Nuclear Quadrupole Resonance Spectra of ^{75}As in Some Dihydrogen Arsenates and of their Deuteriated Analogues

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PURE nuclear quadrupole resonance (n.q.r.) has been observed at room temperature and at 77° K in Na_2HAsO_4 by Jones and Uehling.[1] However, no positive n.q.r. results on dihydrogen arsenates have so far been reported.[2]

We have studied the pure n.q.r. spectra of ^{75}As in some polycrystalline dihydrogen arsenates MH_2AsO_4 (M = Li, K, Na, Rb, Cs, Ag, NH_4, and Me_4N) and of their deuteriated analogues. Measurements were made with a pulse n.q.r. spectrometer IS-2.[3] ^{75}As n.q.r. frequencies at 77° K, spin–lattice (T_1) and spin-phase memory, (T_2) relaxation times are listed in the Table. T_1 and T_2 were measured by a method similar to that of Woessner and Gutowsky.[4] For compounds with weak resonances, T_1 and T_2 have been estimated only approximately.

The n.q.r. frequency is determined by the electric field gradient at the ^{75}As site, and hence can serve as a measure of the distortion of the AsO_4 tetrahedron. This distortion arises mostly from the intermolecular hydrogen bonds O–H $\cdots$ O and their dynamical changes. However, the contribution to the field gradients arising from ionically bonded metal-atoms, M, is not small, since the resonance frequencies depend on M.

For the ferroelectric crystals (M = K, Rb, Cs, and NH_4) the frequencies decrease sharply with increase in temperature. Such a large temperature variation of n.q.r. frequencies cannot be accounted for by the increase in thermal lattice oscillations; it is probably a result of the intrabond protonic mobility. For nonferroelectric crystals no sharp frequency change has been observed.

To establish the character of dynamic effects, it would be of great interest to study the temperature dependences of the n.q.r. frequencies and the relaxation times, and crystals with different H/D isotopic ratio. The results of the experiments in progress will be published later.

TABLE

The nuclear quadrupole resonance spectra of ^{75}*As in polycrystalline dihydrogen arsenates*

Compound	T(°K)	ν_{res}(Mc./sec.)	T_1(msec.)	T_2(μsec.)
KH_2AsO_4	77	35·07	30	25
	90	33·70	—	—
KD_2AsO_4	77	42·62	350	350
RbH_2AsO_4	77	35·70	120	35
	101	32·80	—	—
RbD_2AsO_4	77	42·68	1500	300
CsH_2AsO_4	77	37·23	250	40
	148	30·75	—	—
CsD_2AsO_4	77	42·98	500	330
	196	42·95	—	—
$NH_4H_2AsO_4$	77	35·18	270	40
	196	33·70	10	40
$ND_4D_2AsO_4$	77	38·71	500	15
		39·45	500	60
	196	38·78	—	—
		39·45	—	—
Na_2HAsO_4	77	38·37	<5	30
$Na_2HAsO_4,7H_2O$	77	42·11	1000	60
	196	42·75	50	—
	300	43·70	—	—
NaH_2AsO_4	77	54·50	400	70
	196	54·50	30	60
	300	54·54	—	—
NaD_2AsO_4	77	55·78	100	100
LiH_2AsO_4	77	47·24	15	40
LiD_2AsO_4	77	48·60	5	—
$Me_4NH_2AsO_4$	77	40·75	60	50
	196	40·69	10	50
$Me_4ND_2AsO_4$	77	48·96	25	80
		49·40	25	80
AgH_2AsO_4	77	39·19	1000	150
		38·11	1300	50
	196	39·22	150	—
		37·29	200	—
	300	39·26	—	—
		37·83	—	—

On replacing hydrogen by deuterium a remarkable isotope effect was observed, the difference between the frequencies in K, Rb, and Cs deuteriated arsenates at 77° K nearly vanishing completely.

We thank Dr. I. Rez and Dr. V. Pakhomov for providing some of the samples used.

(*Received, March* 20*th,* 1968; *Com.* 344.)

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