127I Pure Quadrupole Resonance Spectrum of Orthoperiodic acid, H$_5$IO$_6$

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The NQR-spectrum of 127I in orthoperiodic acid, H$_5$IO$_6$, has been studied on powder samples in the temperature range 77 K $\leq T \leq$ 398 K. The resonance frequencies $v_1$ of the transition $m(\pm 3/2)$ $\leftrightarrow$ $m(\pm 1/2)$ are 45.248 $\pm$ 0.005 MHz (77 K) and 44.976 $\pm$ 0.005 MHz (296 K). For the transition $m(\pm 5/2)$ $\leftrightarrow$ $m(\pm 3/2)$ the resonance frequencies $v_2$ are 83.478 $\pm$ 0.005 MHz (77 K) and 83.960 $\pm$ 0.005 MHz (296 K). The corresponding quadrupole coupling constants, $e^2 q Q/h$, are 282.977 $\pm$ 0.005 MHz (296 K), and 281.892 $\pm$ 0.005 MHz (77 K). The asymmetry parameters $\eta$ have been determined as 0.2372 $\pm$ 0.0001 (296 K), and 0.2580 $\pm$ 0.0001 (77 K). A small change of 0.4% for $e^2 q Q/h$ is accompanied by a rather large change of 21% for $\eta$ within the temperature range investigated. $e^2 q Q/h$ shows a maximum at $\sim$ 313 K. No evidence of phase transition has been observed by NQR spectroscopy between 77 K and 398 K.

Introduction

Quite strong electric field gradients act on the 127I nuclei in covalently bonded iodides and nuclear quadrupole coupling constants $e^2 q Q/h$ between 1500 and 2000 MHz are found in aliphatic and aromatic organic iodides. A factor of roughly 2 lower is the nuclear quadrupole interaction energy of pentavalent iodide, I$^{5+}$, in iodates. Still lower nuclear quadrupole coupling constants have been found in periodates of the general type MeI$_x$O$_{4-n}$.

Here the NQ-coupling constants vary between 42.410 MHz for 127I in NaI$_6$O$_4$ (296 K) and 20.760 MHz in KIO$_4$ (296 K) 2-4. Similar low coupling constants and interaction energies have been found for 187Re and 187Re in the perrenates of the MeReO$_4$-type. Comparable electric field gradients can be expected at the X-site in XO$_4$-ions $(X = I, Re)$, since the two ions I$^{7+}$ and Re$^{4+}$ have an outer shell isosctructural electronic configuration.

For the periodic ion several different chemical configurations are known. Besides the tetrahedral surrounding by oxygen in I$^{5-}$, an octahedral surrounding by oxygen ions (atoms) is found in the salts of the type Me$_2$H$_2$IO$_6$ (Me = NH$_4$, Ag). The two compounds crystallize in the hexagonal system, the IO$_6^{6-}$-ions having an almost regular octahedral arrangement of oxygen atoms around the iodine $6,7$. The iodine-oxygen distance within the octahedron is 1.93 Å. Both salts undergo a phase transition below room temperature to antiferroelectric states.

Recent studies of nuclear quadrupole interaction in (NH$_4$)$_2$H$_2$IO$_6$ by the cross-over-relaxation technique reveal that the quadrupole coupling constant, $e^2 q Q/h$, of 127I is 25.35 MHz at room temperature and the asymmetry parameter $\eta$ is zero. The discussion of the NQR results in the periodates and perrenates of the MeXO$_4$-type $(CaWO_4$-structure) gave evidence that in all these isostructural compounds the relatively large quadrupole coupling probably results from contributions to the electric field gradient tensor from both the point charges $q(e)$ in the tetragonal lattice and from partial covalent bonding $q(p)$ in the ion which is distorted from tetrahedral symmetry. It has been found that both $q(e)$ and $q(p)$ are very sensitive to the changes in the oxygen parameter.

4 L. HELMHOLTZ, J. Amer. Chem. Soc. 59, 2036 [1937].
9 M. T. ROGERS and K. V. S. RAMA RAO, Presented at the 156th National ACS Meeting, Atlanta, N. J. 1968 (to be published).
It seemed worthwhile to us to study the NQR-spectrum of $^{127}$I in crystalline H$_5$I$_0$$_6$. Here the different IO$_6$-octahedra are connected to a three-dimensional frame by hydrogen bonds. Detailed crystal structure studies by X-ray and neutron diffraction analysis showed that H$_5$I$_0$$_6$ consists of slightly deformed oxygen octahedra with iodine as the central atom.

Orthoperiodic acid belongs to the monoclinic crystal class, space group P2$_1$/n with $a = 5.28$ Å, $b = 18.35$ Å, $c = 4.95$ Å, $\beta = 111.4^\circ$ and $Z = 4$. The molecule H$_5$I$_0$$_6$ consists of a slightly deformed octahedron with iodine near the centre. Five of the oxygen atoms are directly linked to hydrogens. For these five oxygen atoms the distance to the central iodine atom is 1.89 Å. For the remaining oxygen atom, the distance I—O is 1.78 Å. It has also been suggested, that the bonds within the molecule may be covalent. This gives an indication of the relatively large quadrupole coupling [when compared to (NH$_4$)$_2$H$_3$I$_0$$_6$] at the iodine site resulting from the contribution of both $q(e)$ and $q(p)$. This has indeed been the case, and in this paper we report the values of quadrupole coupling constants obtained at several temperatures by direct observations of $^{127}$I pure quadrupole resonance spectra in polycrystalline samples of H$_5$I$_0$$_6$.

**Experimental**

The resonances reported here were observed using a frequency modulated, externally quenched superregenerative oscillator and an oscilloscope. The quench frequencies were around 50 kHz. No optimum performance of the oscillator can be reached using only one tank coil for the measurement of $v_1$ and $v_2$.

To measure the two transitions

$$v_1 = m(\pm 3/2) \not\ll m(\pm 1/2)$$

and

$$v_2 = m(\pm 5/2) \not\ll m(\pm 3/2)$$

at the same temperature $T_a$, the oscillator was first adjusted for the low frequency line ($v_1$). Then a parallel coil (a shunting coil) of appropriate inductance was soldered at the top of the tuning condenser keeping the main coil in the dewar at $T_a = T$. In this way $v_1$ and $v_2$ could be detected at the same temperature $T$. The intensity of $v_2$ was reduced slightly due to loss of power and filling factor. However, this did not greatly affect our measurements since the signals were fairly strong (at 296 K $S/N = 7$ for $v_1$, and $S/N = 6$ for $v_2$ with the shunting coil).

The frequencies were measured by using a Rhode und Schwarz, WIK BN 4221 type frequency meter; the error in frequency measurements is ±5 kHz and is solely due to the line width of the NQR-lines. The temperatures between room temperature and 115 K were achieved by immersing the sample tube in a dewar containing isopentane and slowly adding liquid nitrogen with constant stirring. The melting points of petroleum ether (184 K) and carbon tetrachloride (250 K) were used as a check.

For the measurement of $v_1$ and $v_2$ at the boiling point of liquid nitrogen, the sample was first precooled to 115 K, using an isopentane liquid nitrogen slush bath. Then, after the sample had reached the temperature of 115 K, it was immersed in liquid N$_2$. In this way a considerable improvement in signal to noise ratio was reached in comparison to samples cooled directly from room temperature to liquid N$_2$.

The temperatures above room temperature were achieved by immersing the sample in paraffin and heating it with a temperature controlled oil bath. The resonances were observable to 398 K after which they began broadening since the sample started melting. Temperatures were measured with a copper constantan thermocouple and were accurate to ±1 degree. The periodic acid (H$_5$I$_0$$_6$ pro analysi) in crystalline form was obtained from E. Merck, Darmstadt.

A plot of the temperature variation of the $^{127}$I-NQR-frequencies in H$_5$I$_0$$_6$ is given in Fig. 1.

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Fig. 1. NQR-frequencies $v_1(m = \pm 1/2 \not\ll m = \pm 3/2)$ and $v_2(m = \pm 3/2 \not\ll m = \pm 5/2)$ of $^{127}$I in H$_5$I$_0$$_6$ as a function of temperature.

12 H. Huthmann, Diplomarbeit, Münster 1971.
Results and Discussion

The quadrupole coupling constant \( (e^2 q Q/h) \) and the asymmetry parameter \( \eta \) were calculated using the tables of Livingston and Zeldes\(^{13}\). The plots are shown in Figs. 2 and 3. The values of \( e^2 q Q/h \) and \( \eta \) calculated at a few different temperatures are given in Table 1, together with the resonance frequencies \( \nu_1 \) and \( \nu_2 \). Within the temperature range 77 K to 398 K, \( \eta \) changes by 21% whereas the \( e^2 q Q/h \) varies by only 0.4%. This clearly shows that the spin 5/2 energy level scheme is more dominated by changes in \( \eta \) and only slightly by the maximum principal axis of the electric field gradient system. A similar effect has been observed by Segel and Anderson\(^{14}\) on \( \text{Re}_2(\text{CO})_{10} \) where the asymmetry parameter of \( \text{Re} \) varies by 43% whereas the coupling constant changes by only 6% in the temperature range 77 K to 340 K.

Since our present work included only powder data, no information was obtained concerning the direction cosines of the electric field gradient tensor at the site of the iodine nucleus. However, from knowledge of the crystal structure, it may be assumed that \( q_{zz} \) is along the short \( I-O \) bond (1.78 Å) within the \( \text{IO}_6 \) octahedron.

In \( (\text{NH}_4)_2\text{H}_3\text{IO}_6 \) the \( \text{IO}_6 \)-octahedron is almost regular. Therefore \( q(e) \), caused by the oxygen atoms within the first coordination sphere around the iodine, should be small and certainly smaller than in \( \text{H}_5\text{IO}_6 \). The large difference in the coupling constants between \( \text{H}_5\text{IO}_6 \) (282.977 MHz at 296 K) and \( (\text{NH}_4)_2\text{H}_3\text{IO}_6 \) (25.35 MHz at 296 K) is probably caused mainly by the difference in \( q(p) \). For the ammonium salt \( q(p) \) should be small due to the high symmetry of the \( \text{IO}_6 \)-ion, whereas in \( \text{H}_5\text{IO}_6 \), \( q(p) \) can reach a comparatively high value.

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\(^{13}\) R. L. Livingston and H. Zeldes, Tables of Eigenvalues for Pure Quadrupole Spectra, Spin 5/2, ORNL-1913 [1955].

The present paper shows how to incorporate the correlation between successive nuclear jumps, which are well known to play a role in defect mechanisms of self-diffusion in crystals, into the calculation of the correlation functions describing the temperature dependence of the nuclear spin relaxation in solids. The treatment is based on an extension of Torrey’s theory of nuclear spin relaxation by randomly migrating nuclei. Explicit and detailed results are given for the mono-vacancy mechanisms of self-diffusion in an isotopically pure face-centred cubic crystal.

I. Introduction

Bloembergen, Purcell and Pound (BPP)\(^1\) showed that the time dependent nuclear magnetic spin-spin coupling is one of the most powerful mechanisms for bringing about spin-lattice relaxation in liquids and solids. In monoatomic solids this time dependence is due to atomic diffusion which may be characterized by the (temperature dependent) mean time of stay of a nucleus on a given lattice site, \(\tau\), henceforth called the “mean jump time”.

Information about diffusional motions may be obtained from the measurement of the temperature dependence of the spin lattice relaxation time either in the laboratory frame, \(T_1\), where the splitting of the Zeeman-levels is due to the constant external magnetic field \(H_0\), or in the rotating frame \(T_{1\Omega}\), where — in resonance — this splitting results from the rotating field with amplitude \(H_1\). If relaxation is observed in relaxation fields \(H_1\) that are large compared with the internal local fields, the temperature variation of \(T_1\) and \(T_{1\Omega}\) may be interpreted by means of perturbation theory. In this way one obtains for \(T_1\) due to the magnetic dipolar interaction of like spins\(^2\)

\[
T_1 = \frac{3}{2} \gamma^4 \hbar^2 I(I + 1) \left[ J^{(1)}(\omega_0) + J^{(2)}(2\omega_0) \right].
\]

(1.1)

Here \(J^{(q)}(\omega)\) is the Fourier-transform of the correlation function\(^2\)

\[
G^{(q)}(\tau) = \sum_I \langle F^{(q)}(t) F^{(q)*}(t + \tau) \rangle_I.
\]

(1.2)

The \(F^{(q)}(t)\) are functions depending on the relative distance and orientation of two spins \(i\) and \(j\). \(q\) may assume the values 0, 1, or 2\(^2\).

For the spin-lattice relaxation time in the rotating frame, \(T_{1\Omega}\), Look and Lowe derived\(^3\)

\[
\frac{1}{T_{1\Omega}} = \frac{3}{8} \gamma^4 \hbar^2 I(I + 1) J_0(2\omega_1).
\]

(1.3)

\(^1\) N. Bloembergen, E. M. Purcell and R. V. Pound, Phys. Rev. 70, 679 [1946].
