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Two Crystal Structures of Ethylene and Acetylene Sorption Complexes of Dehydrated Fully Ca²⁺-Exchanged Zeolite A

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Two crystal structures of ethylene ($a=12.272(2)$ Å) and acetylene ($a=12.245(2)$ Å) sorption complexes of dehydrated fully Ca²⁺-exchanged zeolite A have been determined by single crystal X-ray diffraction techniques in the cubic space group, *Pm3m* at 21(1)°C. Their complexes were prepared by dehydration at 360°C and 2×10^{-6} Torr for 2 days, followed by exposure to 200 Torr of ethylene gas and 120 Torr of acetylene gas both at 24°C, respectively. The structures were refined to final *R* (weighted) indices of 0.062 with 209 reflections and 0.098 with 171 reflections, respectively, for which $I > 3\sigma(I)$. The structures indicate that all six Ca²⁺ ions in the unit cell are associated with 6-oxygen ring of the aluminosilicate framework. Four of these extend somewhat into the large cavity where each is coordinated to three framework oxide ions and an ethylene molecule and/or an acetylene molecule. The carbon to carbon distance in ethylene sorption structure is 1.48(7) Å and that in acetylene sorption structure 1.25(8) Å. The distances between Ca²⁺ ion and carbon atom are 2.87(5) Å in ethylene sorption structure and 2.95(7) Å in acetylene sorption structure. These bonds are relatively weak and probably formed by the electrostatic attractions between the bivalent Ca²⁺ ions and the polarizable π -electron density of the ethylene and/or acetylene molecule.

Introduction

Calcium exchanged zeolite A is very useful industrially for drying and purifying of natural gas, carbon dioxide removal, separation of *n*- and isoparaffine¹, and detergent builder².

Recently, the crystal structure of dehydrated fully Ca²⁺-exchanged zeolite A³ and of their halogen sorption complexes have been determined^{3,4} by single-crystal X-ray diffraction techniques. In these structures, six divalent cations are located on three different threefold axes associated with 6-ring oxygens. Dehydrated Ca²⁺-exchanged zeolite A sorbs *ca.* six

diiodine molecules at 80°C and also sorbs 6 dibromine molecules per unit cell at 24°C, respectively. The structural analyses indicate that each halogen molecule forms a charge transfer complex with framework oxygen (I-I-O=180(2)° Br-Br-Br-O=178(2) Å, I-I=2.72(2) Å, Br-Br=2.64(9) Å, I-O=3.32(3) Å, and Br-O=3.12(7) Å)^{3,4}.

Several ethylene and acetylene sorption structures of transition metal ion exchanged zeolite A have been studied. In the structures of dehydrated Co₄Na₄-A⁵ and Mn₄Na₄-A⁶, the transition metal ions adopt positions close to the anionic zeolite framework where they achieve near-trigonal planar coord-

dinations. Upon treating dehydrated Co₄Na₄-A and Mn₄Na₄-A with ethylene and acetylene molecules⁷⁻⁹, respectively, four ethylene and/or acetylene per unit cell are sorbed. Each of four transition metal ions per unit cell are sorbed. Each of four transition metal ions lies on threefold axes in the large cavity of unit cell, close to three equivalent trigonally arranged zeolite oxygen atoms and symmetrically to both carbon atoms of C₂H₄ molecules and/or C₂H₂ molecules. In the crystal structures of vacuum-dehydrated Cd²⁺-exchanged zeolite A treated with ethylene and acetylene^{10,11}, respectively, Cd²⁺ ions are distributed over two distinguished threefold axes of unit cell. Two of these Cd²⁺ ions are recessed 0.609(3) Å and 0.694(5) Å, respectively, into the sodalite unit from (111) plane of three O(3)'s, and the other four Cd²⁺ ions extend approximately 0.504(1) Å and 0.586(2) Å, respectively, into the large cavity. The distance between Cd²⁺ ion and C (ethylene) is 2.67 (6) Å and that between Cd²⁺ ion and C (acetylene) is 2.74(7) Å. In both structures, four Cd²⁺ ions per unit cell are in near tetrahedral environment with three framework oxide ions and each carbon atom of an ethylene and/or an acetylene molecule (which are here counted as a monodentate ligand).

As part of a continuing study to ascertain more precisely the effects of sorption upon the dehydrated Ca²⁺-exchanged zeolite A (*i.e.*, to determine shifts in cation and framework atomic position, to observe cation-sorbate interactions and perhaps to detect resultant changes in sorbed molecule geometry), the crystal structures of ethylene and acetylene sorption complexes of dehydrated fully Ca²⁺-exchanged zeolite A have been determined by single crystal X-ray diffraction techniques.

Experimental Section

Crystals of zeolite 4A were prepared by a modification of Charnell's method¹², including a second crystallization using seed crystals. Each of two single crystals about 85 μm on an edge was selected and lodged in a fine capillary. An exchange solution of 0.04325 M Ca(NO₃)₂ (Aldrich 99.997%) and 0.00675 M CaO (Aldrich 99.995%) with a total concentration of 0.05 M was filtered through a membrane filter (CaO was added to the exchange solution to increase its pH because the frameworks of zeolite A crystals are usually destroyed by hydronium ions)¹³.

Ion exchange was accomplished by allowing the solution to flow past each crystal at a velocity of approximately 1.0 cm/sec for 3 days at 21(1)°C. Each crystal was placed in a finely drawn Pyrex capillary, attached to a vacuum system and cautiously dehydrated by gradually increasing its temperature (*ca.* 25 °/hr) to 360°C at a constant pressure of 2 × 10⁻⁶ Torr. Finally, the system was maintained at the state for 48 hrs.

To prepare the ethylene and acetylene complexes, each dehydrated crystal of Ca₆-A was treated with 200 Torr zeolitically dried ethylene for 1 hr at 24°C and 120 Torr zeolitically dried acetylene for 2 hrs at 24°C, respectively.

Under these conditions, each crystal in its capillary was removed from the vacuum system by torch. Microscopic examination showed that both crystals remained colorless.

X-ray Data Collection

The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously^{14,15}. Preliminary crystallographic experiments and subsequent data collection were performed with an automated Enraf-Nonius four-circle computer controlled CAD-4 diffractometer, equipped with a graphite monochromator, a pulse-height analyzer, and a PDP micro 11/73 computer. Molybdenum radiation (*K*_{α1}, λ=0.70930 Å, *K*_{α2}, λ=0.71359 Å) was used for all experiments. The unit cell constant, as determined by a least-squares refinement of 25 intense reflections for which 18° < 2θ < 25° is 12.272(2) Å for the ethylene sorption crystal and 12.245(2) Å for the acetylene sorption crystal, respectively.

Reflections from two intensity-equivalent regions of reciprocal space (*hkl*, *h* ≤ *k* ≤ *l*: *hkl*, *h* ≤ *l* ≤ *k*) were examined by using the ω-2θ scan technique over a scan width of (0.80 + 0.344 tan θ)° in ω. The data were collected by using variable scan speeds. Most reflections were observed at slow scan speeds, from 0.17 to 0.28 deg min⁻¹ in ω. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 3 hrs to monitor crystal and X-ray source stability. Only small, random fluctuations of these check-reflections were noted during the course of data collection. For each region of reciprocal space, the intensities of all lattice points for which 2θ < 70° were recorded.

The raw data from each region were corrected for Lorentz and polarization effects including that due to incident beam monochromatization; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each average reflection, by the computer programs, PAINT and WEIGHT¹⁶.

An absorption correction (μ_R=0.036, ρ_{calc}=1.600 g/cm³ and *F*(000)=886 for the ethylene sorption crystal, and μ_R=0.036, ρ_{calc}=1.600 g/cm³ and *F*(000)=878 for the acetylene sorption crystal) was judged to be negligible and was not applied¹⁷. Only those for which *I* > 3σ(*I*) were used for structure solution and refinement. These amounted to 209 of the 874 reflections examined for Ca₆-A·4C₂H₄, and 171 of the 870 reflections for Ca₆-A·4C₂H₂, respectively.

Structure Determination

Ca₆-A·4C₂H₄. Full-matrix least-squares refinement of the structure was initiated using the framework atoms ((Si, Al), O(1), O(2) and O(3)) in dehydrated Ca²⁺-exchanged zeolite A treated with I₂ molecules³.

Anisotropic refinement of the framework atoms converged to an *R*₁ index, (Σ*F*_o-|*F*_d|)/Σ*F*_o of 0.263 and a weighted *R*₂ index, (Σ*w*(*F*_o-|*F*_d|)²/Σ*wF*_o²)^{1/2} of 0.331. A subsequent difference Fourier function revealed one large threefold axis peak at (0.220, 0.220, 0.220) of height 7.93(2) eÅ⁻³. Inclusion of this peak as Ca(1) lowered the error indices to *R*₁=0.095 and *R*₂=0.117. The thermal ellipsoid of Ca(1) became elongated in subsequent refinement, indicating the presence of two nonequivalent Ca²⁺ ions at this position. These were refined at *X*=0.212 and *X*=0.183 on threefold axes.

From a subsequent difference Fourier function, the carbon atoms of the ethylene molecules appeared at the 24 fold position (0.277, 0.359, 0.359) with a peak height of 0.92(1) eÅ⁻³. It was assumed that one C₂H₄ molecule is associated

Table 1. ^aPositional, Thermal, and Occupancy Parameters
(a) Dehydrated Ca₆-A absorbed C₂H₄ molecules

Atom	Wyckoff Position	<i>x</i>	<i>y</i>	<i>z</i>	^b β ₁₁ ^c B _{iso}	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃	Occupancy	
											varied	fixed
(Si, Al)	24(<i>k</i>)	0	1826(3)	3705(3)	36(2)	15(2)	10(2)	0	0	11(5)		24.0 ^d
O(1)	12(<i>h</i>)	0	2170(10)	5000	50(10)	50(10)	29(9)	0	0	0		12.0
O(2)	12(<i>i</i>)	0	2872(7)	2872(7)	100(10)	28(6)	28(6)	0	0	40(20)		12.0
O(3)	24(<i>m</i>)	1121(4)	1121(4)	3365(6)	39(4)	39(4)	31(6)	30(10)	-1(8)	-1(8)		24.0
Ca(1)	8(<i>g</i>)	2122(5)	2122(5)	2122(5)	41(3)	41(3)	41(3)	23(8)	23(8)	23(8)	3.95(6)	4.0
Ca(2)	8(<i>g</i>)	1830(0)	1830(10)	1830(10)	4.5(5)						1.85 (7)	2.0
C(1)	48(<i>n</i>)	3040(40)	3340(50)	3890(40)	6(2)						8.36 (9)	8.0

(b) Dehydrated Ca₆-A absorbed C₂H₂ molecules

Atom	Wyckoff Position	<i>x</i>	<i>y</i>	<i>z</i>	^b β ₁₁ ^c B _{iso}	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃	Occupancy	
											varied	fixed
(Si, Al)	24(<i>k</i>)	0	1821(6)	3715(3)	34(4)	25(4)	15(3)	0	0	15(9)		24.0 ^d
O(1)	12(<i>h</i>)	0	2220(20)	5000	20(20)	50(20)	60(20)	0	0	0		12.0
O(2)	12(<i>i</i>)	0	2900(10)	2900(10)	80(20)	11(9)	11(9)	0	0	50(20)		12.0
O(3)	24(<i>m</i>)	1146(9)	1146(9)	3360(10)	49(8)	49(8)	50(10)	60(20)	10(20)	10(20)		24.0
Ca(1)	8(<i>g</i>)	2040(10)	2040(10)	2040(10)	52(6)	52(6)	52(6)	70(20)	70(20)	80(20)	4.06(8)	4.0
Ca(2)	8(<i>g</i>)	1480(30)	1480(30)	1480(30)	8(2)						1.81 (9)	2.0
C(1)	24(<i>m</i>)	3140(50)	3140(50)	3870(70)	6(3)						7.89 (7)	8.0

^aPositional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. ^bThe anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^cOccupancy factors given as the number of atoms of ions per unit cell. ^dOccupancy for (Si) = 12; occupancy for (Al) = 12. ^eIsotropic thermal parameter in units of \AA^2 .

with each Ca(1) ion, such coordination being the reason that Ca(1) is recessed approximately 0.538(1) \AA into the large cavity at a near-tetrahedral 4-coordinate position. Refinement of about eight carbon atoms per unit cell at this position, constrained to be no more than twice the number of Ca²⁺ ions at Ca(1), converged readily but gave a short C=C bond length (1.23(7) \AA). Hence a trial refinement with carbon atom at a general position (*x*, *y*, *z*) resulted in an opportunity to select a more satisfactory C=C bond length (1.48(7) \AA) and provided a lower isotropic thermal parameter (6(2) \AA^2) for carbon similar to the ethylene sorption complex of Co₄Na₄-A⁷. Simultaneous positional, thermal, and occupancy refinement including this position converged to $R_1=0.062$ and $R_2=0.062$. The largest peak on the final difference function was located at (0.0, 0.0, 0.08) with a peak height of 1.6(5) $\text{e}\text{\AA}^{-3}$.

Ca₆-A·4C₂H₂. Initial full-matrix least-squares refinement was initiated by using the atomic parameters of framework atoms from the previous dehydrated Ca₆-A absorbed C₂H₄ molecules. Anisotropic refinement of the framework atoms converged to $R_1=0.232$ and $R_2=0.266$, respectively.

A subsequent difference Fourier function revealed two large threefold axis peaks at (0.20, 0.20, 0.20) and (0.15, 0.15, 0.15) with heights of 5.42(2) $\text{e}\text{\AA}^{-3}$ and 2.19(2) $\text{e}\text{\AA}^{-3}$, respectively. These two peaks were stable in least-squares refinement.

The occupancies of these cation per unit cell are refined to Ca(1)=4.06(8) and Ca(2)=1.81(9). These were fixed at Ca(1)=4.0 and Ca(2)=2.0, because the cationic charge should not exceed +12 per *Pm3m* unit cell. This model lowered

the error indices to $R_1=0.134$ and $R_2=0.124$, respectively (see Table 1).

A successive difference Fourier map indicated that carbon atoms of 24 fold position (0.30, 0.30, 0.38) with a peak height of 0.96(1) $\text{e}\text{\AA}^{-3}$. This corresponds closely to the final result, that approximately, 8.0 carbon atoms are found very near this position. Refinement of about eight carbon atoms per unit cell at this position, constrained to be no more than twice the number of Ca²⁺ ions at Ca(1), converged readily.

The final *R* values were $R_1=0.102$ and $R_2=0.098$. The final difference function was featureless except 2.7(10) $\text{e}\text{\AA}^{-3}$ at (0.0, 0.5, 0.5). This peak was not refined at the least-squares refinement.

For all structures, the full-matrix least-squares program used minimized $\sum w(F_o - |F_d|)^2$; the weight (*w*) of an observation was the reciprocal square of $\sigma(F_o)$, its standard deviation. Atomic scattering factors^{18,19} for C⁰ (valence), Ca²⁺, O⁻, and (Si, Al)^{1.75+} were used. The function describing (Si, Al)^{1.75+} is the mean of the Si⁰, Si⁴⁺, Al⁰, and Al³⁺ functions. All scattering factors were modified to account for the anomalous dispersion correction²⁰. The final structural parameters and selected interatomic distances and angles are presented in Table 1 and 2, respectively.

Discussion

In both structures, 4 Ca²⁺ ions at Ca(1) and 2 Ca²⁺ ions at Ca(2) occupy 6-ring sites on the three fold axes of unit cells. The 8-ring sites and 4-ring sites are empty. The Ca²⁺

Table 2. Selected Interatomic Distance (Å) and Angles (deg)

Interatom	Ca ₆ -A·4C ₂ H ₄	Ca ₆ -A·4C ₂ H ₂
(Si, Al)-O(1)	1.643(5)	1.65(1)
(Si, Al)-O(2)	1.641(7)	1.66(1)
(Si, Al)-O(3)	1.677(4)	1.69(2)
Ca(1)-O(3)	2.312(6)	2.24(2)
Ca(2)-O(3)	2.26(1)	2.38(2)
Ca(1)-C(1)	2.87(5)	2.95(7)
C(1)-C(1)	1.48(7)	1.25(8)
O(1)-(Si, Al)-O(2)	113.8(5)	109.7(9)
O(1)-(Si, Al)-O(3)	111.9(3)	113.0(7)
O(2)-(Si, Al)-O(3)	104.4(2)	103.7(4)
O(3)-(Si, Al)-O(3)	110.2(3)	112.7(5)
(Si, Al)-O(1)-(Si, Al)	150.5(9)	146(2)
(Si, Al)-O(2)-(Si, Al)	167.2(5)	163.7(8)
(Si, Al)-O(3)-(Si, Al)	141.6(4)	138.5(8)
O(3)-Ca (1)-O(3)	114.8(3)	118.0(3)
O(3)-Ca (2)-O(3)	119.9(3)	108(1)
O(3)-Ca (1)-C(1)	89(2)	84 (1)
Ca(1)-C (1)-C(1)	76(3)	78(4)

Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

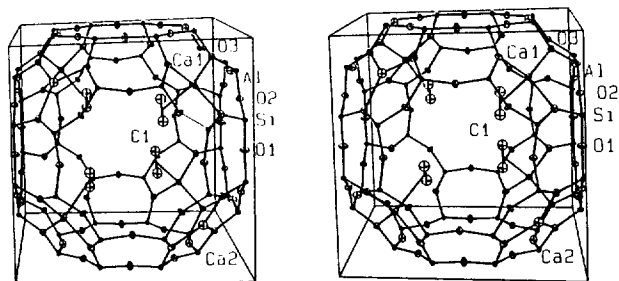


Figure 1. The stereoview of large cavity of vacuum dehydrated Ca₆-A treated with C₂H₄. The hydrogen atoms, whose positions were not determined, are not shown. Four Ca(C₂H₄)²⁺ complexes are shown in large cavity. Ellipsoids of 20% probability are used.

ions at Ca(1) are 2.31(1) Å in the ethylene sorption structure and 2.24(2) Å in the acetylene sorption structure from their nearest framework oxygens, O(3), respectively. For comparison, the sum of the conventional ionic radii of Ca²⁺ and O²⁻ is 2.31 Å²¹. Also, two Ca²⁺ ions at Ca(2) are 2.26(1) Å and 2.38(2) Å from their nearest neighbors, three O(3)'s, respectively (see Table 2).

The cation to O(3) distances presented here have not taken into account the probable but unobserved (due to disorder) conformational difference between three set of O(3). The first set of O(3) is associated with the Ca²⁺ ions at Ca(1), second set with the Ca²⁺ ions at Ca(2) and third set with no Ca²⁺ ions. Only the average 12-membered ring of framework atoms are determined in this study (see Figure 2 and 4).

Certainly the most interesting feature of the present structure is the bonding of ethylene (and/or acetylene) molecules

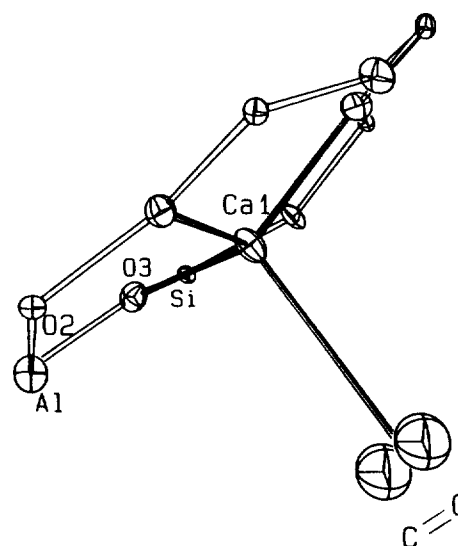


Figure 2. A Ca(C₂H₄)²⁺ complex in the large cavity. The approximately tetrahedral coordination about Ca²⁺ can be seen. The hydrogen atoms, whose positions were not determined, are not shown. Ellipsoids of 20% probability are used.

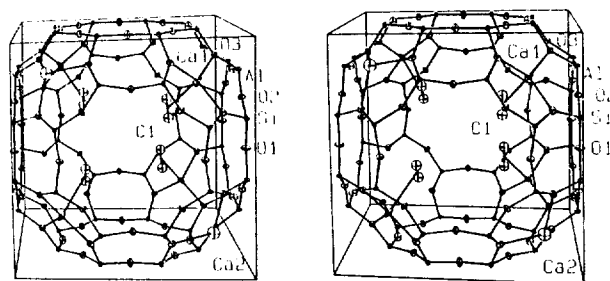


Figure 3. The stereoview of large cavity of vacuum dehydrated Ca₆-A treated with C₂H₂. The hydrogen atoms, whose positions were not determined, are not shown. Four Ca(C₂H₂)²⁺ complexes are shown in large cavity. Ellipsoids of 20% probability are used.

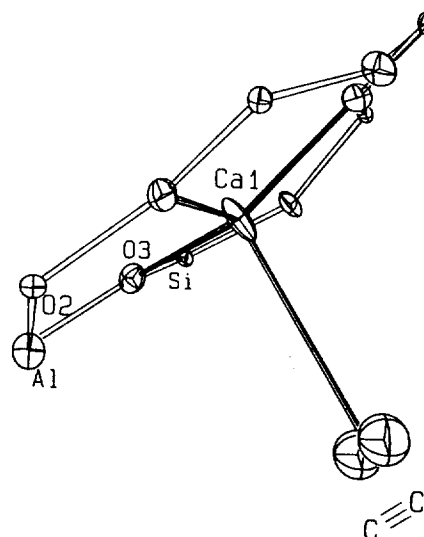


Figure 4. A Ca(C₂H₂)²⁺ complex in the large cavity. The hydrogen atoms, whose positions were not determined, are not shown. Ellipsoids of 20% probability are used.

Table 3. Deviation of Atom (\AA) from The (111) Plane at O(3)

Atom	$\text{Ca}_6\text{A}\cdot 4\text{C}_2\text{H}_4$	$\text{Ca}_6\text{A}\cdot 4\text{C}_2\text{H}_2$
O(2)	0.095(1)	0.111(1)
Ca(1)	0.538(1)	0.323(1)
Ca(2)	-0.088(1)	-0.865(2)
C(1)	3.304(5)	3.186(6)

A negative deviation indicates that the atom lies on the same side of the plane as the origin

by Ca^{2+} ions. All eight carbon atoms (four molecules of C_2H_4 (or C_2H_2)) distributed about one equipoint (Wyckoff position 48(n) for ethylene sorption structure and 24(m) for acetylene sorption structure). Each carbon to carbon bond is normal to and bisected by a plane of symmetry which contains a threefold axis (and here a Ca^{2+} ion), so that both carbon atoms are equidistant from Ca^{2+} ions. However, the bond distance of Ca^{2+} ion at Ca(1) to carbon is relatively long ($\text{Ca}^{2+}\text{-C}=2.87(5)$ \AA for the ethylene sorption complex and $2.95(7)$ \AA for the acetylene sorption complex) and also the concomitant change in Ca^{2+} -framework geometries is relatively small compared with the structure of the dehydrated Ca_6A^3 . The bindings in those complexes may be resulted from the electrostatic interaction between the dipositive Ca^{2+} ions and the polarizable π -electron density of C_2H_4 molecules and/or C_2H_2 molecules. These interactions are relatively weak. The interactions of Ca^{2+} ions with acetylene molecules are weaker than those with ethylene molecules. The Ca^{2+} ions to O(3) distances are also consistent with this conclusion (see Table 2).

Because of the combined effects of disorder (the averaging of the Al and Si positions into a single (Si, Al) position, of the oxide ion positions as though the coordination sphere of Si and Al were the same size) and moderately high thermal motion of the carbon atom, there must be some uncertainty in carbon to carbon distances. The $\text{C}=\text{C}$ bond distance in the ethylene sorption complex is $1.48(7)$ \AA and the $\text{C}\equiv\text{C}$ bond distance in the acetylene sorption complex is $1.25(8)$ \AA (see Table 2). For comparison, the $\text{C}=\text{C}$ distance in gaseous ethylene is 1.334 \AA ²² and the $\text{C}\equiv\text{C}$ distance in gaseous acetylene molecule is $1.201(5)$ \AA ²³. The closest approach distance of carbon atoms to framework oxygens, O(3), is approximately 3.4 \AA . Therefore, the hydrogen atoms would be too far from the nearest oxide ions to interact with them, even if the $\text{O}-\text{H}\cdots\text{O}$ angle were linear. Since the energy of the interaction between ethylene (or acetylene) and Ca^{2+} is not considered great enough to cause an appreciable deviation of the hydrogen atoms from the best ethylene (or acetylene)

plane, $\text{C}-\text{H}\cdots\text{O}$ should be bent (see Figure 2 and 4) and the hydrogen atoms should be far indeed, more than 3.0 \AA , from their nearest oxide neighbor.

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