Ab initio Calculation of the Molecular Structure and Vibration Frequencies of Carbonate Ions Coordinated to Calcium Ions in the Zeolite CaA by Hartree-Fock Methods

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The molecular structures and vibration frequencies of unidentate and bidentate coordinations of carbonate ions to calcium ions in the zeolite CaA have been investigated, using the Hartree-Fock method implementing 6-31 G and 6-311 G basis sets. From the calculations, for both coordinations the structures give rise to theoretical vibration frequencies corresponding well to the experimental results. Therefore the charge of the divalent calcium ion is distributed in the zeolitic structure, and not near the guest carbonate ion. Optimized structural parameters for the two coordinations have been given.

Key words: Carbonate; Calcium; Hartree-Fock Calculation; Vibration Frequencies; Molecular Charge.

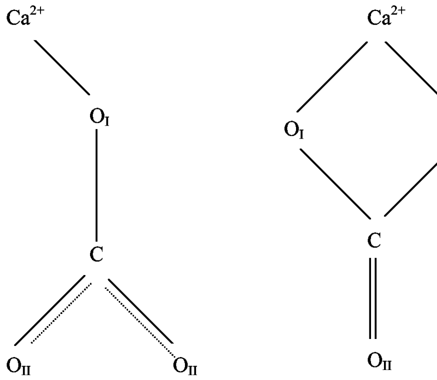
1. Introduction

Cluster models of calcite have been studied by Mao and Siders [1], using Gaussian computer programs. They carried out ab initio Hartree-Fock (HF) calculations and found that the minimum energy geometry of calcite has C_{2v} symmetry. X-ray diffraction of calcite did show that each Ca ion is coordinated by six oxygen atoms in an octahedral configuration [2]. But this symmetry has not been studied theoretically.

In our previous work an infrared study has been made on CaA zeolite reacted with CO_2 gas. It has been found that $CO_3{}^{2-}$ is formed by binding of CO_2 to a zeolitic oxygen atom and that this ion is coordinated to a Ca^{2+} cation in the zeolite in an unidentate way [3 – 4]. In the present study the molecular structures and harmonic frequencies for unidentate and bidentate coordinations of $CO_3{}^{2-}$ to Ca^{2+} in the zeolite CaA have been calculated by using ab initio HF methods implementing 6-31 G and 6-311 G basis sets.

2. Computational Methods

We used the GAUSSIAN 98 computer program [5]. Optimized structural parameters and harmonic frequencies were calculated by using the ab initio HF method at 6-31 G and 6-311 G basic set levels. The scale factors of 0.873 and 0.890 are used for 6-31 and 6-311 G basic sets, respectively [6].



Unidentate (C_s) Bidentate (C_{2v})

Scheme 1.

3. Bidentate and Unidentate Structures

The two binding ways of $CO_3{}^{2-}$ to Ca^{2+} in the zeolite are shown in Scheme 1.

Free $CO_3{}^{2-}$ has 4 vibration modes, two of them are degenerate. The binding of $CO_3{}^{2-}$ to a metal ion takes it to a lower symmetry. In this situation, each of the doubly degenerate vibrations, ν_3 and ν_4, splits into two bands. The splitting of the degenerate vibrations

Table 1. Theoretical and experimental vibration frequencies of CO_3^{2-} on Zeolite CaA, $[Co(NH_3)_5CO_3]Br$, and $[Co(NH_3)_5CO_3]I$. Results are in cm^{-1}. ν shows stretching, δ bending, ρ_r rocking, and π bending out of plane modes. The sum of Mullikan charges is 2−.

Unidentate way (C_s)	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(A_1)$	$\nu_5(B_2)$	$\nu_6(B_2)$	$\nu_7(B_2)$	$\nu_8(B_1)$
Assignment	$\nu(C\text{-}O_{II})$ + $\nu(C\text{-}O_I)$	$\nu(C\text{-}O_I)$ + $\nu(C\text{-}O_{II})$	$\delta\ (O_{II}CO_{II})$	$\nu(C\text{-}O_I)$ [or $\nu(Co\text{-}O_I)$]	$\nu(C\text{-}O_{II})$	$\rho_r\ (O_{II}CO_{II})$	$\delta_r\ (CaO_IC)$ [or $\delta_r\ (CaO_IC)$]	π
CaA + CO_3^{2-} HF 6-31 G	1300	990	670	308	1469	614	86	807
CaA + CO_3^{2-} HF 6-311 G	1291	990	681	313	1477	612	100	822
CaA + CO_3^{2-} [3]	1420	1010	750	340	1470	680	–	834
$[Co(NH_3)_5CO_3]Br$ [7]	1373	1070	756	362	1453	678	–	850
$[Co(NH_3)_5CO_3]I$ [7]	1366	1065	776	360	1449	679	–	850

Table 2. Theoretical and experimental vibration frequencies of CO_3^{2-} on Zeolite CaA, $[Co(NH_3)_4CO_3]Cl$, and $[Co(NH_3)_4CO_3]ClO_4$. Results are in cm^{-1}. ν shows stretching, δ bending, ρ_r rocking, and π bending out of plane modes. The sum of Mullikan charges is 2−.

Bidentate way (C_{2v})	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(A_1)$	$\nu_5(B_2)$	$\nu_6(B_2)$	$\nu_7(B_2)$	$\nu_8(B_1)$
Assignment	$\nu(C\text{-}O_{II})$	$\nu(C\text{-}O_I)$	Ring def. + $\nu(Ca\text{-}O_I)$ [or $\nu(Co\text{-}O_I)$]	$\nu(Ca\text{-}O_I)$ [or $\nu(Co\text{-}O_I)$] + Ring def.	$\nu(C\text{-}O_I)$ + $\delta(O_ICO_{II})$	$\delta(O_ICO_{II})$ + $\nu(Ca\text{-}O_I)$ + $\nu(Ca\text{-}O_I)$ [or $\nu(Co\text{-}O_I)$]	$\nu(Ca\text{-}O_I)$ [or $\nu(Co\text{-}O_I)$]	π
CaA + CO_3^{2-} HF 6-31 G	1501	926	658	239	1208	615	307	786
CaA + CO_3^{2-} HF 6-311 G	1508	928	670	247	1217	621	321	799
$[Co(NH_3)_4CO_3]Cl$ [7]	1593	1030	760	395	1265	673	430	834
$[Co(NH_3)_4CO_3]ClO_4$ [7]	1602	–	762	392	1284	672	428	836

Table 3. Theoretical and experimental vibration frequencies of CO_3^{2-} on Zeolite CaA, $[Co(NH_3)_4CO_3]Cl$, and $[Co(NH_3)_4CO_3]ClO_4$. Results are in cm^{-1}. ν shows stretching, δ bending, ρ_r rocking and π bending out of plane modes. The sum of Mullikan charges is 0.

Bidentate way (C_{2v})	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(A_1)$	$\nu_5(B_2)$	$\nu_6(B_2)$	$\nu_7(B_2)$	$\nu_8(B_1)$
Assignment	$\nu(C\text{-}O_{II})$	$\nu(C\text{-}O_I)$	Ring def. + $\nu(Ca\text{-}O_I)$ [or $\nu(Co\text{-}O_I)$]	$\nu(Ca\text{-}O_I)$ [or $\nu(Co\text{-}O_I)$] + Ring def.	$\nu(C\text{-}O_I)$ + $\delta(O_ICO_{II})$	$\delta(O_ICO_{II})$ + $\nu(Ca\text{-}O_I)$ + $\nu(Ca\text{-}O_I)$ [or $\nu(Co\text{-}O_I)$]	$\nu(Ca\text{-}O_I)$ [or $\nu(Co\text{-}O_I)$]	π
CaA + CO_3^{2-} HF 6-31 G	1607	888	679	348	1076	624	393	765
CaA + CO_3^{2-} HF 6-311 G	1622	895	692	347	1103	628	410	779
$[Co(NH_3)_4CO_3]Cl$ [7]	1593	1030	760	395	1265	673	430	834
$[Co(NH_3)_4CO_3]ClO_4$ [7]	1602	–	762	392	1284	672	428	836

is larger in the bidentate than in the unidentate [7]. If Ca^{2+} in the zeolite CaA is the metal ion, the splitting is small, since the binding of CO_3^{2-} to Ca^{2+} has been found as the unidentate way in the zeolite CaA [3]. But it has been found as the bidentate way for Co^{2+} in $[Co(NH_3)_4CO_3]Cl$ and $[Co(NH_3)_4CO_3]ClO_4$ [7].

4. Results

4.1. Vibrational Frequencies

The calculated and experimental harmonic frequencies for the unidentate way (the C_s symmetry) and the bidentate way (the C_{2v} symmetry) are given in Tables 1 and 2, respectively. As seen from the tables, the theoretical results agree well with the experimental ones. These values are found taking the charge as 2−. If the charge is taken as 0, the calculated frequencies for the bidentate are found in Table 3. As seen, these values are very far from the experimental ones. It also gives a new bond between C and Ca atoms. Therefore we say that the charge of the structure for both coordinations is 2− in the CaA zeolite.

4.2. Optimized Geometry and Atomic Charges

The optimized geometries and atomic charges of both cordinations are given in Tables 4 and 5. These optimized geometries are very close to the ones for the optimize geometry of $(CaCO_3)_2$ in [1]. They have been

Table 4. Optimized geometry and atomic charges for the unidentate way (C_s). The sum of Mullikan charges is 2−.

Unidentate way (C_s)	Bond lengths (Å) and angles (°)		Charge
HF 6-31 G:			
$R_{\mathrm{C-O_I}}$	1.3466	C	0.9454
$R_{\mathrm{C-O_{II}}}$	1.2779	O_I	−1.1097
$R_{\mathrm{O_I-Ca}}$	2.1323	O_{II}	−0.8399
$A_{\mathrm{O_{II}CO_I}}$	117.71	Ca	−0.1558
$A_{\mathrm{O_{II}CO_{II}}}$	124.58		
$A_{\mathrm{CO_ICa}} \sim$	180.00		
HF 6-311 G:			
$R_{\mathrm{C-O_I}}$	1.3497	C	0.8270
$R_{\mathrm{C-O_{II}}}$	1.2738	O_I	−1.1234
$R_{\mathrm{O_I-Ca}}$	2.0830	O_{II}	−0.7867
$A_{\mathrm{O_{II}CO_I}}$	117.53	Ca	−0.1304
$A_{\mathrm{O_{II}CO_{II}}}$	124.94		
$A_{\mathrm{CO_ICa}} \sim$	180.00		

Table 5. Optimized geometry and atomic charges for the bidentate way (C_{2v}). The sum of Mullikan charges is 2−.

Bidentate way (C_{2v})	Bond lengths (Å) and angles (°)		Charge
HF 6-31 G:			
$R_{\mathrm{C-O_I}}$	1.3309	C	0.9358
$R_{\mathrm{C-O_{II}}}$	1.2545	O_I	−0.9689
$R_{\mathrm{C-Ca}}$	2.8054	O_{II}	−0.7900
$R_{\mathrm{O_{II}-Ca}}$	2.3461	Ca	−0.2080
$A_{\mathrm{O_ICO_I}}$	112.64		
$A_{\mathrm{O_ICaO_I}}$	56.36		
HF 6-311 G:			
$R_{\mathrm{C-O_I}}$	1.3302	C	0.8252
$R_{\mathrm{C-O_{II}}}$	1.2500	O_I	−0.9547
$R_{\mathrm{C-Ca}}$	2.7658	O_{II}	−0.7297
$R_{\mathrm{O_{II}-Ca}}$	2.3043	Ca	−0.1861
$A_{\mathrm{O_ICO_I}}$	112.10		
$A_{\mathrm{O_ICaO_I}}$	57.22		

found to be $R_{\mathrm{Ca-O_I}} = 2.33-2.37$ Å, $R_{\mathrm{C-O_I}} = 1.30-1.32$ Å and $R_{\mathrm{C-O_{II}}} = 1.25-1.26$ Å, respectively.

5. Discussion

The zeolite CaA consists of a tetrahedral framework of $[\mathrm{SiO_4}]^{4-}$ and $[\mathrm{AlO_4}]^{5-}$. All four corner oxygen ions of each $[\mathrm{SiO_4}]^{4-}$ tetrahedron are shared with adjacent tetrahedrons. Since each tetrahedron in the framework contains quadrivalent silicon as the central cation, the structure is electrically neutral. But the central cation is trivalent aluminium, this gives rise to a deficiency of positive charge. This charge is balanced by bivalent or divalent cations [8]. For the CaA zeolite this cation is $\mathrm{Ca^{2+}}$. Its unit cell content is given in [9]. Therefore we say that the charge of divalent calcium is distributed in the zeolite structure and not in the guest carbonate ions.

6. Conclusions

The structure of both coordinations of $\mathrm{CO_3}^{2-}$ to $\mathrm{Ca^{2+}}$ ion in the zeolite CaA is seen to have the molecular charge 2−. Because of this, we say that the charge of the divalent calcium ion is distributed in the zeolitic structure and not near the guest carbonate ion.

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