The Crystal Structure of Hydronium Perchlorate at −80 °C.

By C. E. Nordman

Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.

The structure of the low temperature phase of perchloric acid monohydrate, stable below −30 °C., has been determined at −80 °C. The crystals belong to the monoclinic space group $P2_1/n$ with cell parameters

$$a = 7 \cdot 541 \pm 0 \cdot 006, \quad b = 9 \cdot 373 \pm 0 \cdot 011, \quad c = 5 \cdot 359 \pm 0 \cdot 006 \text{ Å}; \quad \beta = 97° 41' \pm 4'.$$

The structure, which consists of hydrogen-bonded layers of perchlorate and hydronium ions, is closely related to the orthorhombic structure stable above −30 °C. The two structures are compared and a disordered model for the high temperature structure is proposed.

Introduction

The early observation (Volmer, 1924) that the X-ray diffraction pattern of perchloric acid monohydrate (m.p. 50 °C.) is very similar to that of ammonium perchlorate led to the belief that the former compound is ionized in the solid state. More recently this belief has been confirmed through nuclear magnetic resonance studies, which have yielded evidence of hydronium ions, H_3O^+, in the solid, at least at low temperature. Proton resonance spectra observed by Kakiuchi *et al.* (1951, 1952) between room temperature and 105 °K. show a gradual change in line shape indicating a decrease in disorder with decreasing temperature. The results were interpreted as showing that the hydronium ions rotate above 150 °K. Independently, Richards & Smith (1951) obtained NMR spectra at 0 °C. and 90 °K. The results at 0 °C. indicated that the hydronium ions undergo reorientation in the solid at a frequency greater than about 50 kc.sec.$^{-1}$, and that the reorientation probably occurs about more than one axis. At the lower temperature no such reorientation was observed. A phase transition was found at an intermediate temperature by Taylor & Vidale (1956), who studied the Raman spectra of large single crystals of perchloric acid monohydrate. Due to the shattering of the crystals at the transition temperature, found by Taylor & Vidale to be −30 °C., the spectra of the low temperature modification were of poor quality. However the results indicated that the low temperature phase is ordered and has hydronium ions occupying sites of lower symmetry than the high temperature, presumably disordered phase.

A complete X-ray structure determination of the room temperature phase has recently been reported by Lee & Carpenter (1959), confirming the presence of hydronium ions. A disorder in the orientation of the hydronium ions is strongly suggested by the coordination of perchlorate oxygens around the hydronium ions, however, in view of the low scattering power of hydrogen an ordered arrangement of the

H_3O^+ ions could not be ruled out. In a very recent neutron diffraction study of the room temperature phase Smith & Levy (1959) have confirmed the presence of orientational disorder in the hydronium ions. While apparently more complicated than free rotation, the detailed nature of the disorder is not known at the present time.

The present X-ray diffraction study of the crystal structure below the −30 °C. phase transition was undertaken in an attempt to shed some additional light on the nature of the transition.

Experimental

Crystals of the room temperature modification of perchloric acid monohydrate were invariably found to shatter on cooling through the transition temperature. It therefore became necessary to devise a method whereby single crystals of the low temperature modification could be grown directly from a solution at a temperature below the transition point (cf. Lipscomb, 1957). Since the monohydrate is the lowest hydrate formed by perchloric acid, and since the anhydrous acid melts at −112 °C. (van Wyk, 1906), the latter may be employed as a solvent from which crystals of the low temperature modification of the monohydrate can be grown.

To a sample of anhydrous perchloric acid was added enough water to give a slush when the mixture was cooled to dry ice temperature. The sample was kept at dry ice temperature for a week or more, whereupon small portions of the now coarsely crystalline slush were transferred to a microscope cold stage cooled from below and blanketed with cold, dry nitrogen gas. A suitable crystal could now be selected and inserted into a glass capillary held in a hole in a small block of dry ice. The capillary was then sealed off, and mounted on the precession camera by transferring it from the dry ice block directly into the stream of cold nitrogen gas which was used to keep it cold during the subsequent X-ray work. From many un-

successful attempts to mount single crystals of the low temperature modification it was concluded that the transition from the low to the high form is essentially instantaneous upon warming to the transition temperature, and invariably results in a shattered crystal. The diffraction data were collected on a standard precession camera at -80 ± 5 °C. using two different single crystal specimens. A total of 811 independent reflections were found to be of measurable magnitude; their intensities were measured by visual comparison with timed calibration exposures. 391 different reflections measured on two or more reciprocal lattice nets

Table 1. *Observed and calculated structure factors*

($\times 10$)

h	k	l	KF_o	F_c
0	0	0	--	2400+
0	0	2	587	614-
0	0	4	401	422+
0	0	6	73	74+
0	1	1	125	127+
0	1	2	260	257+
0	1	3	142	146-
0	1	4	86	94+
0	1	5	241	254+
0	1	6	38	38-
0	1	7	57	58-
0	2	0	682	699+
0	2	1	479	498+
0	2	2	90	98-
0	2	3	223	207-
0	2	4	204	202+
0	2	5	198	204+
0	2	6	90	92-
0	2	7	53	58-
0	3	1	117	112-
0	3	2	124	120-
0	3	3	204	207-
0	3	4	108	114-
0	3	5	176	178+
0	3	6	68	70+
0	4	0	140	142-
0	4	1	164	149-
0	4	2	215	221+
0	4	3	53	60-
0	4	4	154	161+
0	4	6	126	118-
0	4	7	48	46+
0	5	1	210	198-
0	5	2	72	75+
0	5	3	47	43-
0	5	4	264	271-
0	5	5	48	45-
0	5	6	134	125+
0	5	7	77	70-
0	6	0	114	110-
0	6	1	431	459+
0	6	2	136	153-
0	6	3	177	180-
0	6	5	113	125+
0	7	2	94	94+
0	7	7	217	211-
0	8	0	76	69-
0	8	1	222	231+
0	8	3	114	110-
0	8	4	65	60-
0	9	1	98	100+
0	9	2	53	62+
0	9	3	46	46+
0	10	1	98	103+
0	10	3	85	92-
0	11	1	112	124+
0	11	3	103	88-
0	12	0	150	158+
0	12	3	76	87-
1	0	-7	52	49+
1	0	-5	160	157+
1	0	-1	672	637+
1	0	1	673	702-
1	0	3	278	279+
1	0	5	162	166-
1	0	7	56	70+
1	1	-7	56	56-
1	1	-6	187	186+
1	1	-5	122	119+
1	1	-4	412	395-
1	1	-2	526	528+
1	1	0	147	133-
1	1	2	202	193+
1	1	3	84	85+
1	1	4	284	279+
1	1	6	128	117-
1	2	-6	61	53-
1	2	-5	223	202+
1	2	-4	255	240+
1	2	-3	240	232-
1	2	-2	216	199+
1	2	-1	754	724+
1	2	0	238	241+
1	2	1	764	764-
1	2	2	235	227+
1	2	3	253	242+
1	2	5	146	142+
1	2	6	61	63-
1	3	-7	59	60+
1	3	-6	60	55-
1	3	-5	65	70+
1	3	-4	169	165+
1	3	-3	139	140-
1	3	-2	66	63-
1	3	-1	182	176+
1	3	0	194	189-
1	3	1	128	126+
1	3	3	273	272+
1	3	4	59	53-
1	3	5	64	68+
1	3	6	68	61-
1	4	-5	68	70+
1	4	-4	69	79-
1	4	-3	310	307+
1	4	-2	97	103-
1	4	-1	61	37-
1	4	0	732	754+
1	4	1	127	129-
1	4	2	203	196+
1	4	3	55	46+
1	4	4	200	203+
1	4	5	150	159-
1	4	6	99	92-
1	4	7	77	74+
1	5	-7	93	90-
1	5	-6	79	72+
1	5	-5	182	176+
1	5	-4	66	65-
1	5	-3	258	253-
1	5	-2	203	196-
1	5	0	150	144+
1	5	1	62	67-
1	5	2	192	189-
1	5	3	111	109-
1	5	4	74	80+
1	5	5	159	164+
1	5	6	109	113-
1	5	7	75	73-
1	6	-2	104	91-
1	6	-1	93	93-
1	6	0	340	350+
1	6	2	279	296-
1	6	4	126	135+
1	6	5	49	49-
1	6	6	138	139-
1	7	-5	173	153+
1	7	-3	305	282-
1	7	-1	70	69-
1	7	2	77	74-
1	7	2	40	37-
1	7	3	261	274-
1	7	4	49	51-
1	7	5	172	191+
1	8	-4	81	69+
1	8	-3	63	52-
1	8	-1	90	97+
1	8	0	246	250+
1	8	2	313	301-
1	8	3	38	39+
1	8	4	108	109+
1	8	5	71	66+
1	9	-5	64	61+
1	9	-4	65	61+
1	9	-3	123	134-
1	9	0	57	45-
1	9	1	98	96+
1	9	4	38	40-
1	10	-4	116	104+
1	10	-3	106	116+
1	10	-2	152	151-
1	10	0	118	110-
1	10	1	131	129+
1	10	2	177	173+
1	10	2	121	132-
1	11	-3	53	50-
1	11	-1	89	89+
1	11	0	38	37+
1	11	-1	40	37+
1	12	-3	70	70+
1	12	-1	146	130-
1	12	1	196	181+
2	0	-4	230	232-
2	0	-2	56	72+
2	0	0	984	1033-
2	0	2	319	315+
2	0	4	181	170-
2	0	6	64	72+
2	1	-7	115	119+
2	1	-6	55	63+
2	1	-5	253	257-
2	1	-4	43	41-
2	1	-3	514	503+
2	1	-2	195	198+
2	1	-1	551	525-
2	1	0	72	69+
2	1	1	287	283+
2	1	2	390	366+
2	1	3	86	50-
2	1	6	55	55-
2	1	7	80	69+
2	2	-6	34	33-
2	2	-5	119	203+
2	2	-4	100	103-
2	2	-3	41	50-
2	2	-1	218	205+
2	2	0	443	427-
2	2	1	179	163+
2	2	2	265	267+
2	2	4	34	32-
2	2	6	164	160+
2	3	-7	58	57+
2	3	-6	147	137+
2	3	-5	165	160+
2	3	-4	135	136-
2	3	-3	140	144-
2	3	-2	168	147+
2	3	-1	214	218+
2	3	0	241	234+
2	3	1	246	244+
2	3	2	83	82-
2	3	3	223	232+
2	3	4	109	118-
2	4	-8	102	104+
2	4	-7	170	176+
2	4	-6	73	70+
2	4	-4	148	152-
2	4	-3	74	74-
2	4	-2	232	240+
2	4	-1	79	90+
2	4	0	174	187-
2	4	1	157	162-
2	4	2	240	244+
2	4	3	140	141+
2	4	4	112	107-
2	4	5	130	133-
2	4	6	142	148-
2	4	7	106	117+
2	5	-7	66	59+
2	5	-6	111	108+
2	5	-4	262	241-
2	5	-3	67	58+
2	5	-2	196	202+
2	5	-1	90	93+
2	5	1	114	124+
2	5	2	85	77+
2	5	3	41	39-
2	5	4	142	144+
2	5	5	62	65+
2	5	6	89	93-
2	6	-6	55	58+
2	6	-5	86	80+
2	6	-3	213	200-
2	6	-2	210	209+
2	6	-1	285	302+
2	6	2	37	40-
2	6	3	560	584-
2	6	4	120	128+
2	6	5	230	237+
2	6	5	167	182-
2	7	-6	50	38+
2	7	-5	54	53+
2	7	-4	263	251-
2	7	-2	179	181+
2	7	0	194	193-
2	7	1	29	31-
2	7	2	30	34+
2	7	3	74	76+
2	7	4	48	52+
2	8	-4	141	135+
2	8	-2	145	140-
2	8	-1	55	62-
2	8	0	98	96+
2	9	-4	355	373-
2	9	-3	41	38-
2	9	-2	162	167+
2	9	-1	189	182-
2	9	0	173	158-
2	9	-2	50	51-
2	9	-1	59	54+
2	9	0	94	95-
2	10	-4	38	40-
2	10	-3	47	53-
2	10	-2	51	48+
2	10	-1	71	77-
2	10	0	54	54-
2	10	-1	63	69+
2	10	1	91	86+
2	11	-3	96	95-
2	11	-2	116	120-
2	11	-1	77	80+
2	11	0	69	58+
2	11	-3	140	137-
2	11	-2	75	72+
2	11	-1	50	49+
2	11	0	53	55-
2	12	-2	105	99-
2	12	-1	107	91+
2	12	0	159	156+
2	12	2	168	154-
3	0	-7	180	175-
3	0	-5	254	263-
3	0	-1	71	83-
3	0	1	339	348+
3	0	3	391	408-
3	0	5	172	174+
3	0	7	150	165-
3	1	-7	65	61+
3	1	-6	148	158-
3	1	-5	35	35-
3	1	-4	203	204+
3	1	-3	30	32-
3	1	-2	504	492-
3	1	-1	324	309+
3	1	0	151	147-
3	1	1	290	291-
3	1	2	201	193+
3	1	3	73	72+
3	1	4	200	201-
3	1	5	59	53-
3	1	6	92	97+
3	2	-7	65	58-
3	2	-6	104	103-
3	2	-5	41	50-
3	2	-4	41	41+
3	2	-3	105	113+
3	2	-2	142	140-
3	2	-1	260	246-
3	2	0	85	84+
3	2	1	365	365+
3	2	2	24	32-
3	2	3	201	190-
3	2	4	38	39-
3	2	5	130	116+
3	2	6	86	94+
3	2	7	111	112+
3	3	-7	109	124-
3	3	-6	115	124-
3	3	-4	244	241+
3	3	-3	208	197+
3	3	-2	301	264-
3	3	0	234	228+
3	3	2	208	211-
3	3	3	81	67-
3	3	4	77	71+
3	3	5	54	61-
3	4	-5	55	57-
3	4	-4	176	188-
3	4	-3	244	271+
3	4	-1	101	101-
3	4	0	260	261-
3	4	1	296	300+
3	4	2	64	55-
3	4	3	58	63-
3	4	5	145	149+
3	4	6	90	94+
3	5	-7	106	99+
3	5	-6	58	55-
3	5	-5	141	137-
3	5	-4	128	124+
3	5	-3	322	313+
3	5	-1	189	198-
3	5	0	40	43+
3	5	1	141	152+
3	5	2	98	102+
3	5	3	63	64-
3	5	4	79	78-
3	5	5	70	78-
3	5	6	30	34+
3	6	-6	73	70-
3	6	-5	46	43+
3	6	-4	51	53-
3	6	-3	87	100+
3	6	-2	74	61+
3	6	0	348	335-
3	6	1	118	124+
3	6	2	374	379+
3	6	4	211	209-
3	6	5	82	87+
3	6	6	187	167+
3	7	-5	123	125-
3	7	-4	51	51+
3	7	-3	246	252+
3	7	-1	158	158-
3	7	0	147	143-
3	7	1	120	123+
3	7	5	67	80-
3	8	-7	80	74-
3	8	-3	50	49-
3	8	-2	104	100+
3	8	0	209	211-
3	8	1	70	73-
3	8	2	258	251+
3	8	4	147	148-
3	8	5	61	50-
3	9	-4	120	125-
3	9	-2	92	98-
3	9	0	196	196+
3	9	-1	152	160-
3	9	1	129	134+
3	9	3	56	67-
3	10	-4	59	54-
3	10	-3	156	149-
3	10	-2	88	90+
3	10	-1	53	52+
3	10	0	79	80-
3	10	1	170	171-
3	11	-4	188	196+
3	11	-3	46	43-
3	11	-2	108	104+
3	11	0	108	113-
3	11	2	44	44+
3	12	1	179	168+
4	0	-6	70	70-
4	0	-4	43	40+
4	0	-2	205	213+
4	0	0	407	421-
4	0	2	174	174-
4	0	6	171	167-
4	1	-7	128	128-
4	1	-6	78	75-
4	1	-5	94	99+
4	1	-4	41	41+
4	1	-3	366	367-
4	1	-1	140	152-
4	1	1	250	234+
4	1	2	100	91-
4	1	3	33	32-
4	1	4	72	72+
4	2	-7	63	58-
4	2	-6	101	99-
4	2	-5	38	43+
4	2	-4	68	70+
4	2	-2	36	40-
4	2	-1	185	182-
4	2	0	381	362-
4	2	2	90	95+
4	2	4	215	195+
4	2	5	86	173-
4	3	-7	130	116-
4	3	-6	103	108-
4	3	-5	155	129+
4	3	-4	125	120+
4	3	-1	177	177-
4	3	0	307	320-
4	3	2	67	64-
4	3	3	89	87+
4	3	4	76	75-
4	4	-7	120	122-
4	4	-4	106	116+
4	4	-2	83	80-
4	4	-1	144	154-
4	4	0	117	118+
4	4	1	257	251+
4	4	2	43	42-
4	4	3	257	248-
4	4	4	50	45+
4	4	6	52	53-
4	5	-7	93	79-
4	5	-6	112	106-
4	5	-5	176	173+
4	5	-4	169	179+
4	5	-2	307	302-
4	5	1	217	232+
4	5	0	93	76-
4	5	1	113	112-
4	5	2	153	160-
4	5	6	52	48+
4	6	1	269	271+
4	6	3	114	132-
4	6	5	125	120+
4	7	-6	98	96-
4	7	-4	250	266+
4	7	-2	309	318-
4	7	6	318	325+
4	7	2	156	156-
4	7	4	76	74+
4	8	-5	112	106-
4	8	-4	101	113-
4	8	-3	76	67+
4	8	1	231	231+
4	8	4	116	121-
4	8	5	132	148+
4	9	-5	87	77-
4	9	-4	124	127+
4	9	2	95	104+
4	9	0	70	72-
4	9	-1	82	85+
4	9	3	71	64-
4	10	-4	76	68+
4	10	-3	152	143-
4	10	0	54	44+
4	10	1	100	96-
4	10	2	88	92+
4	10	3	92	89-
4	11	-3	39	39+
4	11	-2	76	78-
4	11	-1	83	78-
4	11	0	37	36+
4	12	-1	66	73-
4	12	0	62	82-
5	0	-5	114	129+
5	0	-3	53	42-
5	0	-1	192	186+
5	0	1	380	376-
5	0	3	418	414+
5	0	5	199	193-
5	1	-6	108	107+
5	1	-5	33	28-
5	1	-3	95	97-
5	1	-2	370	362+
5	1	-1	114	100-
5	1	1	40	35+
5	1	4	261	254+
5	2	-6	56	51-
5	2	-5	53	44+
5	2	-3	248	233-
5	2	-2	128	145+
5	2	2	256	258-
5	2	4	154	155+
5	3	-6	90	94+
5	3	-5	146	150+
5	3	-4	50	77+
5	3	-3	244	254-
5	3	-1	66	66+
5	3	0	171	176-
5	3	2	101	100+
5	3	5	47	41-
5	4	-7	31	36+
5	4	-6	56	62+
5	4	-5	39	40+
5	4	-2	67	66-
5	4	1	178	179-
5	4	4	81	94-
5	4	6	125	129+
5	5	-5	118	114+
5	5	-4	294	271-
5	5	-1	244	257+
5	5	0	53	57-
5	5	1	140	147+
5	5	2	62	55-
5	5	3	107	108+
5	5	4	55	47-
5	6	0	102	101+
5	6	1	49	57-
5	6	2	194	198-
5	7	-3	157	143-
5	7	-1	214	224+
5	7	0	78	72-
5	7	1	94	91-
5	7	3	112	125+
5	8	0	75	65+
5	8	1	51	54+
5	8	2	91	89-
5	9	-3	153	149-
5	9	-2	76	77-
5	9	-1	170	176+
5	9	1	77	79-
5	10	-2	55	44-
5	10	1	67	60+
6	0	0	78	81-
6	0	-4	70	82+
6	0	2	212	214+
6	1	-6	85	79+
6	1	-4	84	87-
6	1	-3	101	107+
6	1	-2	307	314+
6	1	-1	158	162+
6	1	0	289	288-
6	1	1	267	286+
6	1	2	52	51+
6	1	3	155	147-
6	2	-6	76	77-
6	2	-4	32	27+
6	2	-3	59	61-
6	2	-1	37	41+
6	2	0	58	52-
6	2	3	38	38+
6	3	-6	103	90+
6	3	-5	79	78-
6	3	-4	106	98-
6	3	-3	107	106+
6	3	-2	86	72+
6	3	-1	141	132-
6	3	0	95	90-
6	3	1	39	39+
6	3	2	129	128+
6	3	4	80	80-
6	4	-6	90	106-
6	4	-5	106	61-
6	4	-4	51	55-
6	4	-2	28	33-
6	4	0	79	72-
6	4	1	152	149-
6	4	3	63	70-
6	4	4	150	155+
6	4	5	76	78-
6	5	-5	121	127+
6	5	-2	225	228+
6	5	-1	120	116-
6	5	0	132	137-
6	5	2	129	126+
6	5	4	63	70-
6	6	-2	46	52-
6	6	-1	37	41+
6	6	0	58	61+
6	6	2	58	46-
6	6	-1	58	46+
6	7	-3	112	104-
6	7	-2	170	154-
6	7	0	161	154-
6	8	-1	73	94-
6	8	0	100	92-
6	9	-2	74	89+
6	9	-1	66	66+
6	9	0	118	119-
7	0	-2	64	60+
7	0	-1	64	60+
7	1	-6	89	86-
7	1	-3	233	237-
7	1	-2	41	40-
7	1	0	237	230+
7	1	1	170	171-
7	1	3	91	92-
7	2	-6	36	44-
7	2	-5	33	43+
7	2	0	86	85+
7	2	1	89	84+
7	2	3	80	71-
7	3	-4	105	104-
7	3	-3	224	196+
7	3	-2	177	170-
7	3	-1	137	125-
7	3	0	103	91+
7	3	1	119	122+
7	3	2	59	53-
7	4	-5	94	100-
7	4	-4	102	110+
7	4	-2	37	35-
7	4	-1	52	55-
7	4	0	102	100+
7	4	1	78	72+
7	4	2	78	72+
7	4	3	90	92-
7	5	-5	51	60-
7	5	-3	124	132+
7	5	-2	54	53-
7	5	-1	170	172-
7	5	0	44	37+
7	5	1	108	105+
7	5	2	46	46-
7	5	3	66	93-
7	6	-1	70	65-
7	6	0	52	48-
7	6	1	59	50+
7	6	2	126	115+
7	7	-5	55	53+
7	7	-1	175	177-
7	7	0	36	23+
7	7	1	95	90-
7	7	3	150	145-
7	8	-3	55	49-
7	9	-3	92	90+
7	9	-2	68	70+
8	0	-4	100	177-
8	0	-2	94	96+
8	0	0	162	166-
8	0	4	34	35+
8	1	-5	48	51+
8	1	-4	46	46-
8	1	-3	132	120-
8	1	-1	142	139+
8	1	1	133	129-
8	1	2	49	43+
8	1	3	77	70+
8	2	-6	95	111+
8	2	-4	76	76-
8	2	-3	38	41-
8	2	-1	100	89+
8	2	0	72	69-
8	2	1	59	49+
8	3	-4	97	99+
8	3	-3	99	85-
8	3	-2	85	93-
8	3	0	169	159+
8	3	1	124	114-
8	4	-5	87	92+
8	4	-4	31	31-
8	4	0	55	55+
8	4	1	36	43+
8	4	2	100	89+
8	5	-4	50	50-
8	5	-3	99	85-
8	5	-2	85	93-
8	5	-1	89	96+
8	5	2	106	102-
8	6	-2	72	67-
8	7	-2	135	136-
9	0	-3	65	69-
9	0	-2	29	24+
9	0	-4	45	45-
9	1	-3	62	26-
9	1	-2	61	70+
9	1	0	141	143+
9	1	-1	32	32-
9	1	2	44	66+
9	2	-1	59	63+
9	2	-4	53	39-
9	2	3	49	37-
9	3	-5	95	96+
9	3	-4	29	52-
9	3	-3	78	68+
9	3	-2	85	62+
9	4	-3	31	45-
9	4	-2	21	31+
9	4	3	52	62-
9	5	-2	108	109+
9	5	1	59	74-
10	0	0	55	50-
10	0	-1	92	98+
10	2	-3	62	62+
10	3	-2	58	38+
10	3	0	95	100-
10	4	-1	40	36-

were used to place the 17 nets on a common scale (Nordman, 1960).

Structure determination

The crystals of the low temperature modification of perchloric acid monohydrate are monoclinic and belong to the space group $P2_1/n$. The lattice parameters, as determined from measurements of high angle diffraction spots on precession photographs of several nets, are, with their estimated standard deviations:

$$a = 7 \cdot 541 \pm 0 \cdot 006, \ b = 9 \cdot 373 \pm 0 \cdot 011, \ c = 5 \cdot 359 \pm 0 \cdot 006 \text{ Å},$$
$$\beta = 97° \ 41' \pm 4'.$$

These values resemble the orthorhombic cell parameters of the high temperature modification reported by Lee & Carpenter, namely

$$c = 7 \cdot 339 \pm 0 \cdot 004, \ a = 9 \cdot 065 \pm 0 \cdot 008, \ b = 5 \cdot 569 \pm 0 \cdot 004 \text{ Å}.$$

The unit-cell volume is $375 \cdot 4 \pm 0 \cdot 7$ Å^3 at -80 °C., and $370 \cdot 5 \pm 0 \cdot 5$ Å^3 at room temperature. It is likely, therefore, that the low-to-high transition itself is accompanied by a slight decrease in molar volume. The unit cell contains four formula units of perchloric acid monohydrate.

The high temperature modification belongs to the orthorhombic space group *Pnma*, with the axes labeled as stated above. This space group contains the symmetry elements $2_1/n$ about a, which evidently becomes the monoclinic b axis in the low temperature form. Thus all the symmetry elements of the low form are contained in the symmetry group of the high form. The effect of the transition on the symmetry of the orthorhombic phase can thus be described as a moderate distortion of the lattice, making it monoclinic, with preservation of all symmetry elements compatible with this distortion.

In view of these clues it was decided to attempt to refine the monoclinic structure directly by least-squares using the atomic coordinates of the orthorhombic structure as starting parameters. Individual isotropic thermal parameters were employed and the off-diagonal terms in the least-squares matrix neglected. The quantity $R' = \Sigma w (KF_o - F_c)^2 / \Sigma w K^2 F_o^2$ was minimized, taking $w(hkl)$ as $3|F_{\min}./F_o(hkl)|$ or unity, whichever was smaller. 250 low angle reflections were included in the early stages. Although somewhat

sluggish in the first several cycles, the procedure yielded the correct structure after generating net shifts of approximately 0·5 Å in the chlorine position, and 0·9, 0·9, 0·4, 0·2 and 0·3 Å in the five oxygen positions. The level of agreement reached in this manner, with all observed reflections included, was $R = 0 \cdot 098$ and $R' = 0 \cdot 0145$. A few additional cycles employing anisotropic thermal parameters improved the agreement to $R = 0 \cdot 062$ and $R' = 0 \cdot 0062$.

At this stage the approximate locations of the three hydrogen atoms could be safely deduced from the presence of three characteristic hydrogen bonded $O \cdots O$ distances between the hydronium oxygen and neighboring perchlorate ions. The hydrogens were located independently, however, as fairly well resolved peaks in a Fourier difference synthesis based on the structure factor output of the anisotropic heavy-atom refinement. The hydrogen atoms, with isotropic temperature factors, were now included in F_c; a few more cycles of refinement reduced the discrepancies to $R = 0 \cdot 052$ and $R' = 0 \cdot 0040$. Finally a small extinction correction was applied. The observed structure factors were multiplied by a correction factor

$$\exp \left[\alpha (KF_o)^2 (1 + \cos^2 2\theta) / \sin 2\theta \right],$$

where α was taken as $1 \cdot 5 \times 10^{-6}$. This correction increased 20 structure factors by 1% or more, 6 by 5% or more, the greatest correction (13%) being applied to $F(200)$. Further refinement produced slight changes in the scale and temperature factors, giving final residuals of $R = 0 \cdot 049$ and $R' = 0 \cdot 0036$. The observed (corrected) and calculated structure factors of the observed reflections are listed in Table 1. The scattering factors used in the refinement were that of Dawson (1960) for Cl, Berghuis *et al.* (1955) for O, and McWeeny (1951) for H.

Table 2. *Atomic coordinates and standard deviations*

Atom	x	y	z
Cl	$0 \cdot 2184 \pm 0 \cdot 0001$	$0 \cdot 4643 \pm 0 \cdot 0001$	$0 \cdot 2779 \pm 0 \cdot 0001$
O_1	$0 \cdot 0523 \pm 0 \cdot 0002$	$0 \cdot 3920 \pm 0 \cdot 0005$	$0 \cdot 2317 \pm 0 \cdot 0005$
O_2	$0 \cdot 1925 \pm 0 \cdot 0004$	$0 \cdot 6152 \pm 0 \cdot 0002$	$0 \cdot 3242 \pm 0 \cdot 0006$
O_3	$0 \cdot 3138 \pm 0 \cdot 0004$	$0 \cdot 4517 \pm 0 \cdot 0002$	$0 \cdot 0619 \pm 0 \cdot 0007$
O_4	$0 \cdot 3258 \pm 0 \cdot 0004$	$0 \cdot 4039 \pm 0 \cdot 0003$	$0 \cdot 4989 \pm 0 \cdot 0005$
O_5	$0 \cdot 3250 \pm 0 \cdot 0002$	$0 \cdot 6926 \pm 0 \cdot 0002$	$0 \cdot 7866 \pm 0 \cdot 0004$
H_1	$0 \cdot 279 \ \pm 0 \cdot 018$	$0 \cdot 679 \ \pm 0 \cdot 009$	$0 \cdot 650 \ \pm 0 \cdot 014$
H_2	$0 \cdot 330 \ \pm 0 \cdot 008$	$0 \cdot 621 \ \pm 0 \cdot 004$	$0 \cdot 876 \ \pm 0 \cdot 010$
H_3	$0 \cdot 274 \ \pm 0 \cdot 006$	$0 \cdot 765 \ \pm 0 \cdot 008$	$0 \cdot 864 \ \pm 0 \cdot 013$

Table 3. *Thermal parameters*

($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
Cl	85 ± 2	35 ± 2	89 ± 2	-5 ± 1	$+6 \pm 1$	$+33 \pm 2$
O_1	102 ± 3	109 ± 4	241 ± 8	-83 ± 5	$+69 \pm 10$	-33 ± 13
O_2	215 ± 6	40 ± 2	160 ± 2	$+65 \pm 7$	-7 ± 14	$+50 \pm 11$
O_3	152 ± 5	64 ± 4	140 ± 3	$+30 \pm 10$	$+18 \pm 10$	$+120 \pm 9$
O_4	105 ± 5	50 ± 1	136 ± 4	-17 ± 5	$+43 \pm 5$	-24 ± 8
O_5	114 ± 5	41 ± 2	140 ± 6	$+7 \pm 6$	-7 ± 4	$+40 \pm 11$
H_1			$B = 2 \cdot 5 \pm 1 \cdot 0$ Å^2			
H_2			$0 \cdot 3 \pm 1 \cdot 2$			
H_3			$0 \cdot 6 \pm 0 \cdot 8$			

The final values of the atomic coordinates and thermal parameters are given in Tables 2 and 3. The six anisotropic thermal parameters given for the non-hydrogen atoms are those in the temperature factor

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+kl\beta_{23}+hl\beta_{13})\right].$$

In order to estimate the standard deviations of the parameters the structure factors were divided into six equal sets with the same distribution in $\sin\theta/\lambda$ but otherwise selected at random. Each such set was refined through four cycles of least-squares, enough to insure virtually complete refinement. In this way six essentially independent values were obtained for each positional and thermal parameter. The estimates of the standard deviations listed in Tables 2 and 3 were taken as

$$\left[\sum_i r_i^2/n(n-1)\right]^{\frac{1}{2}},$$

where $r_i(i=1,\ldots,n)$ is the deviation from the mean of an individual value, and $n=6$ in this case.

Discussion

A schematic representation of the structure viewed along the shortest crystallographic axis (c) is shown in Fig. 1(b). The hydronium and perchlorate ions are arranged in hydrogen-bonded sheets, parallel to the yz plane, in which each hydronium ion is hydrogen bonded to three different perchlorate ions. Fig. 2 shows the arrangement of ions and hydrogen bonds within one such sheet. Interatomic distances and bond angles are given in Table 4.

Considering first the hydronium ion and its surroundings we find the ion to be pyramidal, as expected. The H–O–H angle is approximately 112°, not significantly different from the value 117° found in hydrogen chloride monohydrate (Yoon & Carpenter, 1959). The pyramidal configuration of the H_3O^+ ion also manifests itself in the angles formed by the three O–H$\cdots$O hydrogen bonds about the hydronium oxygen. In an average sense these three angles agree very closely with corresponding angles in nitric acid trihydrate (hydronium nitrate dihydrate) reported as 103, 113 and 118° (Luzzati, 1953) and the value 110·4 found by Yoon & Carpenter for the angles between the three symmetrically equivalent O–H$\cdots$Cl bonds about the OH_3^+ ion in hydrogen chloride monohydrate (hydronium chloride). Our O–H distances appear to be shorter than the value 0.96 ± 0.08 Å reported by Yoon & Carpenter, but in view of the large standard deviations the difference can hardly be considered significant. A similar disagreement exists between the H$\cdots$H distance of about 1·4 Å calculated from the data of Table 4 and the values 1·58 and 1·72 Å (Kakiuchi et al., 1951; Richards & Smith, 1951) found by NMR. The discrepancy could be reduced somewhat by correcting the O–H distances for oscillational motion of the hydronium ion. Although the thermal param-
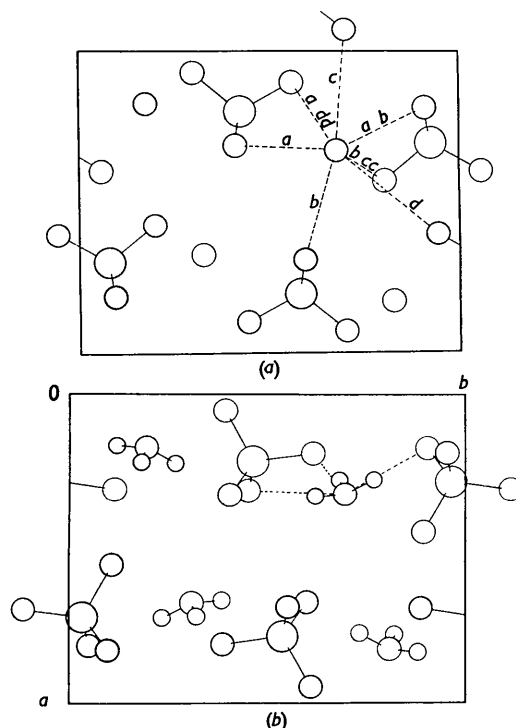
Fig. 1. (a) Schematic projection of the room temperature structure according to Lee & Carpenter, showing $H_3O^+\ldots O$ contacts. (b) Corresponding projection of the low temperature structure showing hydrogen bonds.
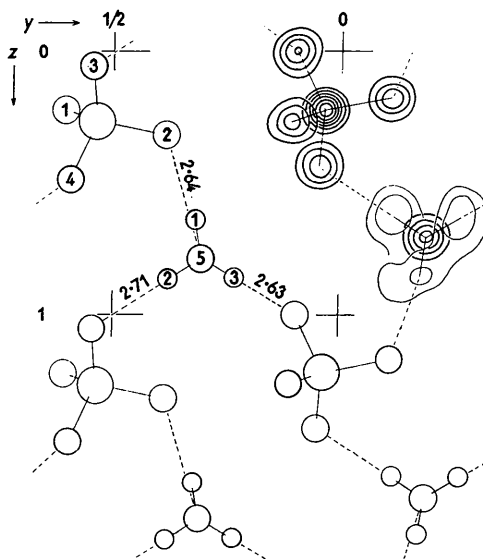
Fig. 2. A portion of the low temperature structure showing the arrangement of perchlorate and hydronium ions within a hydrogen bonded sheet. Electron density contours are at intervals of 4 e.Å^{-3} for O and 8 e.Å^{-3} for Cl. Contours of the electron density of H, as given by a difference Fourier synthesis, are at intervals of 0·25 e.Å^{-3}. Zero contours omitted.

eters of the hydrogen atoms (Table 3) are too inaccurate to yield any reliable estimate of this error,

it could be expected to amount to at least a few hundredths of an Å.

Table 4. *Interatomic distances and bond angles*

(a) Distances (Å)		(b) Angles (°)	
Cl–O$_1$	1·445 ± 0·006	O$_1$–Cl–O$_2$	111·1 ± 0·3
Cl–O$_2$	1·478 ± 0·005	O$_1$–Cl–O$_3$	110·1 ± 0·2
Cl–O$_3$	1·465 ± 0·007	O$_1$–Cl–O$_4$	109·8 ± 0·3
Cl—O$_4$	1·468 ± 0·006	O$_2$–Cl–O$_3$	108·1 ± 0·3
		O$_2$–Cl–O$_4$	108·2 ± 0·2
O$_5$–H$_1$	0·78 ± 0·06	O$_3$–Cl–O$_4$	109·5 ± 0·3
O$_5$–H$_2$	0·82 ± 0·05		
O$_5$–H$_3$	0·91 ± 0·11	H$_1$–O$_5$–H$_2$	113 ± 9
		H$_2$–O$_5$–H$_3$	110 ± 4
O$_5$–H$_1$...O$_2$	2·64 ± 0·01	H$_1$–O$_5$–H$_3$	112 ± 5
O$_5$–H$_2$...O$_3'$	2·71 ± 0·01		
O$_5$–H$_3$...O$_4'$	2·63 ± 0·01	O$_2$–(H$_1$–O$_5$–H$_2$)–O$_3'$	104·3 ± 0·5
		O$_3'$–(H$_2$–O$_5$–H$_3$)–O$_4'$	110·0 ± 0·5
		O$_2$–(H$_1$–O$_5$–H$_3$)–O$_4'$	118·9 ± 0·5

The lengths of the three hydrogen bonds are 2·64, 2·71 and 2·63 Å. The shortest non-hydrogen bonded O · · · O contact made by the hydronium ion is 2·94 Å, roughly along the threefold axis of the H$_3$O$^+$ ion, on its concave side. The next shortest H$_3$O$^+$ · · · O distances are 3·05, 3·12 and 3·16 Å. The three angles formed by the hydrogen bonds with their adjoining Cl–O bonds are very nearly equal, 113, 115 and 115°.

Fig. 1(a) shows the corresponding view of the room temperature modification (Lee & Carpenter, 1959). The similarity of the two structures is quite apparent. Lee & Carpenter found that the hydronium ion is surrounded by twelve oxygen neighbors within 3·40 Å. These contacts are shown as broken lines in Fig. 1(a). Due to the presence of a mirror plane through the hydronium oxygen, parallel to the paper some of these contacts overlap in the figure.

In an attempt to deduce a plausible picture of the behavior of the H$_3$O$^+$ ion in the phase transition we have compiled the comparison of the two structures given in Table 5. Assuming that the hydronium ion in the room temperature form is disordered, or tumbling, among two or more different orientations, we may look for a likely set of such orientations by surveying the distances and angles of the O · · · O

contacts. Among the twelve contacts within 3·40 Å we find four symmetrically independent sets of three, having all three angles in the range 90 to 130°. These are designated (a)–(d) in Table 5 and Fig. 1(a). Each of the first two corresponds to two distinct but symmetrically equivalent sets of contacts due to the presence of mirror symmetry. In columns 3 and 4 of the table are given the angles and distances of these possible H$_3$O$^+$ orientations in the room temperature modifications. Columns 5 and 6 list the corresponding H$_3$O · · · O distances in the low temperature form. Since the two structures are sufficiently similar there is no ambiguity as to which distances 'correspond' to each other.

Although one of the distances in set (a) is longer (3·40 Å) than even a 'partial' hydrogen bond, the other two are the shortest ones present. Furthermore, one of the sets (a) corresponds to the orientation of the hydronium ion in the low temperature structure, as shown by the distances in column 5. It is therefore very reasonable to propose that if the ion is disordered among two or more orientations, the ones represented by (a) are contributing structures.

The angles in set (b) are favorable. One distance (2·86 Å) is common to (a) and (b). The other two are both shorter than either of their respective low temperature counterparts suggesting that the sets (b) represent probable orientations of the disordered H$_3$O$^+$ ion. Set (c) appears somewhat less favorable. While the 2·93 Å distance might be an O–H · · · O contact, it is not greatly lengthened in going to the low temperature form, where the 2·94 Å distance is known *not* to be a hydrogen bond. Finally, the orientation corresponding to (d) is unlikely to have a significantly higher than random probability, on account of its very long H$_3$O$^+$ · · · O distances.

In summary, the preceding argument suggests as an at least plausible model for the room temperature structure one in which the hydronium ions are disordered among the four orientations (a) and (b) with the possible addition of (c). An experimental test of the validity of this model is clearly beyond the power of X-ray diffraction. It is to be hoped that accurate

Table 5. *Possible orientations of the* H$_3$O$^+$ *ion in the room temperature modification*

Designation	Multiplicity	O ... (H$_3$O$^+$) ... O angles	H$_3$O$^+$ ... O distances	H$_3$O$^+$ ... O distances in low temp. phase	
(a)	2	100·5°	2·86	2·63	3·16
		106·2	2·92	2·71	3·12
		121·9	3·40	2·64	3·26
(b)	2	103·0	2·86	2·63	3·16
		106·3	2·99	3·05	3·34
		108·9	3·10	3·57	3·22
(c)	1	102·2	2·93	2·94	
		102·2	3·10	3·22	
		127·7	3·10	3·57	
(d)	1	110·1	3·16	3·29	
		123·2	3·40	2·64	
		123·2	3·40	3·26	

neutron diffraction work will yield the definitive answer.

As expected, the largest r.m.s. amplitudes of thermal vibration of the chlorine and hydronium oxygens, 0·16 and 0·18 Å, respectively, are approximately perpendicular to the yz plane, that is, perpendicular to the hydrogen bonded sheets. The average r.m.s. amplitudes parallel to the sheets are 0·12 and 0·14 Å. The thermal anisotropy of the perchlorate oxygens is very strong. The directions of maximum motion, with r.m.s. amplitudes of 0·19 to 0·25 Å, are in all cases approximately perpendicular to the Cl–O bonds, while the minimum motions with r.m.s. amplitudes of only 0·12 to 0·15 Å are in the directions of these bonds. The r.m.s. amplitudes of chlorine and oxygen atoms along a bond joining them were found to be equal within experimental error in all cases, the differences being apparently random in sign and averaging less than 4% in magnitude. The along-the-bond r.m.s. amplitudes of hydrogen bonded oxygen atoms give a vague indication that the hydronium oxygen vibrates with a smaller amplitude than the perchlorate oxygens, implying some stretching of the hydrogen bond. The differences are small, however, averaging 7% of the r.m.s. amplitudes, and can hardly be considered significant, particularly in view of the errors that might have arisen from the different states of ionization of the perchlorate and hydronium oxygens.

The oscillation corrections (Cruickshank, 1956) to be added to the apparent Cl–O bond lengths range from 0·011 to 0·029 Å considerably exceeding the standard deviations in these distances as calculated from the least-squares coordinates. The corrected Cl–O bond distances given in Table 4 are in good agreement with values found in several other perchlorates and in the room temperature modification of hydronium perchlorate itself (Gillespie, Sparks & Trueblood, 1959; Truter, Cruickshank & Jeffrey, 1960; Truter, 1961). It is interesting to note that the three perchlorate oxygens, O_2, O_3 and O_4, which are hydrogen bonded to the hydronium ion, have Cl–O distances somewhat longer than that of the non-hydrogen bonded oxygen atom O_1.

References

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757.

DAWSON, B. (1960). *Acta Cryst.* **13**, 403.

GILLESPIE, R. B., SPARKS, R. A. & TRUEBLOOD, K. N. (1959). *Acta Cryst.* **12**, 867.

KAKIUCHI, Y., SHONO, H., KOMATSU, H. & KIGOSHI, K. (1951). *J. Chem. Phys.* **19**, 1069.

KAKIUCHI, Y., SHONO, H., KOMATSU, H. & KIGOSHI, K. (1952a). *J. Phys. Soc. Japan*, **7**, 102.

KAKIUCHI, Y., SHONO, H., KOMATSU, H. & KIGOSHI, K. (1952b). *J. Phys. Soc. Japan*, **7**, 380.

LEE, F. S. & CARPENTER, G. B. (1959). *J. Phys. Chem.* **63**, 279.

LIPSCOMB, W. N. (1957). *Norelco Reporter*, **IV**, 54.

LUZZATI, V. (1953). *Acta Cryst.* **6**, 157.

McWEENY, R. (1951). *Acta Cryst.* **4**, 513.

NORDMAN, C. E. (1960). *Acta Cryst.* **13**, 535.

RICHARDS, R. E. & SMITH, J. A. S. (1951). *Trans. Faraday Soc.* **47**, 1261.

SMITH, H. G. & LEVY, H. A. (1959). Abstracts, Cornell Meeting of the American Crystallographic Association. Ithaca, New York, July 1959.

TAYLOR, R. C. & VIDALE, G. L. (1956). *J. Amer. Chem. Soc.* **78**, 5999.

TRUTER, M. R., CRUICKSHANK, D. W. J. & JEFFREY, G. A. (1960). *Acta Cryst.* **13**, 855.

TRUTER, M. R. (1961). *Acta Cryst.* **14**, 318.

VOLMER, M. (1924). *Ann. Chem.* **440**, 200.

WYK, H. J. VAN (1906). *Z. anorg. Chem.* **48**, 1.

YOON, Y. K. & CARPENTER, G. B. (1959). *Acta Cryst.* **12**, 17.