JOURNAL OF CATALYSIS 13, 221-231 (1969)

The Crystal Structure of the Zeolite Hydrogen Faujasite

D. H. OLSON AND E. DEMPSEY

From the Mobil Research and Development Corporation, Research Department,
Central Research Division, Princeton, New Jersey 08540

Received July 31, 1968; revised October 1, 1968

Recent infrared studies of the hydroxyl groups in hydrogen faujasite-type zeolites indicate that there are two acidic, catalytically reactive –OH groups in this structure. These studies also indicate that the two groups have different acidic strengths and are not equally accessible to incoming molecules. Using single-crystal X-ray techniques, we have determined the crystal structure of H faujasite (calcined, ammonium-exchanged natural faujasite).

The hydrogen atom positions were not determined directly, but were deduced from the four independent Si(Al)–O distances. In our model, the hydrogen atoms are bonded to two of the four unique groups of oxygen atoms inherent in the disordered faujasite model. One of the H-atom positions is in the hexagonal prism and the other is on the highly accessible bridging, hexagonal prism oxygen atom. Electrostatic field calculations imply that this model would give rise to two unique IR –OH bands. The model also agrees with the Si,Al ordering scheme proposed earlier for faujasite-type zeolites.

INTRODUCTION

In the past few years, there have been numerous infrared studies of the hydroxyl groups in hydrogen faujasite-type zeolites (*1–8*). In a recent review article, Venuto and Landis have demonstrated that some of these groups are involved in acid-catalyzed reactions (*9*). In HY, –OH bands are observed at about 3750, 3650, and 3550 cm^{-1} (*1–5, 7, 8*); the highest frequency band has been assigned to –OH groups on the external surface of the crystal (*2, 3, 7, 8*), while the two lower frequency bands are associated with acidic, catalytically reactive, –OH groups within the crystal (*1–9*).

White *et al.* (*6*) have studied the effect of physically adsorbed gases (N_2, O_2, CH_4, Ar, Kr) on the position and intensity of –OH bands in HY. These gases were found to perturb the –OH groups, giving rise to the 3650-cm^{-1} band, whereas the 3550-cm^{-1} band was unaffected. On this basis, they assign the former band to –OH groups in the supercages and the latter to –OH groups within the cubooctahedra. Using similar arguments, Hughes and White (*4*) and Eberly (*5*) have assigned positions to the –OH groups based upon the interaction of HY with amines and olefins, respectively. Hughes and White suggest that the 3550-cm^{-1} band orginates from hydrogen atoms attached to O4 oxygen atoms, and the 3650-cm^{-1} band from hydrogen atoms attached to the somewhat more accessible O1 oxygen atoms* (*4*). Eberly assigns these two bands to hydrogen atoms bonded to oxygen atoms near SI sites (centers of hexagonal prisms) and to oxygen atoms in exposed six-rings, respectively (*5*). From a study of the thermal stability of these –OH groups in zeolites X and Y and the variations in their intensity with sodium ion content, Uytterhoeven

---

* The framework oxygen atoms are numbered as follows: O1 is the bridging oxygen atom of the double six-membered ring (hexagonal prism), O2 is the oxygen atom that is in both the hexagonal prism six-ring and the supercage six-ring, O3 is the second oxygen atom of the hexagonal prism six-ring, and O4 is the second oxygen atom of the supercage six-ring (a threefold symmetry axis passing through the six-rings generates the remaining four oxygen atoms of each six-ring).

et al. (*8*) assign the 3650-cm^{-1} band to O1 H groups and the 3550-cm^{-1} band to hydroxyls located on six-membered rings of oxygen atoms in the cubooctahedra.

With the hope of providing more definite information on the distribution of hydrogen atoms in the zeolite, we have determined the crystal structure of H faujasite (calcined, ammonium-exchanged natural faujasite). In addition to trying to locate hydrogen atom positions directly, we are prompted by our chemical intuition and the crystallographic results of Megaw (*10*) and of Jamieson and Glasser (*11*) to examine closely the individual Si(Al)–O distances. These authors have shown that when hydrogen atoms are bonded to oxygen atoms of isolated $H_xSiO_4^{(4-x)-}$ groups, the Si–O bond length of the Si–OH group is increased by about 0.08 Å. Although the magnitude of the increase may be different for SiO_4 (and AlO_4) tetrahedra in a framework structure, it seems certain that an increase in bond length will occur here also.

EXPERIMENTAL

The faujasite single crystal used in this study was prepared from a crystal fragment chipped from a Sasbach mineral specimen. The fragment was ion-exchanged with several batches of 1.0 *M* ammonium acetate solution at 100°C for 38 days. After washing the crystal thoroughly, it was ground into the form of an ellipsoid of revolution with semiaxis of length $a = b = 0.0096$ cm and $c = 0.0140$ cm. The crystal was then mounted in a thin-walled glass capillary that had been attached to a simple Pyrex vacuum apparatus. The crystal was converted to the hydrogen form by the following vacuum calcination steps: 16 hr at 57°C, 4 hr at 150°C, and 17 hr at 376°C. The final dynamic pressure reading at each step was 1×10^{-6} torr. After the apparatus had been cooled slowly to room temperature, the capillary containing the crystal was sealed and mounted on a goniometer head. Based upon reported silica-alumina ratios for natural faujasite, the probable composition of the crystal is $H_{59}(AlO_2)_{59}(SiO_2)_{133}$ (*12*). The diffraction photographs exhibited symmetry and extinctions consistent with the previously assigned *Fd*3*m* space group (*12*). The lattice parameter, $a_0 = 24.756(6)$ Å, was determined by double-scanning diffractometry (*13*) with nickel-filtered copper radiation on a Siemens goniometer equipped with a General Electric Eulerian cradle. The intensity data were collected using the moving-crystal, moving-counter technique and zirconium-filtered molybdenum radiation. One-minute background counts were taken at each end of a 3-degree, 3-min scan; the intensities of 797 reflections were measured. The standard deviations of the structure factors were computed as described earlier (*14*).

Determination and Refinement of the Structure

Framework positional parameters from a structure determination of nickel-exchanged natural faujasite (*14*) were used as the initial trial parameters. The ionic scattering factors computed by Hanson and Pohler (*15*), selected and modified as described elsewhere (*14*), were used in the structure factor calculations. Because of the uncertainty in the ionization state of the atoms and the resultant ambiguity in selecting appropriate form factors, the anisotropic temperature factors were refined (*16*) using data with $\sin\theta/\lambda > 0.3$; in this range, the neutral-atom and ionized-atom form factors are identical. Difference maps computed in the final stages of refinement failed to reveal the positions of the hydrogen atoms. The maps were free of any significant extraneous scattering matter, which indicates that all metal ions associated with the original natural faujasite had been removed by the ammonium acetate ion-exchange treatment described above. The final positional and thermal parameters are given in Tables 1 and 2, respectively. An observed and calculated structure factor listing is given in Table 3; the *R* value for structure factors with an observed value greater than 0 is 6.8%. Interatomic distances and angles and their errors were computed using ORFFE (*17*) and are given in Table 4.

DISCUSSION

The framework positional and thermal parameters (Tables 1 and 2) and interatomic distances and angles (Table 4) are in general

TABLE 1

Final Fractional Coordinates and E. S. D.'s[a]

Atom	Set	X	Y	Z
Si(Al)	i	−0.05339 (3)	0.03619 (3)	0.12535 (4)
O1	h	−0.10607 (12)	0.10607 (12)	0.00000
O2	g	−0.00320 (13)	−0.00320 (13)	0.14224 (15)
O3	g	0.17712 (12)	0.17712 (12)	−0.03310 (19)
O4	g	0.17547 (11)	0.17547 (11)	0.32110 (15)

[a] Estimated Standard Deviations.

agreement with the values expected for a faujasite framework. The thermal parameters, which include disorder effects, are lower than those found for nickel faujasite (*14*), and not significantly larger than those reported for hydrated natural faujasite (*18*). Also, the average Si(Al)–O distance (1.644 Å) agrees very well with the average distances found for nickel faujasite (1.646 Å) (*14*) and hydrated natural faujasite (1.647 Å) (*18*). These two facts indicate that the deamination process did not result in any appreciable amount of bond breakage or disruption of the crystal lattice. Although, as it turned out, the hydrogen atoms in this structure could not be located directly, the bond length data support the hypothesis that hydrogen atoms are attached to only two of the four crystallographically unique framework oxygen atoms. In the ensuing discussion, we shall show that attachment of a hydrogen atom to an oxygen atom of an aluminosilicate increases the associated Si(Al)–O distance and that the individual Si(Al)–O distances in the faujasite structure depend mainly upon the arrangement of cations associated with the structure and are free of any framework restrictions, i.e., variations in the Si(Al)–O distances reflect the presence or absence of hydrogen coordination.

To date, only two silicate structures containing $H_xSiO_4^{(4-x)-}$ units have been well characterized (*10*, *11*). The SiO_4 tetrahedra in both structures are isolated units containing no direct interconnecting bonds. In both structures the hydrogen atom coordination was assigned on the basis of the interatomic distances of the heavy atoms with the main emphasis on the Si–O distances. There is little doubt that this assignment is correct. In $Ca_3(SiO_3OH)_2{\cdot}2H_2O$, Megaw found average Si–O and Si–O(H) distances of 1.61(3) and 1.68(3) Å, respectively (*10*). In the sodium silicate hydrate, $Na_2(H_2SiO_4){\cdot}8H_2O$, Si–O and Si–O(H) distances of 1.591(8) and 1.672(8) Å, respectively, were found by Jamieson and Glasser (*11*). From these distances it appears that an increase of about 0.08 Å in the Si–O distance occurs when a hydrogen atom is bonded to the oxygen atom. Although the same increase in bond length may not apply to the Si(Al)–O distances of tetrahedra in a framework structure, an increase is certain to occur. The analogous increase in Si(Al)–O bond length when oxygen atoms of the faujasite framework interact with metal cations supports this statement and is discussed in detail below.

Table 5 contains a listing of the individual Si(Al)–O distances in four different faujasite-type zeolites. Also listed is the percent of each type of oxygen atom in

TABLE 2

Vibration Tensor Components and E. S. D.'s (Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(Al)	0.0200 (5)	0.0144 (4)	0.0164 (5)	0.0004 (3)	−0.0029 (4)	−0.0036 (4)
O1	0.036 (1)	0.036 (1)	0.042 (2)	−0.008 (2)	−0.012 (1)	−0.012 (1)
O2	0.037 (1)	0.037 (1)	0.030 (2)	0.013 (2)	−0.003 (1)	−0.003 (1)
O3	0.028 (1)	0.028 (1)	0.059 (3)	0.004 (3)	−0.003 (1)	−0.003 (1)
O4	0.029 (1)	0.029 (1)	0.029 (2)	0.008 (1)	0.002 (1)	0.002 (1)

TABLE 3

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR H FAUJASITE

H	*K*	F_{OBS}	F_{CAL}	H	*K*	F_{OBS}	F_{CAL}	H	*K*	F_{OBS}	F_{CAL}	H	*K*	F_{OBS}	F_{CAL}
****L = 0******				20	20	261	267	25	7	197	−239	14	2	0	15
4	0	1062	−997	22	22	2461	−2431	27	7	389	300	16	2	278	−370
8	0	0	−86	****L = 1******				29	7	228	244	18	2	439	−477
12	0	2906	−2979	1	1	7999	−6748	9	9	506	−475	20	2	1452	−1445
16	0	3253	3282	3	1	3042	2637	11	9	350	−237	22	2	175	96
20	0	641	−808	5	1	2563	2317	13	9	801	−779	24	2	1377	1419
24	0	2269	2280	7	1	185	155	15	9	539	−611	26	2	0	−129
28	0	584	593	9	1	596	522	17	9	557	−565	28	2	1106	1133
2	2	4287	3762	11	1	1671	−1650	19	9	1747	1735	30	2	0	56
6	2	1627	1488	13	1	237	134	21	9	794	−834	4	4	375	−458
10	2	153	107	15	1	0	−22	23	9	189	70	6	4	2675	−2668
14	2	1690	−1679	17	1	1541	−1521	25	9	751	838	8	4	581	587
18	2	85	114	19	1	593	610	27	9	0	42	10	4	516	484
22	2	1320	1313	21	1	1107	1076	29	9	0	243	12	4	897	884
26	2	506	532	23	1	1646	1625	11	11	3799	3783	14	4	369	−356
30	2	352	−407	25	1	217	252	13	11	1001	972	16	4	577	−595
4	4	4714	−4429	27	1	0	77	15	11	216	328	18	4	488	569
8	4	2316	2262	29	1	144	−156	17	11	1058	−1080	20	4	256	−254
12	4	631	−632	31	1	222	−139	19	11	0	−265	22	4	997	1081
16	4	1027	999	3	3	4261	−3841	21	11	1298	1286	24	4	0	112
20	4	830	−798	5	3	506	476	23	11	1898	−1939	26	4	498	496
24	4	0	−114	7	3	570	583	25	11	0	−109	28	4	0	−87
28	4	672	−731	9	3	1427	1358	27	11	497	481	30	4	421	−362
6	6	3635	3851	11	3	492	−535	29	11	411	467	6	6	0	−27
10	6	987	1009	13	3	922	−925	13	13	476	454	8	6	546	590
14	6	0	−87	15	3	840	863	15	13	389	380	10	6	664	−625
18	6	1385	−1360	17	3	342	−299	17	13	734	711	12	6	772	−784
22	6	1924	−1914	19	3	932	−922	19	13	680	−752	14	6	1604	1579
26	6	650	−633	21	3	722	−785	21	13	200	241	16	6	490	511
30	6	465	540	23	3	683	666	23	13	515	−513	18	6	428	−429
8	8	2708	2665	25	3	535	500	25	13	667	−716	20	6	1810	−1847
12	8	487	474	27	3	277	101	27	13	276	122	22	6	194	55
16	8	621	−641	29	3	39	146	15	15	522	−528	24	6	855	818
20	8	3581	3574	5	5	1577	1629	17	15	74	−77	26	6	0	83
24	8	943	−951	7	5	1015	1009	19	15	398	432	28	6	0	−48
28	8	368	334	9	5	496	506	21	15	235	271	30	6	59	−6
10	10	3326	−3489	11	5	567	556	23	15	0	−48	8	8	0	2
14	10	760	−729	13	5	825	−851	25	15	346	−382	10	8	2225	2215
18	10	0	−3	15	5	569	535	27	15	307	129	12	8	1060	−1050
22	10	2790	2736	17	5	504	−444	17	17	645	654	14	8	481	−466
26	10	0	267	19	5	198	−172	19	17	0	70	16	8	831	840
12	12	5052	5110	21	5	952	−925	21	17	486	437	18	8	1285	−1276
16	12	1014	−1003	23	5	968	−949	23	17	525	544	20	8	222	171
20	12	207	−86	25	5	212	257	25	17	344	−274	22	8	790	−763
24	12	1583	−1605	27	5	503	−412	19	19	0	102	24	8	113	−122
28	12	1364	1339	29	5	491	424	21	19	272	−174	26	8	0	−66
14	14	1698	1631	7	7	332	−362	23	19	370	372	28	8	235	166
18	14	644	−658	9	7	850	843	21	21	290	−371	30	8	299	271
22	14	0	23	11	7	532	554	****L = 2******				10	10	0	−269
26	14	978	−1012	13	7	127	−75	2	2	96	−182	12	10	375	−282
16	16	1190	−1223	15	7	290	−272	4	2	121	277	14	10	517	−488
20	16	125	88	17	7	0	−84	6	2	0	59	16	10	742	−737
24	16	303	328	19	7	752	711	8	2	1584	1551	18	10	237	−197
18	18	890	926	21	7	288	202	10	2	823	−857	20	10	965	−977
22	18	278	272	23	7	386	267	12	2	350	235	22	10	150	−58

TABLE 3 (*Continued*)

H	*K*	F_{OBS}	F_{CAL}	H	*K*	F_{OBS}	F_{CAL}	H	*K*	F_{OBS}	F_{CAL}	H	*K*	F_{OBS}	F_{CAL}
24	10	598	565	23	5	0	-128	23	17	0	164	28	10	0	6
26	10	0	-136	25	5	635	596	25	17	1293	-1250	12	12	336	-310
28	10	588	635	27	5	325	-233	19	19	561	614	14	12	230	218
12	12	130	-160	29	5	206	-75	21	19	344	357	16	12	891	-906
14	12	1857	1877	7	7	0	27	23	19	994	942	18	12	0	-176
16	12	188	80	9	7	805	-806	21	21	819	761	20	12	459	379
18	12	287	355	11	7	874	881	****L = 4******				22	12	65	32
20	12	178	243	13	7	631	622	4	4	1669	-1580	24	12	279	-363
22	12	638	-582	15	7	813	822	6	4	488	-508	26	12	0	144
24	12	457	-433	17	7	490	-530	8	4	1057	1028	28	12	290	267
26	12	886	-860	19	7	1256	-1229	10	4	102	114	14	14	1176	1181
28	12	0	63	21	7	454	432	12	4	371	427	16	14	238	-23
14	14	215	138	23	7	473	-380	14	4	854	851	18	14	1204	-1183
16	14	1116	1107	25	7	528	-501	16	4	359	-345	20	14	210	-41
18	14	62	-206	27	7	511	-520	18	4	359	378	22	14	501	-497
20	14	888	861	29	7	453	450	20	4	1521	-1543	24	14	326	-319
22	14	311	410	9	9	964	983	22	4	166	-77	26	14	646	-672
24	14	854	-897	11	9	3252	-3206	24	4	79	100	16	16	1076	1056
26	14	251	-169	13	9	1077	-1061	26	4	0	-111	18	16	159	30
16	16	21	27	15	9	204	-173	28	4	0	3	20	16	649	591
18	16	420	-467	17	9	2474	-2489	30	4	303	127	22	16	0	-53
20	16	169	-170	19	9	200	251	6	6	3537	-3394	24	16	310	-261
22	16	265	281	21	9	664	-670	8	6	968	-894	26	16	178	-166
24	16	209	276	23	9	355	329	10	6	385	336	18	18	402	-344
26	16	796	-743	25	9	436	354	12	6	238	-224	20	18	111	151
18	18	0	-97	27	9	579	584	14	6	1304	1312	22	18	689	731
20	18	422	416	29	9	423	394	16	6	161	-116	24	18	169	-183
22	18	0	-48	11	11	0	-88	18	6	1059	1039	20	20	515	-493
24	18	212	-217	13	11	847	782	20	6	0	145	22	20	66	160
20	20	277	-105	15	11	1703	1679	22	6	758	-800	****L = 5******			
22	20	1022	1019	17	11	66	-117	24	6	85	103	5	5	7453	-7347
****L = 3******				19	11	225	-243	26	6	0	-95	7	5	920	-926
3	3	980	898	21	11	542	535	28	6	0	-141	9	5	572	-595
5	3	4370	-4118	23	11	0	95	30	6	0	-79	11	5	398	389
7	3	2182	-2159	25	11	1484	-1461	8	8	2500	-2424	13	5	0	128
9	3	0	113	27	11	365	-254	10	8	368	-344	15	5	1309	-1280
11	3	2111	2039	13	13	1485	1472	12	8	1688	-1666	17	5	3816	3759
13	3	634	598	15	13	291	240	14	8	0	72	19	5	318	270
15	3	959	-991	17	13	614	620	16	8	1419	-1431	21	5	710	-708
17	3	568	-572	19	13	0	11	18	8	459	-491	23	5	0	-163
19	3	774	778	21	13	961	886	20	8	787	813	25	5	290	-180
21	3	1013	1052	23	13	500	-434	22	8	254	-195	27	5	1112	1161
23	3	1708	1750	25	13	537	-523	24	8	128	-193	29	5	1260	-1313
25	3	41	36	27	13	258	-285	26	8	0	122	7	7	1560	1554
27	3	906	921	15	15	769	743	28	8	535	563	9	7	766	-751
29	3	978	-1007	17	15	1001	-984	10	10	435	-489	11	7	1430	-1400
5	5	574	-596	19	15	772	-780	12	10	0	-10	13	7	609	682
7	5	1110	1085	21	15	0	76	14	10	581	632	15	7	143	98
9	5	571	-581	23	15	517	-576	16	10	180	-111	17	7	2133	2156
11	5	0	106	25	15	383	-340	18	10	0	-49	19	7	0	141
13	5	198	-58	27	15	466	-481	20	10	0	94	21	7	0	100
15	5	1691	1709	17	17	251	63	22	10	0	154	23	7	857	847
17	5	140	47	19	17	418	285	24	10	0	-8	25	7	379	-435
19	5	1946	-1948	21	17	307	312	26	10	384	-367	27	7	790	-822
21	5	344	-381												

TABLE 3 (*Continued*)

H	K	F_{OBS}	F_{CAL}	H	K	F_{OBS}	F_{CAL}	H	K	F_{OBS}	F_{CAL}	H	K	F_{OBS}	F_{CAL}
29	7	609	−626	24	6	254	185	11	7	1138	−1160	10	8	604	623
9	9	2662	2573	26	6	142	−219	13	7	691	−641	12	8	2717	2667
11	9	312	273	28	6	2647	−2752	15	7	0	−255	14	8	231	−103
13	9	839	−839	8	8	1264	1231	17	7	812	−766	16	8	2175	2210
15	9	1162	−1171	10	8	805	741	19	7	0	211	18	8	386	476
17	9	294	134	12	8	192	125	21	7	84	−73	20	8	411	−426
19	9	312	392	14	8	2131	−2150	23	7	480	474	22	8	99	238
21	9	412	−482	16	8	214	80	25	7	751	781	24	8	573	−501
23	9	142	−91	18	8	210	52	27	7	193	−211	26	8	0	−15
25	9	1089	1065	20	8	314	−359	29	7	0	171	28	8	191	−186
27	9	227	269	22	8	195	283	9	9	525	564	10	10	1774	1757
29	9	310	−352	24	8	364	299	11	9	1088	1070	12	10	98	−145
11	11	2975	−2948	26	8	963	980	13	9	247	−307	14	10	1268	−1254
13	11	597	−603	28	8	76	−40	15	9	691	726	16	10	373	355
15	11	568	−571	10	10	781	−784	17	9	998	982	18	10	0	−80
17	11	2138	−2206	12	10	2160	−2162	19	9	603	−597	20	10	234	−162
19	11	307	384	14	10	131	−100	21	9	244	12	22	10	691	−646
21	11	434	−412	16	10	869	−915	23	9	104	−179	24	10	142	154
23	11	269	389	18	10	428	−448	25	9	344	346	26	10	330	295
25	11	87	7	20	10	548	−533	27	9	210	−285	28	10	248	104
27	11	489	547	22	10	−0	−61	11	11	467	−412	12	12	1010	−1015
13	13	0	−51	24	10	733	753	13	11	0	163	14	12	599	−621
15	13	1470	1465	26	10	92	−92	15	11	1234	−1261	16	12	304	238
17	13	56	−175	28	10	343	292	17	11	648	651	18	12	204	172
19	13	747	−726	12	12	464	507	19	11	479	504	20	12	586	−616
21	13	365	381	14	12	337	333	21	11	0	11	22	12	103	20
23	13	474	352	16	12	648	−646	23	11	293	224	24	12	653	548
25	13	762	−741	18	12	1067	1128	25	11	211	297	26	12	194	−244
27	13	134	−113	20	12	0	−159	27	11	154	271	14	14	293	−290
15	15	507	541	22	12	705	772	13	13	452	473	16	14	419	395
17	15	1006	1007	24	12	220	44	15	13	0	59	18	14	1100	1125
19	15	116	173	26	12	99	63	17	13	171	71	20	14	0	98
21	15	312	187	28	12	137	−147	19	13	181	126	22	14	1077	1084
23	15	79	156	14	14	2794	2839	21	13	136	93	24	14	270	−78
25	15	0	−154	16	14	485	−411	23	13	214	211	26	14	502	481
17	17	2002	−1967	18	14	262	−286	25	13	227	−84	16	16	148	258
19	17	497	−472	20	14	1108	1113	27	13	233	217	18	16	90	−31
21	17	276	116	22	14	234	122	15	15	1036	−1096	20	16	811	−735
23	17	291	396	24	14	603	−583	17	15	0	17	22	16	0	−24
25	17	215	122	26	14	570	515	19	15	750	766	24	16	327	245
19	19	753	−750	16	16	416	417	21	15	95	61	18	18	548	−561
21	19	233	−312	20	16	0	47	23	15	455	380	20	18	138	−53
23	19	159	−170	22	16	669	698	25	15	648	574	22	18	418	−453
21	21	405	403	24	16	0	92	17	17	1772	−1742	24	18	0	156
****L = 6******				26	16	408	−417	19	17	244	−138	20	20	270	−154
6	6	5104	5061	18	18	328	−380	21	17	215	54	22	20	120	−132
8	6	359	358	20	18	602	−641	23	17	465	−340	****L = 9******			
10	6	267	−342	22	18	108	39	25	17	455	460	9	9	1661	1738
12	6	964	−967	24	18	207	116	19	19	748	−761	11	9	1277	1274
14	6	73	−42	20	20	0	−93	21	19	210	16	13	9	1458	−1439
16	6	4980	5001	22	20	194	198	23	19	454	−443	15	9	478	492
18	6	274	211	****L = 7******				21	21	59	2	17	9	637	−619
20	6	0	43	7	7	0	−145	****L = 8******				19	9	0	−23
22	6	1115	1124	9	7	1735	1699	8	8	1945	2072	21	9	724	−682

TABLE 3 (*Continued*)

H	*K*	F_{OBS}	F_{CAL}	H	*K*	F_{OBS}	F_{CAL}	H	*K*	F_{OBS}	F_{CAL}	H	*K*	F_{OBS}	F_{CAL}
23	9	1007	−984	22	14	247	44	18	16	180	−298				
25	9	629	627	24	14	736	−775	20	16	−0	25				
27	9	103	12	16	16	397	389	22	16	192	−246				
11	11	737	708	18	16	271	203	18	18	438	−453				
13	11	1104	−1075	20	16	0	−9	20	18	64	−35				
15	11	257	340	22	16	636	624	22	18	487	−484				
17	11	287	−372	24	16	223	9	20	20	1191	1217				
19	11	619	−559	18	18	0	−88	****L = 13******							
21	11	0	4	20	18	0	17	13	13	979	−989				
23	11	0	−237	22	18	96	−150	15	13	62	−313				
25	11	60	167	20	20	241	242	17	13	787	−749				
27	11	0	−12	****L = 11******				19	13	212	371				
13	13	845	803	11	11	5003	5249	21	13	559	−559				
15	13	470	433	13	11	1351	−1316	23	13	301	304				
17	13	1042	1059	15	11	0	−157	25	13	439	457				
19	13	341	−371	17	11	174	157	15	15	419	−370				
21	13	499	507	19	11	68	−76	17	15	318	−315				
23	13	403	406	21	11	1417	−1449	19	15	0	168				
25	13	580	−579	23	11	1489	−1540	21	15	104	−131				
15	15	768	746	25	11	0	124	23	15	678	623				
17	15	483	483	13	13	0	−28	17	17	112	−43				
19	15	365	−281	15	13	544	−518	19	17	203	232				
21	15	316	259	17	13	567	536	21	17	696	−674				
23	15	564	−534	19	13	604	529	19	19	0	−26				
25	15	193	128	21	13	264	−91	****L = 14******							
17	17	206	−62	23	13	703	733	14	14	0	−167				
19	17	597	−592	25	13	503	−533	16	14	1131	−1113				
21	17	296	413	15	15	667	−614	18	14	255	232				
23	17	385	311	17	15	602	614	20	14	381	−296				
19	19	279	211	19	15	745	737	22	14	1054	1006				
21	19	438	−339	21	15	108	−95	24	14	776	783				
21	21	444	393	23	15	0	−113	16	16	220	164				
****L = 10******				17	17	85	136	18	16	560	593				
10	10	0	17	19	17	309	−355	20	16	319	−305				
12	10	1969	1963	21	17	448	423	22	16	0	148				
14	10	520	−524	23	17	1074	−1074	18	18	307	−242				
16	10	659	−668	19	19	618	−638	20	18	845	−783				
18	10	0	−125	21	19	541	536	****L = 15******							
20	10	414	−399	****L = 12******				15	15	0	−282				
22	10	233	−264	12	12	3146	−3173	17	15	187	181				
24	10	205	−72	14	12	283	−233	19	15	441	435				
26	10	243	−127	16	12	643	678	21	15	319	224				
12	12	361	331	18	12	335	369	17	17	503	−509				
14	12	878	812	20	12	207	40	19	17	499	−477				
16	12	213	−214	22	12	102	170	21	17	0	−86				
18	12	156	89	24	12	798	793	19	19	659	−647				
20	12	0	−23	26	12	0	−87	****L = 16******							
22	12	1491	−1522	14	14	1360	−1361	16	16	1744	−1869				
24	12	30	−12	16	14	0	−74	18	16	403	462				
26	12	267	−232	18	14	241	245	20	16	306	−374				
14	14	75	149	20	14	0	97	18	18	986	1013				
16	14	326	328	22	14	136	−161	****L = 17******							
18	14	274	−246	24	14	0	−23	17	17	2965	2970				
20	14	949	1006	16	16	592	588	19	17	483	482				

TABLE 4

INTERATOMIC DISTANCES AND ANGLES FOR H FAUJASITE

Distances (Å)		Angles (Deg.)	
Si(Al)–O1	1.653 (2)	Si(Al)–O1–Si(Al)	138.6 (3)
Si(Al)–O2	1.634 (1)	Si(Al)–O2–Si(Al)	147.4 (3)
Si(Al)–O3	1.663 (2)	Si(Al)–O3–Si(Al)	139.7 (3)
Si(Al)–O4	1.623 (2)	Si(Al)–O4–Si(Al)	145.3 (3)
Mean value	1.644		142.7
O1–O2	2.702 (4)	O1–Si(Al)–O2	110.5 (2)
O1–O3	2.683 (5)	O1–Si(Al)–O3	108.0 (2)
O1–O4	2.667 (2)	O1–Si(Al)–O4	109.0 (2)
O2–O3	2.655 (3)	O2–Si(Al)–O3	107.2 (2)
O2–O4	2.685 (3)	O2–Si(Al)–O4	111.0 (2)
O3–O4	2.710 (4)	O3–Si(Al)–O4	111.1 (2)
Mean value	2.683		109.5

direct contact with a cation (these values differ from the idealized values of 0% and 100% because of partial occupancy of sites by cations). Without exception, the oxygen atoms experiencing cation contact have Si(Al)–O distances greater than those having no direct cation contact; this increase is consistent with a decrease in bond order. It is also clear that as the polarizing power of the cation increases, there is a corresponding increase in the differences between individual Si(Al)–O distances; Table 5 shows that these can be as great as 0.08 Å. Note that in hydrated faujasite (*18*), where there is little direct cation framework oxygen atom contact, deviations from the average Si(Al)–O distance are small. This implies that the main factors influencing the individual Si(Al)–O distances are the polarizing power of the cation and the degree of direct interaction between the cation and the structural oxygen atoms. We thus conclude that restrictions imposed upon the framework Si(Al)–O distances by the framework configuration itself are minimal or nonexistent which, in turn, leads us to believe that the differences in Si(Al)–O distances observed in H faujasite reflect bond formation between oxygen and hydrogen atoms.

Interpreting the H faujasite Si(Al)–O distances (Table 4) on the basis of the foregoing discussion, we conclude that most of

TABLE 5

SILICON (ALUMINUM)–OXYGEN DISTANCES AND PERCENT CATION CONTACT[a] IN VARIOUS FAUJASITE-TYPE ZEOLITES

	Hydrated faujasite[b]		Dehydrated nickel-exchanged faujasite[c,d]		Dehydrated CaX[c,e]		Dehydrated SrX[c,e]	
	D (Å)	P.C.	D (Å)	P.C.	D (Å)	P.C.	D (Å)	P.C.
Si(Al)–O1	1.643 (3)	0	1.633 (1)	0	1.653 (7)	0	1.655 (6)	0
Si(Al)–O2	1.645 (3)	0	1.641 (1)	26	1.673 (6)	82	1.682 (4)	74
Si(Al)–O3	1.657 (3)	50	1.695 (1)	76	1.678 (8)	100	1.680 (5)	92
Si(Al)–O4	1.642 (3)	0	1.613 (1)	0	1.650 (6)	0	1.654 (4)	0
Average	1.647		1.646		1.664		1.668	

[a] Percent of the particular oxygen atom experiencing short-range interactions with a cation.

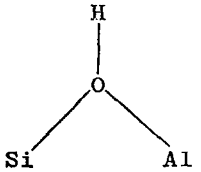
[b] Reference (*18*).

[c] There is evidence for a trace of water in these structures (*23*).

[d] Reference (*14*).

[e] Reference (*19*).

the protons are on the O3 oxygen atoms and that the remainder are on the O1 oxygen atoms. If we assume that the arrangement



is planar, it seems reasonable to suggest that a hydrogen atom will be associated with only one of the three O3 oxygen atoms of each hexagonal prism six-ring: putting two hydrogen atoms on the same ring results in a short 2.0-Å H–H nonbonding interaction, which is unfavorable electrostatically. With one hydrogen atom per six-ring, 32 hydrogen atoms per unit cell are accounted for, leaving 59 minus 32 or 27 for the O1 oxygen atoms. These would be expected to have a distribution giving maximum separation of positive charge. Figure 1 is a stereoscopic view of an idealized model depicting this hydrogen atom distribution.

The placing of the hydrogen ions in the regular array of Fig. 1 has implications for the silicon-aluminum ion arrangement, in that the hydrogen ions must associate with oxygen ions linking a silicon to an aluminum ion. It is easy to demonstrate that the hydrogen distribution of Fig. 1 requires the silicon-aluminum ion arrangement in the hexagonal prisms of the zeolite to be centrosymmetric and the aluminum ions in the hexagonal faces of the prisms to be in meta configurations (*20*), as is shown in Fig. 1.

In ref. (*20*), a discussion is given of the energies of ordered faujasite-type zeolites having a range of Si/Al ratios. There it was shown that a progression from the ideal zeolite having Si/Al = 1/1 towards materials having higher Si/Al ratios led to the meta, para (mp) model for the zeolite having Si/Al = 2/1. It was found that the mp model was more stable than any of the other models considered. An investigation of these models in the light of the hydrogen distribution described above showed that only the preferred model, and one of the mm models, were consistent with the model of Fig. 1. The mm model can be discounted, however, on energetic grounds, in that it has been shown (*20*) that the mp model is more stable than the mm model. Furthermore, the results of ref. (*21*) (which explains breaks in a plot of Si/Al ratio versus crystal lattice parameter for hydrated sodium X and Y zeolites in terms of Si/Al ordering) also support the mp model; breaks in the plot occur at Si/Al = 1.4/1 and ~2/1 and are explained in terms of a progression away from mm models towards mp models. [The results of ref. (*21*) also give some justification for relating results on a faujasite crystal of Si/Al = 2.25/1 to a model having Si/Al = 2/1.] It thus appears that the only ordered model of faujasite that is fully consistent

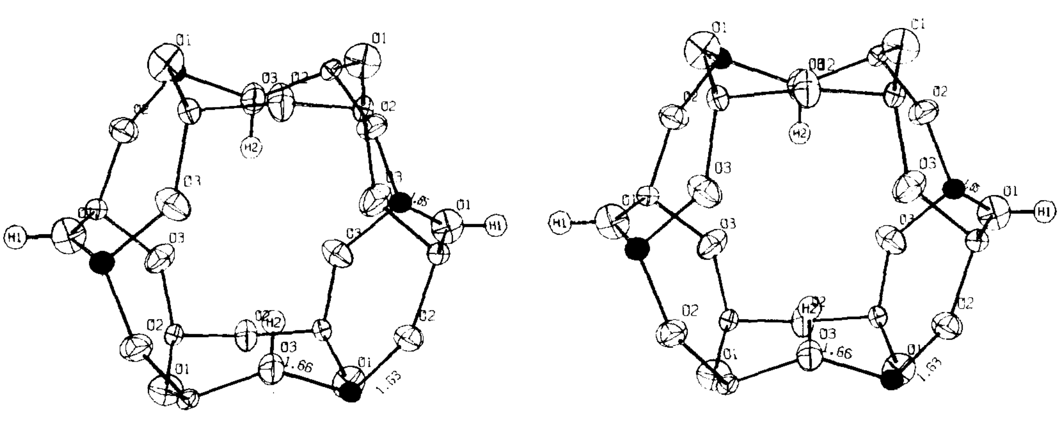


FIG. 1. Proposed HY model for a Si/Al = 2 zeolite showing the hydrogen atom positions in a hexagonal prism (the six-rings of the prims lie in the plane of the paper. The small back circles denote the tetrahedral atom sites assigned to Al atoms in the electrostatic field calculations).

with the hydrogen model of Fig. 1 is the mp one. To this extent, the present results give further support for silicon/aluminum ordering in faujasites.

In Fig. 2, a plot of the fields at the 48 oxygen ions of a typical sodalite cage shows the symmetry of the mp hydrogen zeolite* (Si/Al = 2/1). It may be seen that the oxygen ions fall into twelve groups of four each† (four of the groups being accidentally degenerate in pairs), and that the oxygen ions carrying the H ions lie in two well-separated groups.

The hydrogen distribution described above is clearly consistent with the experimental results on hydrogen faujasite-type zeolites mentioned in the Introduction. As Fig. 2 indicates, placing the hydrogen atoms on the two crystallographically unique groups of oxygen atoms of Fig. 1 agrees with the observation of just two distinct -OH bands in the infrared spectra of HY. [This model is similar to the more general ones already presented for HY (*4–6*, *8*).] From Fig. 1 it is obvious that the two hydrogen atoms in the model are not equally accessible to molecules entering the zeolite. The hydrogen atom on the O3 oxygen atom is in the hexagonal prism and, in this position, is not available to react with large molecules. However, the hydrogen atom attached to the bridging oxygen atom projects into the large cavity and is highly accessible. This model is in complete agreement with the results and conclusions reached by White, Jelli, André, and Fripiat, who found that small, physically adsorbed molecules (that are nevertheless too large to enter the sodalite cages) perturbed only the -OH group, giving rise to the 3650-cm^{-1} band (*6*). We thus assign this band to the -O1-H group and the 3550-cm^{-1} band to the -O3-H group—in agreement with the more general positional assignments given in ref. (*6*). The model also agrees with Eberly's (*5*) observations on olefin interactions with H faujasites and is in general agreement with his positional assignments. Disappearance of the lower frequency -O3-H group band with the adsorption of large molecules like piperidine, observed by Hughes and White (*4*) and Ward (*7*), can

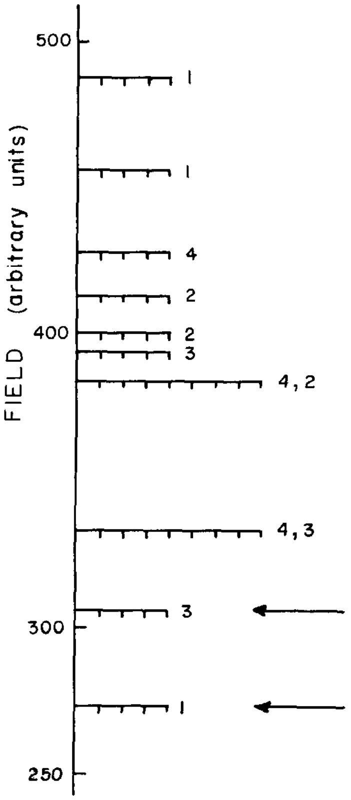


FIG. 2. Plot of electrostatic field at 48 oxygen ion positions in a sodalite cage of an ordered (Si/Al = 2/1) hydrogen zeolite. Each point on the field levels represents an oxygen ion. The silicon and aluminum ions are arranged in accordance with the pm model of ref. (*21*), and the hydrogen ions are located at fixed points relative to appropriate oxygen ions in accordance with Fig. 1. The diagram illustrates the reduced symmetry of the ordered model relative to that of a hypothetical high symmetry Si/Al = 1/1 model. The numbers adjacent to the field levels relate the twelve oxygen groups to the four groups of the high symmetry model. Arrows indicate the oxygen ions that carry the hydrogens.

---

* For this calculation a point-charge model was used and the procedure of ref. (*20*) was followed. The framework coordinates of Table 1 were used, and the hydrogen ions were located at fixed points relative to the centers of appropriate oxygen ions in accordance with Fig. 1.

† This brings out the point that, strictly speaking, it is valid to talk in terms of four crystallographically distinct oxygen ions in faujasites only if the Si/Al ratio is unity, or if the silicon and aluminum ions are arranged at random in the structure.

be explained by mobility of the protons on the zeolite surface, which has been shown to be appreciable at 250–300°C (*22*). The fact that the –O1–H group band disappears when pyridine is adsorbed while the –O3–H group band is unaffected (*4*, *7*) suggests, as pointed out by others (*4*, *7*), that the latter is a weaker acid than the former. This also agrees with the observation that the lower frequency band appears first when HY is deaminated (*6*).

Several workers (*1*, *6*, *8*) have observed that the 3550-cm^{-1} band increases in intensity as the residual sodium content decreases. This again agrees with our model, since residual sodium ions occupying sites in the hexagonal prism six-rings would make –O3–H interactions energetically unfavorable.

In conclusion, we should point out that although the H faujasite model presented above is implied by the Si(Al)–O distances obtained and is consistent with other experimental data, additional work, such as a single crystal neutron diffraction study, is required for an unequivocal conclusion.

Acknowledgments

We wish to acknowledge many helpful discussions with Dr. H. S. Sherry and Dr. E. L. Wu and the experimental assistance of Mr. N. H. Goeke.

References

1. Uytterhoeven, J. B., Christner, L. G., and Hall, W. K., *J. Phys. Chem.* **69**, 2117 (1965).
2. Angell, C. L., and Schaffer, P. C., *J. Phys. Chem.* **69**, 3463 (1965).
3. Liengme, B. V., and Hall. W. K., *Trans. Faraday Soc.* **62**, 3229 (1966).
4. Hughes, T. R., and White, H. M., *J. Phys. Chem.* **71**, 2192 (1967).
5. Eberly, P. E., *J. Phys. Chem.* **71**, 1717 (1967).
6. White, J. L., Jelli, A. N., André, J. M., and Fripiat, J. J., *Trans. Faraday Soc.* **63**, 461 (1967).
7. Ward, J. W., *J. Catalysis* **9**, 225 (1967).
8. Uytterhoeven, J. B., Jacobs, P., Makay, K., and Schoonheydt, R., *J. Phys. Chem.* **72**, 1768 (1968).
9. Venuto, P. B., and Landis, P. S., *Advan. Catalysis* **18**, 259 (1968).
10. Megaw, H. D., *Acta Cryst.* **5**, 477 (1952).
11. Jamieson, P. B., and Dent Glasser, L. S., *Acta Cryst.* **20**, 688 (1966).
12. Bergerhoff, G., Baur, W. H., and Nowacki, W., *Neues Jahrb. Mineral Monatsh.*, p. 193 (1953).
13. King, H. W., and Vassamillet, L. F., *in* "Advances in X-Ray Analysis" (W. M. Mueller, G. R. Mallett, and M. J. Fox, eds.), Vol. 5, pp. 78–79. Plenum Press, New York. 1961.
14. Olson, D. H., *J. Phys. Chem.* **72**, 4366 (1968).
15. Hanson, H. P., and Pohler, R. F., *Acta Cryst.* **21**, 435 (1966).
16. Busing, W. R., Martin, K. O., and Levy, H. A., *ORFLS,* Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.
17. Busing, W. R., Martin, K. O., and Levy, H. A., *ORFFE,* Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1964.
18. Baur, W. H., *Amer. Mineralogist* **49**, 697 (1964).
19. Olson, D. H., unpublished research, Mobil Research and Development Corporation, Research Department, Central Research Division, Princeton, New Jersey.
20. Dempsey, E., *in* "Molecular Sieves," pp. 293–303. Society of Chemical Industry, London, 1968.
21. Dempsey, E., Kuehl, G. H., and Olson, D. H., *J. Phys. Chem.* **73**, in press (1969).
22. Uytterhoeven, J. B., Schoonheydt, R., and Fripiat, J. J., *Proc. Intern. Symp. Reaction Mechanisms of Inorganic Solids.* Chemical Society, London, England, 1966.
23. Olson, D. H., *J. Phys. Chem.* **72**, 1400 (1968).