the asymmetry is smaller in the former than in the latter. The OCO

angle of **13** is nearly equal to those of **1** and **2**. In the unidentate form also, the interaction between  $\text{COO}^-$  and  $\text{Ca}^{2+}$  is smaller than that between  $\text{COO}^-$  and  $\text{Mg}^{2+}$ .

When a water molecule interacts with both the  $\text{COO}^-$  group and  $\text{Ca}^{2+}$  in the pseudobridging form (**14**), the asymmetry of the  $\text{COO}^-$  group is smaller than that of **13** but is larger than that in **6**. The  $\text{COO}^-$  group is even less asymmetric in the acetate ion interacting with  $\text{Ca}^{2+}$  and  $\text{Na}^+$  in the bridging form (**15**). In both of these cases, the OCO angles are smaller than those of **6** and **13** but are larger than those of **10** and **11**.

**Comparison with the X-ray Crystal Structures.** Since the present calculations have been performed on simple models, the calculated results cannot be quantitatively compared with some appropriate X-ray crystal structures. In a qualitative manner, however, the following comparisons are possible.

In a crystal of sodium acetate trihydrate,<sup>18</sup> the CO bond lengths are  $1.253$  and  $1.257 \text{ \AA}$  and the OCO angle is  $123.7^\circ$ . The acetate ion in this crystal is in a typical ionic state similar to those in **3** and **4**. In a crystal of calcium acetate monohydrate,<sup>19</sup> there are two types of acetate groups; one in the pseudobridging form and the other acting as ligands in both a bidentate form and a bridging form. For the acetate ion in the pseudobridging form, the CO bond lengths are  $1.222$  and  $1.239 \text{ \AA}$  and the OCO angle is  $125.7^\circ$ . These structure parameters are similar to those of **14**. For the acetate ion acting as ligands in both a bidentate form and a bridging form, the CO bond lengths are in the range of  $1.240-1.263 \text{ \AA}$  and the OCO angle is  $120.9-122.2^\circ$ . This acetate ion is similar to those in **11** and **12**.

The acetate ion in a crystal of  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CMe})_2$  is in a typical unidentate form.<sup>20</sup> The CO bond lengths are  $1.298$  and  $1.214 \text{ \AA}$ , and the OCO angle is  $121.6^\circ$ . This acetate ion is similar to those in **9** and **13**, in that the two CO bond lengths are significantly different. By contrast, the acetate ion in a crystal of  $\text{Sn}(\text{O}_2\text{CMe})_4$  is a representative example of the bidentate form.<sup>21</sup> The two CO bond lengths are  $1.264 \text{ \AA}$  on the average, and the OCO angle is  $118.3^\circ$ . This acetate ion is similar to that in **7**.

**3.2. Vibrational Frequencies.** The calculated frequencies of the  $\text{COO}^-$  antisymmetric and symmetric stretches for species **1–15** are shown Table 1. The frequencies change significantly with the metal ion and the coordination type. They range from  $1648$  to  $1485 \text{ cm}^{-1}$  in the case of the  $\text{COO}^-$  antisymmetric stretch and from  $1462$  to  $1302 \text{ cm}^{-1}$  in the case of the  $\text{COO}^-$  symmetric stretch. The difference between the highest and lowest frequencies among the species in Table 1 is therefore about  $160 \text{ cm}^{-1}$  for both modes. In the following, we discuss the characteristic features of these modes for each coordination type.

**Acetate Ion in the Ionic State.** The calculated frequencies of the  $\text{COO}^-$  antisymmetric and symmetric stretches for species **1–6** are in the  $1580-1560$  and  $1410-1355 \text{ cm}^{-1}$  regions, respectively. The widths of these frequency regions ( $20$  and  $55 \text{ cm}^{-1}$ , respectively) are significantly small compared with the difference between the highest and lowest frequencies among the species in Table 1 (about  $160 \text{ cm}^{-1}$  for each mode). Therefore, it may be said that these frequency regions are characteristic of the  $\text{COO}^-$  stretches for the species in the ionic state. The values of  $\Delta\nu_{\text{a-s}}$  for these species are calculated to be in the range of  $150-210 \text{ cm}^{-1}$ .

The frequencies of the  $\text{COO}^-$  antisymmetric and symmetric stretches observed for sodium acetate- $d_3$  in aqueous solution are  $1545$  and  $1405 \text{ cm}^{-1}$ , respectively.<sup>3</sup> The observed value of  $\Delta\nu_{\text{a-s}}$  is therefore  $140 \text{ cm}^{-1}$ . The calculated results for species **1–6** are in reasonable agreement with the experimental result.

**TABLE 1: Calculated Frequencies (in cm<sup>−1</sup>) of the COO<sup>−</sup> Symmetric and Antisymmetric Stretches of the Acetate Ion Interacting with Metal Ions**

	species	coordination type	ab initio MO <sup>a</sup>			eq 1
			COO <sup>−</sup> antisym str	COO <sup>−</sup> sym str	$\Delta\nu_{a-s}$	$\Delta\nu_{a-s}$
1	CD <sub>3</sub> COO <sup>−</sup>	free ion	1566	1358	208	193
2	CD <sub>3</sub> COO <sup>−</sup> D <sub>2</sub> O	hydrogen bonded (ionic)	1560	1382	178	178
3	CD <sub>3</sub> COO <sup>−</sup> Na <sup>+</sup>	bidentate (ionic)	1560	1409	151	140
4	CD <sub>3</sub> COO <sup>−</sup> Na <sup>+</sup> D <sub>2</sub> O	bidentate (ionic)	1578	1401	177	151
5	CD <sub>3</sub> COO <sup>−</sup> Na <sup>+</sup>	unidentate (ionic)	1568	1373	195	207
6	CD <sub>3</sub> COO <sup>−</sup> Na <sup>+</sup> D <sub>2</sub> O	pseudobridging (ionic)	1578	1399	179	184
7	CD <sub>3</sub> COO <sup>−</sup> Mg <sup>2+</sup>	bidentate	1485	1459	26	35
8	CD <sub>3</sub> COO <sup>−</sup> Mg <sup>2+</sup> D <sub>2</sub> O	bidentate	1497	1462	35	40
9	CD <sub>3</sub> COO <sup>−</sup> Mg <sup>2+</sup>	unidentate	1649	1303	346	318
10	CD <sub>3</sub> COO <sup>−</sup> Mg <sup>2+</sup> Na <sup>+</sup>	bridging	1595	1344	251	252
11	CD <sub>3</sub> COO <sup>−</sup> Ca <sup>2+</sup>	bidentate	1542	1440	102	90
12	CD <sub>3</sub> COO <sup>−</sup> Ca <sup>2+</sup> D <sub>2</sub> O	bidentate	1543	1441	102	94
13	CD <sub>3</sub> COO <sup>−</sup> Ca <sup>2+</sup>	unidentate	1602	1342	260	278
14	CD <sub>3</sub> COO <sup>−</sup> Ca <sup>2+</sup> D <sub>2</sub> O	pseudo-bridging	1588	1391	197	215
15	CD <sub>3</sub> COO <sup>−</sup> Ca <sup>2+</sup> Na <sup>+</sup>	bridging	1556	1393	163	194

<sup>a</sup> Calculated at the HF (SCRF) level, with the SVDP basis set for Ca<sup>2+</sup> and the 6-31+G\*\* basis set for the other atoms. Frequencies are scaled by 0.89.

**TABLE 2: Changes in the COO<sup>−</sup> Symmetric and Antisymmetric Stretches upon Coordination to Metal Ions**

	shift from the frequency of the ionic species/cm <sup>−1</sup>		$\Delta\nu_{a-s}/\text{cm}^{-1}$
	COO <sup>−</sup> antisym str	COO <sup>−</sup> sym str	
ionic <sup>a</sup>			150–195
bidentate (Mg <sup>2+</sup> )	−80 ± 10	70 ± 20	~30
bidentate (Ca <sup>2+</sup> )	−25	50	~100
unidentate (Mg <sup>2+</sup> )	80	−90	~350
unidentate (Ca <sup>2+</sup> )	35	−50	~260
pseudobridging (Ca <sup>2+</sup> )	20	0	~200

<sup>a</sup> Species 2–6 in Figure 1.

Among the calculated six species, the difference between the calculated and observed values of  $\Delta\nu_{a-s}$  is the largest for species 1. It is reasonable that the species having a hydrogen-bonded water molecule (2 and 6) and/or interacting with Na<sup>+</sup> (3–6) reproduce the experimental result in aqueous solution more closely.

The average frequencies of the COO<sup>−</sup> antisymmetric and symmetric stretches for species 2–6 are 1568 and 1393 cm<sup>−1</sup>, respectively. We discuss below the frequencies in various forms by comparing with these average frequencies obtained for the ionic species.

**Acetate Ion Interacting with Mg<sup>2+</sup> or Ca<sup>2+</sup> in the Bidentate Form.** For the acetate ion interacting with Mg<sup>2+</sup> in the bidentate form (7 and 8), the calculated frequencies of the COO<sup>−</sup> antisymmetric and symmetric stretches are ~1490 and ~1460 cm<sup>−1</sup>, respectively, as shown in Table 1. The former is lower by about 80 cm<sup>−1</sup> and the latter is higher by about 70 cm<sup>−1</sup> than the frequency of the corresponding mode in the ionic state, as shown in Table 2. In the case of the acetate ion interacting with Ca<sup>2+</sup> in the bidentate form (11 and 12), the calculated frequencies of the COO<sup>−</sup> antisymmetric and symmetric stretches are ~1545 and ~1440 cm<sup>−1</sup>, respectively. Therefore, the frequencies of the two modes become closer to those of the ionic species when the metal ion is changed from Mg<sup>2+</sup> to Ca<sup>2+</sup>, probably because the interaction between COO<sup>−</sup> and Ca<sup>2+</sup> is weaker than that between COO<sup>−</sup> and Mg<sup>2+</sup>. In this respect, the results for the vibrational frequencies are consistent with those for the structure parameters.

The value of  $\Delta\nu_{a-s}$  is about 30 cm<sup>−1</sup> for 7 and 8 and is about 100 cm<sup>−1</sup> for 11 and 12. These are significantly smaller than that for the ionic species (150–195 cm<sup>−1</sup>). This result supports

the empirical rule obtained by Deacon and Phillips for the relative magnitude of  $\Delta\nu_{a-s}$  in various forms.<sup>1</sup>

**Acetate Ion Interacting with Mg<sup>2+</sup> or Ca<sup>2+</sup> in the Unidentate Form.** For the acetate ion interacting with Mg<sup>2+</sup> in the unidentate form (9), the calculated frequencies of the COO<sup>−</sup> antisymmetric and symmetric stretches are 1649 and 1303 cm<sup>−1</sup>, respectively, as shown in Table 1. For each mode, the shift from the frequency of the ionic species is 80–90 cm<sup>−1</sup> in the direction opposite to that for the bidentate form, as shown in Table 2. When the metal ion is changed from Mg<sup>2+</sup> to Ca<sup>2+</sup> (13), the frequency shifts become as small as 35–50 cm<sup>−1</sup>, indicating that the interaction between COO<sup>−</sup> and Ca<sup>2+</sup> is weaker than that between COO<sup>−</sup> and Mg<sup>2+</sup>. The calculated frequencies of the COO<sup>−</sup> antisymmetric and symmetric stretches of 13 are 1602 and 1342 cm<sup>−1</sup>, respectively.

The values of  $\Delta\nu_{a-s}$  for 9 and 13 are about 346 and 260 cm<sup>−1</sup>, respectively, which are significantly larger than that for the ionic species (150–195 cm<sup>−1</sup>). This result is also consistent with the empirical rule obtained by Deacon and Phillips.<sup>1</sup>

**Systems in the Bridging or Pseudobridging Form.** Species 10 and 15 (in the bridging form) are generated from 9 and 13 (in the unidentate form) by adding Na<sup>+</sup> which interacts with the free CO bond of the unidentate species. The interaction between COO<sup>−</sup> and Na<sup>+</sup> induces a low-frequency shift of the COO<sup>−</sup> antisymmetric stretch by 45–55 cm<sup>−1</sup> and a high-frequency shift of the COO<sup>−</sup> symmetric stretch by 40–50 cm<sup>−1</sup>. As a result, the values of  $\Delta\nu_{a-s}$  for 10 and 15 (251 and 164 cm<sup>−1</sup>, respectively) are smaller than those for 9 and 13 by about 95 cm<sup>−1</sup>. Clearly, the value of  $\Delta\nu_{a-s}$  for the bridging form may be larger than or comparable to that for the ionic species depending on the divalent metal cation contained. As will be shown in section 3.3, the larger value of  $\Delta\nu_{a-s}$  for 10 is related to the substantial asymmetry in the COO<sup>−</sup> group, which is induced by a stronger interaction with Mg<sup>2+</sup>.

The frequency of the COO<sup>−</sup> antisymmetric stretch of 14 (in the pseudobridging form) is calculated to be 1588 cm<sup>−1</sup>, which is higher by about 20 cm<sup>−1</sup> than that of the ionic species. By contrast, the frequency of the COO<sup>−</sup> symmetric stretch of 14, which is calculated to be 1391 cm<sup>−1</sup>, is essentially the same as that of the ionic species. From these frequencies, the value of  $\Delta\nu_{a-s}$  is calculated to be about 200 cm<sup>−1</sup>.

**Comparison with the Experimental Results for Ca<sup>2+</sup>-Binding Proteins.** In the previous studies,<sup>9,10</sup> the COO<sup>−</sup> antisymmetric stretching band has been observed at 1553 cm<sup>−1</sup> for Ca<sup>2+</sup>-bound calmodulin and parvalbumin. This band has been assigned to

the glutamic acid residues interacting with  $\text{Ca}^{2+}$  in the bidentate form in the  $\text{Ca}^{2+}$ -binding sites. The observed frequency of this band is lower by  $14\text{ cm}^{-1}$  than that of a free glutamate ion in aqueous solution ( $1567\text{ cm}^{-1}$ ). The above assignment is consistent with the result of the present study shown in Table 2, which indicates that the frequency of the  $\text{COO}^-$  antisymmetric stretch for the  $\text{Ca}^{2+}$ -bound bidentate species is lower than that for the ionic species by about  $25\text{ cm}^{-1}$ .

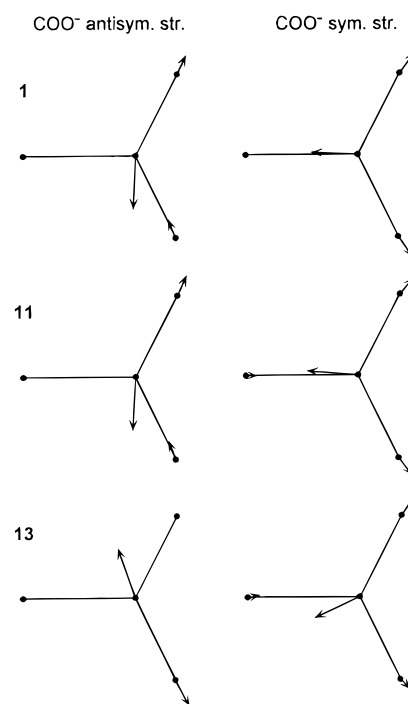
For  $\text{Ca}^{2+}$ -bound calmodulin and parvalbumin, another  $\text{COO}^-$  antisymmetric stretching band has been observed at  $\sim 1605\text{ cm}^{-1}$ . It has been suggested,<sup>9</sup> as one of the possibilities, that this band is due to the aspartic acid residues in the  $\text{Ca}^{2+}$ -binding sites interacting with  $\text{Ca}^{2+}$  and water molecules in the pseudo-bridging form. Since the frequency of this band is higher by about  $20\text{ cm}^{-1}$  than that of a "free" aspartate ion in aqueous solution ( $1584\text{ cm}^{-1}$ ), the above tentative assignment is consistent with the result of the present study shown in Table 2.

It is more difficult to assign the  $\text{COO}^-$  symmetric stretching bands based on the comparison of the observed and calculated shifts of the frequencies from those of the ionic species, since the calculated frequency range of this band for the species in the ionic state (2–6) is as wide as  $55\text{ cm}^{-1}$ . For  $\text{Ca}^{2+}$ -bound calmodulin and parvalbumin, the  $\text{COO}^-$  symmetric stretching band has been observed at about  $1424\text{ cm}^{-1}$ , which is higher by about  $20\text{ cm}^{-1}$  than the observed frequency of the "free"  $\text{COO}^-$  group in the proteins. This  $1424\text{ cm}^{-1}$  band has been assigned in the previous studies to the  $\text{COO}^-$  groups interacting with  $\text{Ca}^{2+}$  in the bidentate form. As shown in Table 2, the calculated frequency shift of the  $\text{COO}^-$  symmetric stretch for the  $\text{Ca}^{2+}$ -bound bidentate species is larger ( $50\text{ cm}^{-1}$ ).

The rather large difference (about  $30\text{ cm}^{-1}$ ) between the observed and calculated shifts of the  $\text{COO}^-$  symmetric stretch upon  $\text{Ca}^{2+}$ -binding in the bidentate form cannot be explained at present, although the direction of the calculated shift is in agreement with the observed upshift. Calculations on other carboxylate ions with longer  $n$ -alkyl chains as models of the glutamate and aspartate side chains may give useful information on this problem, because the  $\text{COO}^-$  symmetric stretch is more or less mixed with the neighboring CC stretch, which is likely to be influenced by vibrations of the group(s) bonded to the CC bond or even by those of farther groups. On the other hand, the coordination number of  $\text{Ca}^{2+}$  might be another origin of the large difference in question. In the structures treated in the present calculations,  $\text{Ca}^{2+}$  in the bidentate form is either 2-coordinate (species 11) or 3-coordinate (species 12), whereas  $\text{Ca}^{2+}$  in the  $\text{Ca}^{2+}$ -binding sites of the proteins is 7-coordinate.<sup>22</sup> In the latter case, the  $\text{Ca}^{2+}$ -induced upshift of the bidentate  $\text{COO}^-$  symmetric stretching frequency may be smaller than those for species 11 and 12.

**3.3. Relationship between the Structures and the  $\text{COO}^-$  Stretching Frequencies of the Acetate Ion.** As shown in section 3.1, in the acetate–metal systems in the unidentate form (9 and 13), the CO bond interacting with a metal ion is longer than the other CO bond. Such asymmetry in the structure of the  $\text{COO}^-$  group is more significant in the  $\text{Mg}^{2+}$ -bound species (9) than in the  $\text{Ca}^{2+}$ -bound species (13). In section 3.2, it has been shown that the value of  $\Delta\nu_{\text{a-s}}$  for the former ( $346\text{ cm}^{-1}$ ) is larger than that of the latter ( $260\text{ cm}^{-1}$ ), which is in turn larger than that for the ionic species ( $150\text{--}210\text{ cm}^{-1}$ ) having a nearly symmetric  $\text{COO}^-$  group. These results indicate that the value of  $\Delta\nu_{\text{a-s}}$  is correlated with the asymmetry in the structure of the  $\text{COO}^-$  group.

By contrast, in the acetate–metal systems in the bidentate form (7, 8, 11, and 12), the OCO angle is smaller than that of



**Figure 4.** Vibrational patterns of the  $\text{COO}^-$  antisymmetric and symmetric stretches for species 1 (ionic), 11 (bidentate), and 13 (unidentate).

the ionic species. The results shown in Table 1 and Figures 1–3 indicate that the value of  $\Delta\nu_{\text{a-s}}$  decreases as the OCO angle becomes smaller. Therefore, the value of  $\Delta\nu_{\text{a-s}}$  is considered to be correlated also with the magnitude of the OCO angle of the  $\text{COO}^-$  group.

Taking into account the above two factors, we have obtained an equation for the relationship between the structure of the  $\text{COO}^-$  group and the value of  $\Delta\nu_{\text{a-s}}$  (in  $\text{cm}^{-1}$ ), which is given as

$$\Delta\nu_{\text{a-s}} = 1818.1 \delta r + 16.47(\theta_{\text{OCO}} - 120) + 66.8 \quad (1)$$

where  $\delta r$  is the difference between the two CO bond lengths (in Å) and  $\theta_{\text{OCO}}$  is the OCO angle (in deg). The values of  $\Delta\nu_{\text{a-s}}$  obtained from eq 1 are shown in the last column in Table 1. These values agree reasonably well with those obtained from the *ab initio* MO calculations. According to eq 1, the variation of  $0.01\text{ Å}$  in  $\delta r$  or  $1^\circ$  in  $\theta_{\text{OCO}}$  gives rise to a change of  $16\text{--}18\text{ cm}^{-1}$  in the value of  $\Delta\nu_{\text{a-s}}$ .

The correlation between  $\delta r$  and  $\Delta\nu_{\text{a-s}}$  is rationalized by examining the vibrational patterns in the  $\text{COO}^-$  antisymmetric and symmetric stretching modes. In Figure 4 are shown the vibrational patterns of these modes for the ionic species (1) and for the  $\text{Ca}^{2+}$ -bound bidentate (11) and unidentate (13) species. In the case of species 13, the amplitude of the stretching of the free CO bond is far larger than that of the  $\text{Ca}^{2+}$ -bound CO bond in the  $\text{COO}^-$  antisymmetric stretching mode, whereas the reverse is the case in the  $\text{COO}^-$  symmetric stretching mode. This result indicates that, in contrast to the cases of the ionic and bidentate species, the characters of the two CO bonds of the unidentate species are so different that they vibrate almost independently. In the case of the unidentate species, the free CO bond is short and has the character of a double bond, while the  $\text{Ca}^{2+}$ -bound CO bond is long and has the character of a single bond. Therefore, as the asymmetry in the structure of the  $\text{COO}^-$  group becomes larger, the two modes approach the  $\text{C=O}$  and  $\text{C-O}$  stretching modes, respectively, so that their frequency difference increases. The changes in the force

constants of the two CO stretches and in the potential energy distributions of the two modes (not shown) are in accord with this conclusion.

The correlation between  $\theta_{\text{OCO}}$  and  $\Delta\nu_{\text{a-s}}$  is considered to originate mainly from the following two factors. One is the change in the interaction force constant between the stretches of the two CO bonds. As  $\theta_{\text{OCO}}$  becomes smaller, this interaction force constant becomes larger. The value of this constant is 1.312, 1.421, and 1.535 mdyn Å<sup>-1</sup> for species **1**, **11**, and **7**, respectively. As shown in Figures 1–3, the  $\theta_{\text{OCO}}$  of species **7** is smaller than that of **11**, which is in turn smaller than that of **1**. The other factor is the change in the mixing of the OCO bend and the CC stretch with the COO<sup>-</sup> symmetric stretch. The OCO bend and the CC stretch are more strongly mixed with the COO<sup>-</sup> symmetric stretch in a species having a smaller value of  $\theta_{\text{OCO}}$ . Since the strong mixing of these vibrations raises the frequency of the COO<sup>-</sup> symmetric stretch,  $\Delta\nu_{\text{a-s}}$  decreases as  $\theta_{\text{OCO}}$  becomes smaller.

#### 4. Concluding Remarks

In the present work, we have studied the structures and vibrational frequencies of the acetate ion interacting with a metal ion by the *ab initio* MO method. The physical basis of the correlation between the structure of the COO<sup>-</sup> group and the frequency of the COO<sup>-</sup> antisymmetric and symmetric stretching bands has been clarified. The previous assignments of the bands observed in the infrared spectra of the Ca<sup>2+</sup>-binding proteins have been supported by the present theoretical calculations.

In order to obtain more detailed information on the ligand–protein interactions from vibrational spectra than what has been obtained in the present study, calculations on more realistic systems (compared with the acetate ion) should be performed. It may be required to take more than one water molecule into account in realistic systems. It is also important to compile experimental data on the COO<sup>-</sup> antisymmetric and symmetric stretching bands of various model molecules (anions) interacting with metal ions.

It may be worth pointing out that the strength of the metal–ion binding to the carboxylate ion qualitatively discussed in this paper does not seem to be correlated at all with the magnitude of the binding constant of the same metal ion in a protein. For example, the results of calculations indicate that Mg<sup>2+</sup> binds

the acetate ion more strongly than Ca<sup>2+</sup> does. However, the binding constant between Mg<sup>2+</sup> and parvalbumin is 3–4 orders of magnitude smaller than that between Ca<sup>2+</sup> and the same protein.<sup>23,24</sup> Quantum chemical studies of the metal–ion binding to active sites in proteins seem to be an interesting problem to be treated in the future.

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