

## Crystal Structure of an Acetylene Sorption Complex of Zeolite 4A

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The crystal structure of an acetylene sorption complex of zeolite A has been determined by single-crystal X-ray techniques. Fully vacuum-dehydrated zeolite A of approximate composition  $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$  per unit cell was exposed to dry acetylene for 24 hr at a pressure of 650 Torr. The cubic space group  $Pm\bar{3}m$  was used with  $a = 12.260(5)$  Å. Approximately six  $\text{C}_2\text{H}_2$  molecules are absorbed per unit cell and occupy two or perhaps three kinds of sites in the large cavity. Three  $\text{C}_2\text{H}_2$  molecules participate in a symmetric approach to threefold axis sodium ions; each carbon atom in each of these three molecules is 2.8(1) Å from a sodium ion. Two other carbon positions have been determined and refined, but the assignment of molecular positions to these is uncertain. One  $\text{C}_2\text{H}_2$  appears to be symmetrically associated with the twofold axis sodium ion at distances of 2.6(1) Å and simultaneously asymmetrically associated with a sodium ion in the eight-oxygen window with distances of 2.6(1) and 3.0(1) Å. Crystallographically refined occupancy parameters indicate that the remaining two  $\text{C}_2\text{H}_2$  molecules are (nearly) equivalent to this one except that each associates with only one ion, one of the remaining two sodium ions in the eight-oxygen windows. However, a chemically more reasonable distribution of occupancy parameters for these two carbon positions would allow each of these latter two  $\text{C}_2\text{H}_2$  molecules to be symmetrically associated (2.6(1) Å) with an eight-window sodium ion. In each case, the sorption mechanism involves an ion to induced dipole interaction between  $\text{Na}^+$  and the laterally polarizable  $\pi$  system of acetylene.

### Introduction

Zeolites find extensive commercial application as catalysts for hydrocarbon cracking or for specific high yield rearrangement reactions involving hydrocarbons and other organic molecules.<sup>1</sup> In order to determine the sorption sites (these may be catalytic sites as well in some cases) selected by a hydrocarbon in a zeolite, this structure was studied. Because unsaturated hydrocarbons are sorbed more tenaciously than saturated ones, and because the carbon atoms in acetylene were likely to be equivalent in the complex,  $\text{C}_2\text{H}_2$  was selected as the sorbate material. Previous sorption measurements<sup>2,3</sup> indicated that approximately six  $\text{C}_2\text{H}_2$  molecules are sorbed per unit cell in zeolite 4A; the effect of less absorbent binder materials contained in the commercial pellets was taken into account.

The mechanism for sorption could involve a direct ion to induced dipole interaction<sup>4</sup> between the cations and the polarizable  $\pi$  systems in these hydrocarbons as spectroscopic<sup>5-7</sup> and nuclear magnetic resonance<sup>8</sup> evidence indicates, and/or weak hydrogen bonding between the very weakly acidic protons, whose acidity might be enhanced by the former interaction, and the negatively charged zeolite framework oxygen atoms. Specific results<sup>9</sup> for acetylene on variously exchanged zeolite A samples support the former mechanism for zeolite 4A. Ethylene sorbed onto variously exchanged samples<sup>10</sup> was found to be freely rotating except in the case of Ag(I)-exchanged zeolite.<sup>11</sup> Further work on alkene sorption<sup>12,13</sup> and subsequent catalytic oxidation<sup>14</sup> has been reported. In partially Co(II)- and Ni(II)-exchanged zeolite A, olefins and cyclopropane have been found<sup>15-19</sup> to change the symmetry of these transition metal ions to  $C_{3v}$  upon sorption.

In all of these studies, involving a wide range of systems, problems, and physical methods, specific structural information has not been available; accordingly this work was undertaken.

### Experimental Section

Single crystals of zeolite A were prepared by a modification of Charnell's<sup>20</sup> method, to include a second crystallization using seed crystals from the first preparation, and have the approximate stoichiometry of  $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$  per unit cell in the dehydrated form.<sup>21</sup> A relatively large single crystal, a cube approximately 75  $\mu$  on an edge, was dehydrated for 48 hr at 350° and a pressure of  $3 \times 10^{-6}$  Torr. The crystal was then exposed to 650 Torr of zeolitically dried 99.6% pure acetylene (from Matheson Co.) for 20 hr. Concurrent measurements of  $\text{C}_2\text{H}_2$  uptake by 0.25-inch spherical pellets of Linde 4A indicated that the sorption was essentially complete in 15 hr. The sample in its fine Pyrex capillary tube was then sealed off from the vacuum system at 650 Torr by torch and mounted onto a goniometer head for X-ray investigation.

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A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation ( $K\alpha_1$ ,  $\lambda$  0.70926 Å;  $K\alpha_2$ ,  $\lambda$  0.71354 Å) and a pulse-height analyzer was used throughout for preliminary experiments and for the collection of diffraction intensities. The cubic cell constant (12.260(5) Å at 20°) was determined by a least-squares refinement of 11 intense reflections with  $2\theta$  values up to 23.6°. The space group  $Pm\bar{3}m$  (no systematic absences) was used instead of  $Fm\bar{3}c$  because Gramlich and Meier<sup>22</sup> have shown that deviations from the former space group are small, and because previous checks of Gramlich and Meier's most intense b reflections in related materials from the same crystallizations<sup>21,23,24</sup> indicated that they would be absent here. The  $\theta$ - $2\theta$  scan technique was employed at a constant scan rate of 0.5°/min (in  $2\theta$ ). The scan range varied from 2.0° at  $2\theta = 3^\circ$  to 2.5° at  $2\theta = 70^\circ$ . All 881 unique reciprocal lattice points for which  $2\theta < 70^\circ$  were examined. A time equal to half of the scan time for each reflection was spent counting background at each end of the scan range. Two check reflections which were measured periodically during data collection showed no significant trend in intensity.

Standard deviations were assigned according to the formula

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated count obtained in a scan time of  $t_c$ ,  $B_1$  and  $B_2$  are the background counts each obtained in time  $t_b$ , and  $I = CT - 0.5(t_c/t_b)(B_1 + B_2)$ . A value of 0.02 was assigned to the empirical parameter  $p$  to account for instrument instability. The net counts were then corrected for Lorentz and polarization effects. An absorption correction ( $\mu R = 0.02$ ) was unnecessary. All 171 reflections for which the net count exceeded three times its standard deviation were used in the final cycles of least-squares refinement.

### Structure Determination

Initial full-matrix least-squares refinement using the framework and the cation positions near the centers of the six- and eight-oxygen windows found for the 32 ammonia complex<sup>23</sup> of zeolite 4A converged quickly to an  $R_1$  index ( $R_1 = (\sum |F_o| - |F_c|)/\sum F_o$ ) of 0.078, using anisotropic thermal parameters for Na(1) only. The corresponding generalized weighted  $R_2$  index ( $R_2 = (\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$ ) was 0.080. Introducing six carbon atoms at position C(1), as suggested by a difference Fourier function, allowed  $R_1$  and  $R_2$  to decrease to 0.072 and 0.078, respectively. Increasing the occupancy of C(1) (although not suggested by the difference Fourier) to 12 carbon atoms caused the error indices to rise to 0.073 and 0.080 and caused its isotropic thermal parameter to diverge upward, confirming the incorrectness of this higher occupancy. Because concurrent results<sup>21</sup> on dehydrated zeolite 4A indicated that a third Na<sup>+</sup> position was present in our samples, Na(3) was introduced with an occupancy parameter of one ion per unit cell. This position behaved well in least-squares refinement, and caused  $R_1$  to increase by 0.001 and  $R_2$  to decrease by the same amount. Introducing three carbon atoms at C(2) caused  $R_1$  and  $R_2$  to decrease further to 0.064 and 0.073. Allowing Na(2) to refine anisotropically and introducing three more carbon atoms at C(3) yielded the final error indices of 0.062 and 0.071 at convergence. Calculated and observed structure factors are presented in Table I, and the final structural parameters are presented in Table II. The goodness-of-fit  $((\sum w(F_o - |F_c|)^2/(m - s))^{1/2})$  is 0.97;  $m$  is the number of observa-

TABLE I: Observed and Calculated Structure Factors<sup>a</sup>

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
1	1284	1312	16	452	433	5	262	193	12	351	326	8	333	323					
2	155	-223	3	454	445	6	262	-253	13	351	-326	9	333	-323					
3	1415	1335	6	570	523	7	443	-425	14	351	326	10	333	323					
4	1671	1655	8	373	355	8	412	203	15	351	-326	11	333	-323					
5	834	834	10	347	363	9	298	-298	16	351	326	12	351	-326					
6	540	648	11	633	656	10	1184	1223	17	351	326	13	351	326					
7	1121	1164	16	355	325	11	1121	1164	18	351	326	14	351	326					
8	560	590	5	514	-507	12	351	326	19	351	326	15	351	326					
9	1043	-1044	10	295	-271	13	351	-326	20	351	326	16	351	326					
10	763	-787	13	338	-287	14	351	-326	21	351	326	17	351	326					
11	416	-536	14	338	-287	15	351	-326	22	351	326	18	351	326					
12	610	225	5	514	-507	16	351	326	23	351	326	19	351	326					
13	765	-755	11	633	656	17	351	326	24	351	326	20	351	326					
14	242	-251	16	348	328	18	351	326	25	351	326	21	351	326					
15	540	-546	1	1127	-1120	19	351	326	26	351	326	22	351	326					
16	345	-413	3	1263	1116	20	351	326	27	351	326	23	351	326					
17	455	-505	4	452	-433	21	351	326	28	351	326	24	351	326					
18	526	-178	5	217	-281	22	351	326	29	351	326	25	351	326					
19	206	-206	7	486	-487	23	351	326	30	351	326	26	351	326					
20	443	-459	8	353	293	24	351	326	31	351	326	27	351	326					
21	330	-375	10	476	-475	25	351	326	32	351	326	28	351	326					
22	255	-152	2	526	881	26	351	326	33	351	326	29	351	326					
23	452	-375	3	787	750	27	351	326	34	351	326	30	351	326					
24	730	394	4	216	257	28	351	326	35	351	326	31	351	326					
25	289	-301	5	231	184	29	351	326	36	351	326	32	351	326					
26	523	-504	7	257	253	30	351	326	37	351	326	33	351	326					
27	283	204	8	313	335	31	351	326	38	351	326	34	351	326					
28	121	285	9	280	315	32	351	326	39	351	326	35	351	326					
29	542	553	5	384	-314	33	351	326	40	351	326	36	351	326					
30	536	502	7	739	723	34	351	326	41	351	326	37	351	326					
31	622	-155	8	302	320	35	351	326	42	351	326	38	351	326					
32	747	-483	9	249	254	36	351	326	43	351	326	39	351	326					
33	605	-606	10	346	369	37	351	326	44	351	326	40	351	326					
34	352	-357	5	611	-555	38	351	326	45	351	326	41	351	326					
35	320	-244	6	423	-615	39	351	326	46	351	326	42	351	326					
36	1743	1735	8	436	461	40	351	326	47	351	326	43	351	326					
37	605	607	11	331	-346	41	351	326	48	351	326	44	351	326					
38	458	-481	12	254	-275	42	351	326	49	351	326	45	351	326					
39	400	-382				43	351	326	50	351	326	46	351	326					
40	472	494				44	351	326	51	351	326	47	351	326					

<sup>a</sup> The running index is  $l$ ; values of  $h$  and  $k$  for each group immediately precede that group. The central column is 10F<sub>o</sub>; the right-hand column is 10F<sub>c</sub>.

tions (171), and  $s$  (28) is the total number of independent parameters. As was the case for dehydrated zeolite 4A,<sup>21</sup> structural models involving only 11 sodium ions always demonstrated  $R$  values greater than or equal to that of the 12 Na<sup>+</sup> structure.

Least-squares refinement of the occupancy parameters of the three carbon positions caused  $R_1$  and  $R_2$  to become 0.061 and 0.070, respectively, and indicated that approximately five molecules were present per unit cell, insignificantly different from the assumed value of six. In fact, a full occupancy parameter refinement for all atoms in the structure lowered  $R_1$  and  $R_2$  to 0.060 and 0.069, presumably an effect caused by the aluminum-silicon disorder or alternation which was not taken into account by the assumed space group; all framework atoms refined unrealistically to occupancies of 0.90. The thermal parameters of C(2) and C(3), which tended to become slightly negative, were fixed at 0.1 Å<sup>2</sup> in the final cycles of least-squares refinement. The inclusion of 12 hydrogen atoms in the structure factor calculation at positions (Table II) calculated assuming that the acetylene molecule is 3.32 Å in length (1.06 + 1.20 + 1.06 Å) had no effect on the final error indices.

The C(2) and C(3) positions are each 24-fold equipoints which contain three and three, or two and four atoms, respectively, to give the final error indices ( $R_1 = 0.062$  and  $R_2 = 0.071$ ). The apportioning of so few atoms among so many equipoints cannot be done unambiguously in this case. In addition, a consideration of possible chemically

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TABLE II: Positional, Thermal, and Occupancy Parameters<sup>a</sup>

Atom	Position	x	y	z	B, Å <sup>2</sup> or appropriate b's	Occupancy factor
(Si,Al)	24(k)	0	0.1829(4)	0.3704(3)	1.46(5)	1
O(1)	12(h)	0	0.222(1)	1/2	2.5(3)	1
O(2)	12(i)	0	0.291(1)	0.291(1)	2.6(3)	1
O(3)	24(m)	0.1129(7)	0.1129(7)	0.339(1)	3.1(2)	1
Na(1)	8(g)	0.2037(7)	0.2037(7)	0.2037(7)	0.0060(6) <sup>b</sup> 0.0056(12)	1
Na(2)	12(i)	0	0.430(5)	0.430(5)	0.026(12) <sup>c</sup> 0.013(4)	1/4
Na(3)	12(j)	0.270(7)	0.270(7)	1/2	3(2)	1/12
C(1)	24(m)	0.312(6)	0.312(6)	0.371(8)	6(3)	1/4
C(2)	24(m)	0.225(7)	0.476(3)	0.476(3)	0(3)	1/8
C(3)	24(l)	0.160(5)	0.448(6)	1/2	0(3)	1/8
H(1) <sup>d</sup>	48(n)	0.2455	0.3119	0.4375	6	1/8
H(2) <sup>d</sup>	48(n)	0.3098	0.4449	0.4870	6	1/16
H(3) <sup>d</sup>	48(n)	0.0749	0.4113	0.4686	6	1/16

<sup>a</sup> Standard deviations are in the units of the least significant digit given for the corresponding parameter. See Figures 1 and 2 for the identities of the atoms. <sup>b</sup> For Na(1), the anisotropic temperature factor =  $\exp[-b_{11}(h^2 + k^2 + l^2) - b_{12}(hk + hl + kl)]$ . <sup>c</sup> For Na(2), the anisotropic temperature factor =  $\exp[-b_{11}h^2 - b_{22}(k^2 + l^2)]$ . <sup>d</sup> Calculated positions and assigned thermal and occupancy factors are given.

reasonable solutions, especially in view of the two nonequivalent sodium ions, suggests strongly that more than these two equipoints must exist. The positions C(2) and C(3) might be averages of more general closely clumped positions; another very low occupancy equipoint might remain unlocated. Fortunately, of the several chemically plausible arrangements, all indicate the same general type of lateral approach as was indicated for the C(1)-C(1) molecule, namely, an ion to induced dipole interaction between Na<sup>+</sup> and the laterally polarizable  $\pi$  system of acetylene.

The solution most consistent with the crystallographic results involves three carbon atoms at C(2) and three at C(3). They form three equivalent molecules with a bond length of 0.92(10) Å; each of these would asymmetrically approach one of the three Na(2) ions near the center of the eight-oxygen window with carbon to Na<sup>+</sup> distances of 2.6(1) and 3.0(1) Å. This solution is demonstrated in Figures 1 and 2. One (or possibly two) of these three molecules probably also makes a symmetric approach to the lone Na(3) ion with distances of 2.57(8) and 2.61(8) Å.

If C(2) is discarded altogether, six carbon atoms may be placed at C(3) to form three C<sub>2</sub>H<sub>2</sub> molecules, each with a bond length of 0.90 Å and each approaching a Na(2) ion symmetrically with a C(3) to Na(2) distance of 2.6 Å. For this solution,  $R_1 = 0.062$  and  $R_2 = 0.073$ , and the x coordinate for C(3) has shifted to 0.193, the average of those for C(2) and C(3). The isotropic temperature factor for this position becomes 25 Å<sup>2</sup>. Na(3), whose position indicates that it is associated with a sorbed molecule, is unaccommodated by this model.

With five atoms at C(3) and one at C(2), one C(2)-C(3) acetylene molecule can associate with Na(3) symmetrically and Na(2) asymmetrically. Two C(3)-C(3) molecules can then associate symmetrically with Na(2). The distances are as given in the above two paragraphs; this solution is a plausible composite of those two. The values of  $R_1$  and  $R_2$  for this model are 0.065 and 0.072, respectively.

With four atoms at C(3) and two at C(2), two solutions can be envisioned. For the first one, a C(2)-C(2) molecule must exist. Na(3) cannot be associated with an acetylene molecule, and the C<sub>2</sub>H<sub>2</sub> molecules would associate in nonequivalent ways with Na(2).  $R_1$  and  $R_2$  are 0.062 and 0.071 for this least reasonable of these solutions.

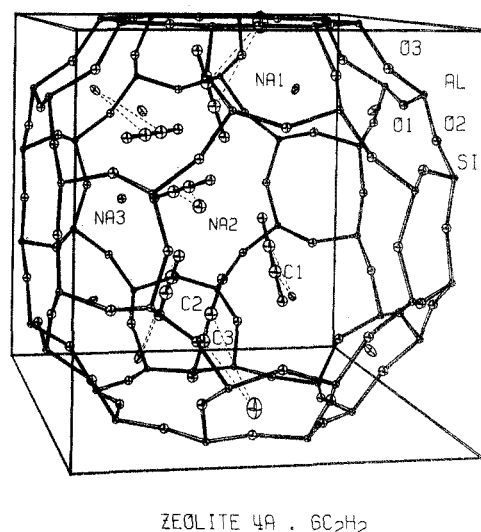


Figure 1. The unit cell (large cavity) of zeolite 4A·6C<sub>2</sub>H<sub>2</sub>. Sodium ions and acetylene molecules are statistically placed within their positions of partial occupancy so as to avoid unreasonably close approaches. Carbon to sodium ion approaches are shown with dashed lines. Thermal parameters of 6 Å<sup>2</sup> have been assigned to C(2) and C(3), and of 4 Å<sup>2</sup> to hydrogen atoms, for the preparation of these drawings only. Ellipsoids of 10% probability are used.

If a model with two C<sub>2</sub>H<sub>2</sub> molecules symmetrically associated with Na(3) and each further associated with Na(2) is considered, in the sequence Na(2), C(2)-C(3), Na(3), C(2)-C(3), Na(2), the third C<sub>2</sub>H<sub>2</sub> molecule, C(3)-C(3), could symmetrically associate with the remaining Na(2). This solution does offer the lowest  $R$  indices, as does the first, and offers an explanation for the asymmetric C(2)-C(3) approach to Na(2).

An exhaustive search of the final difference Fourier function by least-squares methods failed to reveal any other positions or structural alternatives.

The standard deviation of the electron density on Fourier functions was approximately 0.1 e<sup>-</sup>/Å<sup>3</sup>, and the largest unassigned peak on the difference Fourier synthesis was 0.3 e<sup>-</sup>/Å<sup>3</sup> in height. (No phase changes had occurred

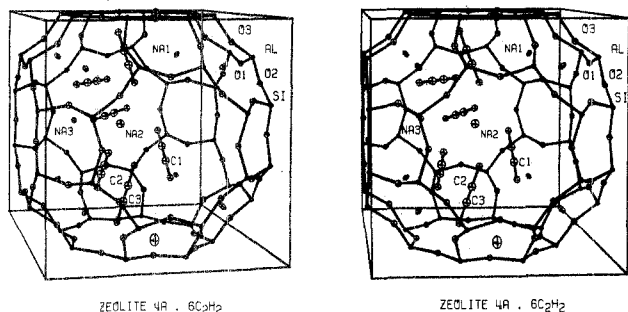


Figure 2. A stereoview<sup>27</sup> of the unit cell of zeolite 4A·6C<sub>2</sub>H<sub>2</sub>. The comments with Figure 1 apply, except that carbon to sodium ion approaches are not shown.

since the preparation of the first difference Fourier function.) The full-matrix least-squares program used<sup>25</sup> minimizes  $\sum w(\Delta|F|)^2$ ; the weights were the reciprocal squares of  $\sigma$ , the standard deviation for each observation. Atomic scattering factors<sup>26</sup> for Si<sup>2+</sup>, Al<sup>1.5+</sup>, Na<sup>+</sup>, O<sup>-</sup>, and C<sup>0</sup> (valence) were used. In the last cycle of least-squares refinement, all shifts were less than 0.6% of their corresponding esd's, except those involving the positional coordinates of Na(3) which were 1.4% of their esd's. The structure is shown<sup>27</sup> in Figures 1 and 2.

### Discussion

Six acetylene molecules occupy two or more nonequivalent sorption sites in the zeolite 4A structure. Three molecules are symmetrically associated with Na(1) ions, and the remaining three are associated with the Na(3) and Na(2) ions. In each case the cation approaches an acetylene molecule equatorially, indicating that the principal interaction is between the cationic charge and the laterally polarizable  $\pi$  electron system of the unsaturated hydrocarbon. Significant contacts between acetylenic hydrogen atoms and framework oxygen atoms are entirely absent. Each Na(2) ion is associated with an acetylene molecule, indicating that this site is energetically more favorable than the site involving Na(1), which is partially filled since, from packing considerations, it might ideally hold eight instead of three C<sub>2</sub>H<sub>2</sub> molecules. The sorption isotherm is, in fact, nonrectangular and still has a positive slope at 650 Torr, suggesting that the sorption sites are not filled by the six C<sub>2</sub>H<sub>2</sub> molecules sorbed per unit cell of zeolite 4A.

It is expected that the single Na<sup>+</sup> ion at Na(3) has disrupted the structure to some extent. A single molecule of C<sub>2</sub>H<sub>2</sub> might well be associated with Na(3) because that ion is the least stable<sup>21</sup> one in the structure and would accordingly tend to achieve more symmetric coordination more readily than the other sodium ions. The location of that single molecule is beyond the resolution of this investigation; however, one or two of the C<sub>2</sub>H<sub>2</sub> molecules associated with Na(2) might also be associated with Na(3) as well, approaching it with distances of 2.61(8) Å to C(2) and 2.57(8) Å to C(3). Such a situation would cause the C(2) and C(3) positions reported to be averages for two nonequivalent C<sub>2</sub>H<sub>2</sub> molecules.

A C<sub>2</sub>H<sub>2</sub> molecule associated with Na(1) lies off the three-fold axis and occupies two of three equivalent atomic sites available near each Na(1) position. Once this is done, that Na<sup>+</sup> ion does not have a molecular site available for further complexation. Actually, the three atomic sorption sites associated with each Na(1) imply three molecular sites (involving six atoms) as well, so that each

TABLE III: Interatomic Distances (Å) and Angles (degrees)<sup>a</sup>

(Si,Al)-O(1)	1.659(6)
(Si,Al)-O(2)	1.645(5)
(Si,Al)-O(3)	1.674(5)
Na(1)-O(3)	2.28 (1)
Na(1)-O(2)	2.92 (1)
Na(2)-O(2)	2.40 (9)
Na(2)-O(1)	2.69 (4)
Na(3)-O(1)	3.36 (11)
Na(3)-O(3)	3.36 (11)
O(1)-(Si,Al)-O(2)	109.3 (7)
O(1)-(Si,Al)-O(3)	111.6 (4)
O(2)-(Si,Al)-O(3)	106.2 (8)
O(3)-(Si,Al)-O(3)	111.5 (8)
(Si,Al)-O(1)-(Si,Al)	146.6 (5)
(Si,Al)-O(2)-(Si,Al)	162.0 (13)
(Si,Al)-O(3)-(Si,Al)	142.6 (8)
C(1)-C(1)	1.03 (15)
C(2)-C(3)	0.92 (10)
C(1)-Na(1)	2.78 (10)
C(2)-Na(2)	3.04 (8)
C(3)-Na(2)	2.61 (7)
C(2)-Na(3)	2.61 (8)
C(3)-Na(3)	2.57 (8)
C(2)-C(3)-Na(2)	109 (4)

<sup>a</sup> Standard deviations are in the units of the least significant digit given for the corresponding parameter.

atomic position reported should be the average of two close positions. This expected effect does not manifest itself strongly and would affect only the acetylenic bond length and neither the sorption site symmetry nor the sodium approach distance of this C<sub>2</sub>H<sub>2</sub>.

A C<sub>2</sub>H<sub>2</sub> molecule associated with Na(2) is presented with a less symmetrical sorption site than one associated with Na(1) because Na(2) occupies a position of only *mm* symmetry and lies away from the center of the eight-oxygen window. While the first C<sub>2</sub>H<sub>2</sub> molecule lies parallel to the window to which Na(1) is coordinated, this second C<sub>2</sub>H<sub>2</sub> may not and appears to occupy a position of no molecular symmetry, even though each of its carbon atoms has been placed on a symmetry element in refinement.

The triple bond lengths found (Table III) are about 1.0 Å in length and are not to be considered significantly shorter than that usually accepted<sup>28</sup> (1.20 Å) for such a bond, for reasons involving already discussed approximations. The average C-Na<sup>+</sup> approach distances, 2.6(1) to 2.8(1) Å, are approximately the sum, 2.65 Å, of the ionic radius of Na<sup>+</sup> and the van der Waals radius of carbon as found in graphite (0.95 + 1.70 Å).<sup>28</sup> In complexes between Na<sup>+</sup> ions and neutral sulfur atoms, a distance equal to the corresponding sum is observed,<sup>24</sup> and in cyclic polyether (crown ether) complexes involving O<sup>0</sup> and Na<sup>+</sup> approaches, a distance 0.35 Å greater than such a sum is found.<sup>29</sup> Accordingly, the acetylene to Na<sup>+</sup> ap-

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TABLE IV: Deviations<sup>a</sup> of Atoms from Planes in Å

	111	100		111	100
O(1)		0.0	Na(2)		0.0
O(2)	0.13	0.0	C(1)	3.05	
O(3)	0.0		C(2)		2.76
Na(1)	0.33		C(3)		1.96

<sup>a</sup> A negative deviation indicates that the atom lies on the same side of the plane as the origin.

proach distance observed here is indicative of a moderately energetic interaction.

The zeolite framework has undergone small framework distortions upon acetylene sorption, with respect to the dehydrated state,<sup>21</sup> which are qualitatively the same as those found for the 32 NH<sub>3</sub> complex<sup>23</sup> of zeolite 4A. The largest angular changes have been of only -4° at O(2) and O(3), and the average Si or Al to O bond has increased by 0.01 Å even though no hydrogen bonding occurs. This latter increase has been considered to be an effect<sup>30</sup> of hydrogen bonding in other structures. The Na(1) position has moved further into the large cavity by 0.13 Å upon partial coordination by acetylene while the Na(1)-O(3) distance has decreased slightly by 0.04 Å. Actually the Na(1) position must be the average of two positions corresponding to associated and unassociated Na<sup>+</sup> ions. The

Na(2) to oxygen approach distances have not changed significantly. The Na(3) to O(1) and to O(3) distances have increased dramatically to 3.4 Å, 0.9 Å more than the distances found in the dehydrated structure,<sup>21</sup> indicating strongly that this ion participates in the complexation of an acetylene molecule. Increases in these Na(3)-O distances of 0.5 Å have been observed in the eight NH<sub>3</sub> and the two or three trimethylamine complexes<sup>31</sup> of zeolite 4A.

In a study of the adsorption of acetylene and methylated acetylenes on dried  $\gamma$ -alumina,<sup>32</sup> a sorption mechanism similar to that found in this work was suggested which involved Al<sup>3+</sup> ions and dimethylacetylene. In general, however, chemisorption with the elimination of a hydrogen atom was the principal sorption process when acetylene or methylacetylene were used.

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## Ultraviolet Absorption Spectrum of Pentaerythritol Tetranitrate

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The absorption spectrum of pentaerythritol tetranitrate (PETN) has been measured in acetonitrile from 3900 to 1825 Å. Absorption bands were observed at ca. 1935, 2600, and 2900 Å. Molecular orbital calculations were performed to facilitate assignment of these absorption bands. The following assignments were made: 1935 ( $\pi \rightarrow \pi^*$  localized on the -NO<sub>2</sub> groups), 2600, and 2900 Å ( $n \rightarrow \pi^*$  transitions of the -NO<sub>2</sub> groups).

The physical and chemical properties of the secondary explosive pentaerythritol tetranitrate (PETN), C(CH<sub>2</sub>O-NO<sub>2</sub>)<sub>4</sub>, have been studied previously.<sup>1</sup> However, only limited spectral data are available based on work using a single crystal of PETN which did not transmit below 2800 Å.<sup>2</sup> In this paper an experimental and theoretical investigation of the electronic absorption spectrum of PETN is reported. Similar work on the secondary explosive hexahydro-1,3,5-trinitro-s-triazine has been published.<sup>3</sup>

A sample of PETN, available in this Laboratory as a slurry with 10% ethanol, was dried *in vacuo*. The absorption spectrum in Eastman spectrograde acetonitrile was obtained from 3900 to 2000 Å using a Cary 14R spectrophotometer and from 2250 to 1825 Å using a Jarrell-Ash vacuum scanning spectrometer. The vacuum ultraviolet

instrumentation and solution cell have been described previously.<sup>2,3</sup> The concentrations of PETN solutions were between 10<sup>-2</sup> and 10<sup>-4</sup> M. The melting characteristics of the PETN sample were obtained using a microscope hot stage (Mettler FP-2). The sample was heated at 10°/min up to 135.0°, 1.0°/min from 135.0 to 139.5°, and at 0.2°/min from 139.5° until melt was completed. We observed three distinct particle shapes and a melting range from 139.5 to 140.4°. PETN has been reported to melt at 140–141° with the pure compound melting at 141.3°.<sup>4</sup>

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