

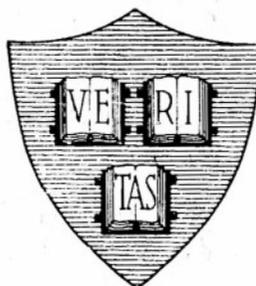
AD NO. 34779

ASTIA FILE COPY

Office of Naval Research

Contract N50RI-76 • Task Order No.1 • NR-071-012

THE NUCLEAR QUADRUPOLE RESONANCE AND
CRYSTAL STRUCTURE OF SOLID IODINE



By

K. W. H. Stevens

April 20, 1954

Technical Report No. 197

Cruft Laboratory
Harvard University
Cambridge, Massachusetts

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE,
DISTRIBUTION UNLIMITED.

JOINT SERVICE CONTRACT (Navy, SigO, AF) N5ori-07601 & 28

CRUFT LABORATORY, HARVARD UNIVERSITY

Tech Rpt 197 dd 20 Apr 54 "The Nuclear Quadrupole Resonance and Crystal Structure of Solid Iodine"

SCEL DISTRIBUTION

<u>No. Cvs</u>	<u>To</u>
1	Chief, Radar Dev Br.ESL
1	Chief, GM Instru Br.ESL
1	Chief, Radar Systems Br.ESL
1	Chief, App Phys Br.ESL
1	Chief, Thermionics Br.ESL
1	Chief, Met Br.ESL
1	Chief, Math & Met Br.ESL
1	Chief, Solid State Devices Br.ESL
1	Chief, Special Projects Br.ESL
1	Chief, C/M Eqt Br.ESL
1	C/M Div. Attn: Mr. J.J.Slattery
1	Chief, Vulnerability Br.ESL
1	Chief, C/M Systems Br.ESL
1	Tech Documents Center, ESL
1	Chief, Wire Comm Br.CSL
1	Chief, SCGE Br.CSL
2	Chief, Radio Comm Br.CSL
1	Chief Engineer's Sec. Attn: Mr. Lindner
1	Tech Documents Center, CSL
1	Chief, Power Sources Br.SSL
2	Chief, C&M Br. SSL
1	Chief, Chem Physics Br.SSL
1	Chief, Frequency Control, Br.SSL
1	Mr. F. Dickson, Chief, Radio Prop Agency, Bldg 463, Ft Mon
2	AF Liaison Office, Bldg 611, Ft Mon.
1	Records Holding Area Sec. Watson - File 102B
1	Tech Documents Center, SSL
1	Routing to Dir of Eng, All Sec Chiefs of Eng Div. (Ultimate file SIGEL-DR)
1	OCSigO - SIGEF
1	OCSigO - SIGGD-P1
1	Signal P&O Div. SIGOL-2D - OCSigO
1	Tech Intelligence Library, ERDL, Ft Belvoir, Va.
1	Aberdeen Proving Ground, Md. Attn: Tech Info Unit
1	C/O 9560 ISU, EDL, P.O. Box 205, Mountain View, Calif.
1	Prof. W.G. Dow, Univ of Michigan, Ann Arbor, Michigan
1	Signal Representative, Officer Group #1, USA Box 65, N.Y.
1	Chief, Plans & Operations Br. SIGOP-3 - OCSigO
5	ASTIA, Doc. Service Center, Knott Bldg, Dayton 2, Ohio

NOTE: Any questions re distribution of reports resulting from this contract, or additional copies, please call the Office of Director of Research, Ft Monmouth, N.J. Eatontown 3-1000 X52135.

SIGEL-DR
12 JUL 54

Office of Naval Research

Contract N5ori-76

Task Order No. 1

NR-078-011

Technical Report

on

The Nuclear Quadrupole Resonance and Crystal Structure

of Solid Iodine

by

K. W. H. Stevens

April 20, 1954

The research reported in this document was made possible through support extended Cruft Laboratory, Harvard University, jointly by the Navy Department (Office of Naval Research), the Signal Corps of the U. S. Army, and the U. S. Air Force, under ONR Contract N5ori-76, T. O. 1 and 28.

Technical Report No. 197

Cruft Laboratory

Harvard University

Cambridge, Massachusetts

The Nuclear Quadrupole Resonance and Crystal Structure
of Solid Iodine

by

K. W. H. Stevens

Cruft Laboratory, Harvard University

Cambridge, Massachusetts

Abstract

Previous attempts to explain the anisotropy of the quadrupole resonance in solid iodine are critically reviewed and an attempt is made to set up a valence bond description of the iodine molecule which contains the possibility that additional weak bonds are formed in crystalline iodine. This is primarily accomplished by introducing d-hybridization. The observed bond angles are then used to estimate some of the parameters in the orbits. Use is made of knowledge about nuclear quadrupole interaction in solid I_2 and in the iodine atom to determine further parameters, and in this way a picture of the iodine molecule and its behavior in a crystal is obtained. An interesting possibility which then arises is that the lobes of the wave-function of different iodine molecules do not overlap very strongly because a maximum of one molecule seems to be directed towards a minimum of another. This does not correspond to the usual ideas about bonds, but as the theory passes smoothly from the notion of maximum overlap to this new situation, no discussion is given about how it should be described. It is also seen that the observation of the quadrupole resonance in single crystals of iodine (if this becomes possible) would provide very useful information and checks on the theory.

The Nuclear Quadrupole Resonance and Crystal Structure of Solid Iodine

K. W. H. Stevens*

Cruft Laboratory, Harvard University
 Cambridge 38, Massachusetts

Introduction

The observation of pure nuclear quadrupole resonances in solid iodine has been reported by a number of authors [1], who find that there are considerable departures from axial symmetry in the charge distributions near the iodine nuclei. At first sight this is rather surprising, for iodine forms a molecular crystal of I_2 molecules, and one would expect that the charge distributions would show cylindrical symmetry about the I-I bond, as is certainly true for a free I_2 molecule. An explanation of the origin of this asymmetry has been put forward by Townes and Dailey [2], who point out that the I-I bond length in the solid is greater than in the free molecule, a fact which can be understood if additional weak bonds are formed in the crystal, thus weakening the main bond. A study of the crystal structure, see Figs. 1 and 2, shows that the iodine molecules lie in planes which are fairly well spaced, and that in the planes there are two directions for the I-I bond, the different sorts of molecules lying in chains. In Fig. 2 we show an enlarged picture of an iodine molecule with the positions of a pair of nearest neighboring iodines, and if, following Townes and Dailey, we assume that the additional bonds are formed in these directions, it seems fairly clear that the charge distribution near an iodine nucleus will not have an axis of symmetry. The rest of the treatment of this problem by Townes and Dailey is more difficult to understand. They assume that the charge distribution around each of the three bonds made by any iodine has cylindrical symmetry about the bond, so that only one parameter is needed to describe the quadrupole interaction with the charge in each bond (if z is a bond direction $\partial^2 V / \partial x^2 = \partial^2 V / \partial y^2 = -\frac{1}{2} \partial^2 V / \partial z^2$), and then, because the two weak bonds are of equal length, they weight them

 *On leave from Nottingham University, England

each with a total charge a and the main bond with $1-2a$. In this way the total quadrupole interaction of an iodine nucleus is described by two parameters, a and $\partial^2V/\partial z^2$; a is found from the anisotropy and $\partial^2V/\partial z^2$ from the magnitude of the interaction. The final step is then to show that $\partial^2V/\partial z^2$ found in this way agrees with the field gradient expected for a free iodine molecule. Our main criticism of this procedure is that there is no reason to suppose that because the two additional bonds are equal in length they must have equal weight, nor is there any a priori reason to assume that, apart from the different charges, $\partial^2V/\partial z^2$ is the same for the weak and strong bonds. This latter assumption becomes plausible if one assumes that the bonds are made of hybridized s and p orbitals, but there is then the difficulty that three bonds in a plane cannot be made from s and p alone. The first criticism can be illustrated very simply (see Fig. 3) where the dotted lines now represent the charge densities in the additional bonds in a schematic way. The bonds will clearly have equal lengths but they do not set up equal field gradients at a given iodine: we believe that this sort of behavior is more likely to occur than equal gradients.

With these difficulties about the validity of Townes and Dailey's model we decided to try to set up a more specific model, based on the Pauling ideas of directed valence. What is needed is a reasonable description of a free iodine molecule, then a study of how such molecules might come together to form a crystal and finally a calculation of the nuclear quadrupole interaction. This ambitious programme proves to be too difficult to carry through completely, but quite a lot of progress can be made and a number of useful results obtained.

Since this work was completed another theory about the origin of the anisotropy has been presented by Robinson, Dehmelt and Gordy [3]. This differs significantly from the previous theory and from the one we propose to give. While we do not know which theory is nearest the true solution, we feel that ours has at least a more fundamental approach than the other two and that something of this sort is required, rather than further semi-empirical speculations.

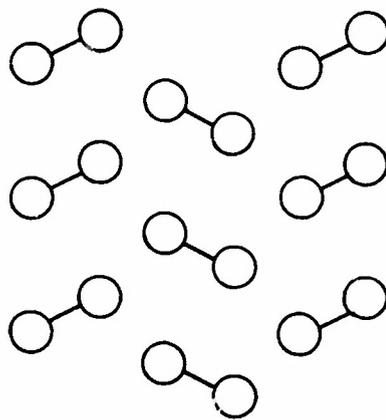


FIG. 1 THE ARRANGEMENT OF IODINE MOLECULES IN A PLANE

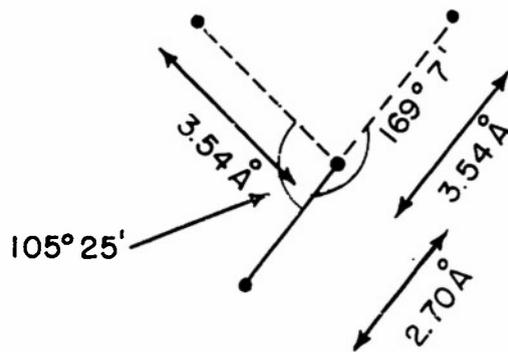


FIG. 2 RELATIVE POSITION OF IODINE ATOMS IN SOLID I_2

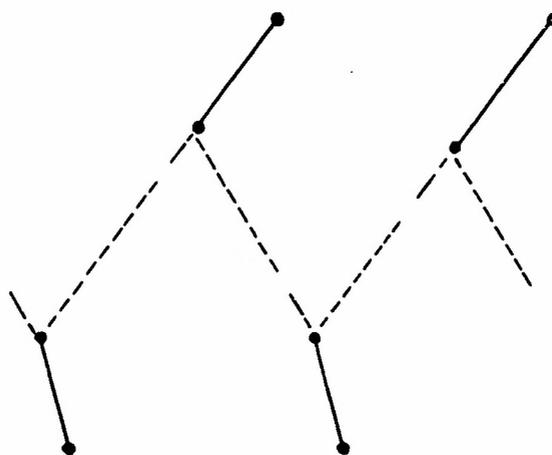


FIG. 3 AN EXAMPLE WHICH SHOWS SCHEMATICALLY HOW BOND DISTANCES CAN BE EQUAL BUT GIVE RISE TO DIFFERENT CHARGE DISTRIBUTION AT A GIVEN NUCLEUS

The Free Molecule

Each iodine atom has five 5p electrons outside closed shells and we might expect that in the molecule four of these pair off in p_π orbitals and the remaining one goes into a p_σ orbit and pairs up with a similar electron from the other iodine. This is too simple because hybridization is expected and to allow for this we shall generalize the above orbits by expressing them in a series of spherical harmonics. Thus, if the positive direction of z is taken towards the other iodine, we have:

$$2 \text{ electrons in } \frac{1}{N_1} \left\{ |y\rangle + a |yz\rangle \right\}$$

$$2 \text{ electrons in } \frac{1}{N_1} \left\{ |x\rangle + a |xz\rangle \right\}$$

$$1 \text{ electron in } \frac{1}{N_2} \left\{ \cos \gamma \left\{ \cos \alpha |z\rangle + \sin \alpha |3z^2 - r^2\rangle \right\} + \sin \gamma |s\rangle \right\}$$

where allowance is made for s, p, d hybridization, $|yz\rangle$ etc., denotes the angular variation of a normalized wave-function, N_1 and N_2 are normalizing factors and a , α and γ describe the relative admixtures of orbitals of different symmetries. The normalization is such that N_2 will probably be near unity (not exactly because this orbit overlaps strongly with the similar one on the other iodine), while N_1 will depart from unity according as a is large or small.

The bonding orbit (i.e., the orbit with only one electron) is expected to have a strong maximum in the positive direction of z, but this is not the only direction of maximum charge concentration, particularly with d-hybridization. In fact, if θ is measured from the positive direction of z the angular variation of the amplitude of the wave-function at some radius r is proportional to:

$$u \cos \alpha \sqrt{3} \cos \theta + v \sin \alpha \frac{\sqrt{5}}{2} (3 \cos^2 \theta - 1)$$

where u and v denote the values of the radial parts of the p and d orbitals respectively (u and v are usually taken to be equal). This function has turning values at $\theta = 0, 180^\circ$ and $\theta_0 = \cos^{-1} \left\{ -\frac{1}{\sqrt{15}} \frac{u}{v} \cot \alpha \right\}$. To make $\theta = 0$, a

strong maximum $\cot \alpha$ must be positive, so that θ_0 lies between 90° and 180° . Thus as a result of using d-hybridization, the bonding orbit has subsidiary turning values on the cone of directions corresponding to θ_0 as well as at $\theta = 180^\circ$. It is convenient to have a notation for the directions of these turning values, so we shall refer to them by the angles they make, i.e., 0° , 180° , and θ_0 directions.

Crystalline Iodine

Suppose two iodine molecules are coming together; then we may ask how they will arrange themselves. If we neglect for the moment the disturbances of their charge clouds by their mutual interactions, it seems not unlikely that they either have their θ_0 directions pointing towards one another, or that the θ_0 of one will point towards a 180° direction of the other. Referring to the crystal structure (Figs. 1 and 2) it is seen that one of the subsidiary bonds is only 10° away from the 180° direction and that the other lies between 90° and 180° . Thus a semi-empirical understanding of why iodine has the structure it does is obtained if we assume that the molecules arrange themselves so that the 180° direction of one is directed towards the θ_0 direction of another. This hypothesis will be further strengthened if we can show that the mutual interactions of the molecules reduce the strength of the main I-I bond and move the 180° direction in the right direction. To consider this we suppose that the interactions cause mixing of our original three orbitals, so that in the crystal the electrons are distributed in orbitals as follows:

$$\begin{aligned}
 & 2 \text{ in } \frac{1}{N_1} \left\{ |y\rangle + a |yz\rangle \right\} \\
 & 2 \text{ in } \frac{\cos \beta}{N_1} \left\{ |x\rangle + a |xz\rangle \right\} + \frac{\sin \beta}{N_2} \left\{ \cos \gamma (\cos \alpha |z\rangle + \sin \alpha |3z^2 - r^2\rangle) \right. \\
 & \qquad \qquad \qquad \left. + \sin \gamma |s\rangle \right\} \\
 & 1 \text{ in } \frac{\cos \beta}{N_2} \left\{ \cos \gamma (\cos \alpha |z\rangle + \sin \alpha |3z^2 - r^2\rangle) + \sin \gamma |s\rangle \right\} \\
 & \qquad \qquad \qquad - \frac{\sin \beta}{N_1} \left\{ |x\rangle + a |xz\rangle \right\}
 \end{aligned}$$

where the plane of the iodine molecules is taken as xz , so the orbit which is primarily perpendicular to this is unaltered. (We are, for the present,

neglecting the 3-dimensional nature of the problem and considering only a plane of iodine molecules). If we assume that β is small, the turning points of the modified bonding orbital, in the xz plane, are along $\theta = \phi, \pi + \psi, \pm \theta_0 + \chi$ where

$$\phi = \frac{-\tan \beta}{\cos \gamma} \frac{N_2}{N_1} \frac{(u + av\sqrt{5})}{(u \cos \alpha + \sqrt{15} v \sin \alpha)}$$

$$\psi = \frac{-\tan \beta}{\cos \gamma} \frac{N_2}{N_1} \frac{(u - av\sqrt{5})}{(u \cos \alpha - \sqrt{15} v \sin \alpha)}$$

$$\text{and } \chi = \frac{-\tan \beta}{\cos \gamma} \frac{N_2}{N_1} \frac{\{\sqrt{3}u \cos \theta_0 + av\sqrt{15} \cos 2\theta_0\}}{\{\sqrt{3}u \cos \alpha \cos \theta_0 + 3\sqrt{5} v \sin \alpha \cos 2\theta_0\}}$$

With some rearrangement, and using the definition of θ_0 , these become:

$$\phi = \frac{-\tan \beta}{X} \frac{\cos \theta_0 (1+A)}{(\cos \theta_0 - 1)}$$

$$\psi = \frac{-\tan \beta}{X} \frac{\cos \theta_0 (1-A)}{(\cos \theta_0 + 1)}$$

$$\chi = \frac{-\tan \beta}{X} \frac{\cos \theta_0 \{\cos \theta_0 + A \cos 2\theta_0\}}{1 - \cos^2 \theta_0} = \frac{\psi \{\cos \theta_0 + A \cos 2\theta_0\}}{(1 - \cos \theta_0)(1 - A)}$$

where

$$X = \cos \alpha \cos \gamma \frac{N_1}{N_2} \quad \text{and} \quad A = a\sqrt{5} \frac{v}{u} .$$

β is positive if the bond along $+\theta_0$ is strengthened, but whether the 180° bond is bent in the required direction depends on whether A is less than, or greater than, unity. Alternatively we can identify ψ with its experimental value, $10^\circ 53'$ and $\theta_0 + \chi$ similarly with $105^\circ 25'$ and use the above equations to determine θ_0 and $\tan \beta/X$ as functions of A . The results of this are given in Table 1.

Table 1

Values of parameters needed to fit the bond angles				
A	0	.2	.4	.6
θ_0	108°	110°	113.7°	120°
$\frac{\tan \beta}{X}$.425	.457	.471	.475

The fact that ϕ is different from zero means that the main iodine bond is not directed straight towards the other iodine, which suggests that the main I-I bond is weakened in the crystal, as required. Further, to have a stable arrangement, the main bonds from the two iodines in a molecule must be deflected on opposite sides of the I-I axis, which means that the midpoint of a molecule is a center of symmetry.

One point which has been glossed over and which must now be considered is the use of the turning values of the angular part of the wave-function to determine bond directions. In so far as the Pauling-directed-bond method is valid, it would seem reasonable to associate bond directions with maxima, but in the above reasoning we have not shown that our various directions, 0 , θ_0 and 180° are really directions in which the electron distribution is large. In particular it seems not unlikely that the actual orbits will be such that the charge in the 180° direction is very small, for presumably the bulk of the charge is located in $\theta = 0$. If, then, we assume that the charge concentration is a minimum in $\theta = 180$ we may picture a free iodine molecule as having a lot of charge along the main axis and with subsidiary cones of charge at about 105° with this axis. The crystal is then built up by having a point on the cone of one molecule on the axis of the cone of another. In this way the molecules pack fairly closely without their charges overlapping too strongly, i. e., without the formation of extra bonds. It also seems not unreasonable to suppose that this would lead to planes of fairly closely interlocked iodine molecules, with weaker forces between the planes.

The above ideas are based on physical arguments about charge densities, and it is seen that the introduction of d-hybridization is mainly responsible for the results obtained. It is clearly going to be a formidable task to try and substantiate these ideas by actual calculation of orbits, so we propose instead to

investigate the results of the nuclear quadrupole resonance to see what information this can give.

The Nuclear Quadrupole Interaction

If (x, y, z) is the position of an electron with respect to a nucleus at the origin, the contribution which it makes to the electric quadrupole interaction is:

$$\frac{e^2 Q}{2I(2I-1)} \left[\left(\frac{3x^2 - r^2}{r^5} \right) I_x^2 + \left(\frac{3y^2 - r^2}{r^5} \right) I_y^2 + \left(\frac{3z^2 - r^2}{r^5} \right) I_z^2 + \frac{3xy}{r^5} (I_x I_y + I_y I_x) \right. \\ \left. + \frac{3y^2}{r^5} (I_y I_z + I_z I_y) + \frac{3zx}{r^5} (I_z I_x + I_x I_z) \right]$$

To obtain the full interaction this must be summed over all electrons and averaged over their orbits. Using

$$\langle z | \frac{3z^2 - r^2}{r^5} | z \rangle = \frac{4}{5} \left(\frac{1}{r^3} \right)_p \\ \langle z | \frac{zx}{r^5} | x \rangle = \frac{1}{5} \left(\frac{1}{r^3} \right)_p, \quad \langle 3z^2 - r^2 | \frac{3z^2 - r^2}{r^5} | 3z^2 - r^2 \rangle = \frac{4}{7} \left(\frac{1}{r^3} \right)_d \\ \langle xz | \frac{3z^2 - r^2}{r^5} | xz \rangle = \frac{2}{7} \left(\frac{1}{r^3} \right)_d, \quad \langle xz | \frac{zx}{r^5} | 3z^2 - r^2 \rangle = \frac{1}{7\sqrt{3}} \left(\frac{1}{r^3} \right)_d$$

and other quantities derived from them, the interaction in the present case becomes:

$$\frac{e^2 Q}{2I(2I-1)} \left[a_{11} I_x^2 + a_{22} I_y^2 + a_{33} I_z^2 + a_{13} (I_z I_x + I_x I_z) \right]$$

where

$$a_{11} = \left(\frac{1}{r^3} \right)_p \left[\begin{aligned} & \frac{4}{N_1^2} \left(+\frac{1}{5} - \frac{1}{7} \lambda a^2 \right) - \frac{2 \cos^2 \gamma}{N_2^2} \left(\frac{1}{5} \cos^2 a + \frac{1}{7} \lambda \sin^2 a \right) \\ & + \sin^2 \beta \left[\frac{-2}{N_1^2} \left(\frac{2}{5} + \frac{1}{7} \lambda a^2 \right) + \frac{2 \cos^2 \gamma}{N_2^2} \left(-\frac{1}{5} \cos^2 a - \frac{1}{7} \lambda \sin^2 a \right) \right] \end{aligned} \right]$$

$$a_{22} = \left(\frac{1}{r^3}\right)_p \left[\begin{aligned} & \frac{4}{N_1^2} \left(\frac{1}{5} - \frac{1}{7} \lambda a^2 \right) - \frac{2 \cos^2 \gamma}{N_2^2} \left(\frac{1}{5} \cos^2 \alpha + \frac{1}{7} \lambda \sin^2 \alpha \right) \\ & + \sin^2 \beta \left\{ \frac{-2}{N_1^2} \left(-\frac{1}{5} - \frac{2}{7} \lambda a^2 \right) + \frac{2 \cos^2 \gamma}{N_2^2} \left(-\frac{1}{5} \cos^2 \alpha - \frac{1}{7} \lambda \sin^2 \alpha \right) \right\} \end{aligned} \right]$$

$$a_{33} = \left(\frac{1}{r^3}\right)_p \left[\begin{aligned} & \frac{4}{N_1^2} \left(-\frac{2}{5} + \frac{2}{7} \lambda a^2 \right) - \frac{2 \cos^2 \gamma}{N_2^2} \left(-\frac{2}{5} \cos^2 \alpha - \frac{2}{7} \lambda \sin^2 \alpha \right) \\ & + \sin^2 \beta \left\{ \frac{-2}{N_1^2} \left(-\frac{1}{5} + \frac{1}{7} \lambda a^2 \right) + \frac{2 \cos^2 \gamma}{N_2^2} \left(\frac{2}{5} \cos^2 \alpha + \frac{2}{7} \lambda \sin^2 \alpha \right) \right\} \end{aligned} \right]$$

$$a_{13} = \left(\frac{1}{r^3}\right)_p \frac{2 \cos \beta \sin \beta \cos \gamma}{N_1 N_2} \left(\frac{1}{5} \cos \alpha + \frac{1}{7 \sqrt{3}} \lambda a \sin \alpha \right)$$

where

$$\lambda = \left(\frac{1}{r^3}\right)_d / \left(\frac{1}{r^3}\right)_p$$

These formulae are too complicated to be handled easily, so as $\left(\frac{1}{r^3}\right)$ probably varies as t^{-3} for electrons with the same principal quantum number, it seems reasonable to approximate by taking λ as zero. Considerable simplification follows if ratios are then used, giving:

$$\frac{a_{11}}{a_{33}} = \frac{1 - \frac{1}{2} X^2 - \frac{1}{2} \sin^2 \beta (2 + X^2)}{-2 + X^2 + \frac{1}{2} \sin^2 \beta (1 + 2X^2)}$$

$$\frac{a_{22}}{a_{33}} = \frac{1 - \frac{1}{2} X^2 + \frac{1}{2} \sin^2 \beta (1 - X^2)}{-2 + X^2 + \frac{1}{2} \sin^2 \beta (1 + 2X^2)}$$

$$\frac{a_{13}}{a_{33}} = \frac{3}{2} \frac{\cos \beta \sin \beta X}{-2 + X^2 + \frac{1}{2} \sin^2 \beta (1 + 2X^2)}$$

These relations are not independent since $a_{11} + a_{22} + a_{33} = 0$, but a full investigation of the quadrupole interaction would determine β and X , and then (see Table 1) A and θ_0 which are properties of the free molecule. There are, however, a number of experimental difficulties in this, so that present information extends only to the magnitude of A_{33} and the anisotropy $|A_{11} - A_{22}|/A_{33}$, where capital A's mean that the quadrupole interaction is referred to its principal axes (i.e., $A_{13} = 0$). If we assume that a_{13} is small so that the original axes are close to the principal axes, the anisotropy is approximately $|a_{11} - a_{22}|/a_{33}$

$$= \frac{\frac{3}{2} \sin^2 \beta}{|-2 + X^2 + \frac{1}{2} \sin^2 \beta (1 + 2X^2)|}$$

To get the bond angles right, we see (Table 1) that $\tan \beta / X$ is probably of order .45, so taking $\tan^2 \beta = .18 X^2$ the observed value of .15 for the anisotropy gives $X^2 \sim .75$ and $\tan \beta \sim .37$. Thus, although the theory contains a good many parameters, some numerical values can be obtained with some precision. Continuing, with $X^2 = .75$, $N_1/N_2 \cos \alpha \cos \gamma = .866$, and using $\cos \theta_0 = -1/\sqrt{15} u/v \cot \alpha$ and setting $u = v$, $\theta_0 = 110^\circ$, we obtain $\alpha \sim 37^\circ$ and $N_1/N_2 \cos \gamma \sim 1.1$. If the nonbonding orbitals contain no d-wave functions, N_1 is probably less than N_2 and this last relation will not be satisfied. It therefore seems that, with our model, it is necessary to have enough d-character in the nonbonding orbitals to make $N_1 > N_2$, and also we may expect $\gamma \sim 0$. With $\alpha \sim 37^\circ$, $\gamma \sim 0$ the bonding orbit contains very little s-character and approximately equal amounts of p and d, which means that $\theta = 180^\circ$ is a direction in which there is very little charge. In other words, the p and d admixtures are such that the p approximately cancels the d in the $\theta = 180^\circ$ direction. This situation was anticipated in the discussion earlier in the paper. A more surprising result is that the π -orbitals, i.e., those which contain pairs of electrons moving perpendicular to the axis, have $\sim 10\%$ d-character (amplitude of admixture, from N_1), but on examination this is seen to make the electrons concentrate towards the middle of the molecule, which does not seem unreasonable.

The above numerical estimates were obtained by taking $\lambda = 0$ and neglecting a_{13} . If we now use the above numerical values and do not make

these assumptions it is found that the theoretical anisotropy might be reduced to .14, depending on the value of λ . The observed value can be restored by increasing X slightly, a change which will not affect the main conclusions.

Finally, it is of interest to consider the actual magnitude of the quadrupole interaction. Our equations give:

$$\frac{(a_{33})_{\text{crystal}}}{(a_{33})_{\text{free mol}}} \sim \frac{-2 + X^2 + \frac{1}{2} \sin^2 \beta (1 + 2X^2)}{-2 + X^2} \sim 1 - \frac{1}{2} \sin^2 \beta \left(\frac{1 + 2X^2}{2 - X^2} \right)$$

$$\sim .876$$

The measured value of the quadrupole coupling in the solid is 2140 Mc/s so this ratio predicts that the free iodine value should be 2440 Mc/s. The other thing which can be done is to compare $(a_{33})_{\text{crystal}}$ with the corresponding value for a free iodine atom, since a free atom will be described by letting $\alpha = \beta = \gamma = a = 0$ and $N_1 = N_2 = 1$.

Then

$$\frac{(a_{33})_{\text{crystal}}}{(a_{33})_{\text{free atom}}} \sim \frac{-2 + X^2 + \frac{1}{2} \sin^2 \beta (1 + 2X^2)}{-2N_1^2} = \frac{1.23}{N_1^2}$$

$(a_{33})_{\text{free atom}}$ can be obtained from the analysis of the hyperfine structure of free iodine by Jaccarino [4], whence $N_1^2 = \frac{1.23 \cdot 2292}{2140} = 1.32$. The departure of N_1 from unity gives a measure of the amount of d-character in the nonbonding orbit, and this agrees well with our earlier estimate of this.

Conclusion

Starting with elementary ideas about the nature of chemical bonds, it has proved possible to set up a plausible model of a free iodine molecule which enables one to understand how iodine molecules may come together to form a solid having the observed structure. The theory is then tested by examining the predictions which it makes about the nuclear quadrupole interaction. A number of approximations are made in this, but it is found that the anisotropy and magnitude of the quadrupole interaction can be

correlated in a satisfactory way with the crystal structure and wave functions, thus helping to confirm the initial assumptions. The final picture of the origin of the anisotropic quadrupole interactions then differs significantly from the models of Townes and Dailey and of Robinson, Dehmelt and Gordy.

Acknowledgements

I would like to thank Professor R. V. Pound for a number of stimulating discussions and pure quadrupole resonance and O. N. R. for financial support.

References

1. H. G. Dehmelt, Naturwiss 17, 398 (1950). R. V. Pound, Phys. Rev. 82, 343 (1951).
2. C. H. Townes and B. P. Dailey, J. Chem. Phys. 20, 35 (1952).
3. H. Robinson, H. G. Dehmelt and W. Gordy, J. Chem. Phys. 22, 511 (1954).
4. V. Jaccarino, Quarterly Progress Report, Research Laboratory of Electronics, Massachusetts Institute of Technology, July 1953, p. 31.

DISTRIBUTION LIST

Technical Reports

2	Chief of Naval Research (427) Department of the Navy Washington 25, D. C.
1	Chief of Naval Research(460) Department of the Navy Washington 25, D. C.
1	Chief of Naval Research (421) Department of the Navy Washington 25, D. C.
6	Director (Code 2000) Naval Research Laboratory Washington 25, D. C.
2	Commanding Officer Office of Naval Research Branch Office 150 Causeway Street Boston, Massachusetts
1	Commanding Officer Office of Naval Research Branch Office 1000 Geary Street San Francisco 9, California
1	Commanding Officer Office of Naval Research Branch Office 1030 E. Green Street Pasadena, California
1	Commanding Officer Office of Naval Research Branch Office The John Crerar Library Building 86 East Randolph Street Chicago 1, Illinois
1	Commanding Officer Office of Naval Research Branch Office 346 Broadway New York 13, New York
3	Officer -in-Charge Office of Naval Research Navy No. 100 Fleet Post Office New York, N. Y.

- 1 Chief, Bureau of Ordnance (Re4)
Navy Department
Washington 25, D. C.
- 1 Chief, Bureau of Ordnance (AD-3)
Navy Department
Washington 25, D. C.
- 1 Chief, Bureau of Aeronautics (EL-1)
Navy Department
Washington 25, D. C.
- 2 Chief, Bureau of Ships (810)
Navy Department
Washington 25, D. C.
- 1 Chief of Naval Operations (Op-413)
Navy Department
Washington 25, D. C.
- 1 Chief of Naval Operations (Op-20)
Navy Department
Washington 25, D. C.
- 1 Chief of Naval Operations (Op-32)
Navy Department
Washington 25, D. C.
- 1 Director
Naval Ordnance Laboratory
White Oak, Maryland
- 2 Commander
U. S. Naval Electronics Laboratory
San Diego, California
- 1 Commander (AAEL)
Naval Air Development Center
Johnsville, Pennsylvania
- 1 Librarian
U. S. Naval Post Graduate School
Monterey, California
- 50 Director
Signal Corps Engineering Laboratories
Evans Signal Laboratory
Supply Receiving Section
Building No. 42
Belmar, New Jersey

3 Commanding General (RDRRP)
Air Research and Development Command
Post Office Box 1395
Baltimore 3, Maryland

2 Commanding General (RDDDE)
Air Research and Development Command
Post Office Box 1395
Baltimore 3, Maryland

1 Commanding General (WCRR)
Wright Air Development Center
Wright-Patterson Air Force Base, Ohio

1 Commanding General (WCRRH)
Wright Air Development Center
Wright-Patterson Air Force Base, Ohio

1 Commanding General (WCRE)
Wright Air Development Center
Wright-Patterson Air Force Base, Ohio

2 Commanding General (WCRET)
Wright Air Development Center
Wright-Patterson Air Force Base, Ohio

1 Commanding General (WCREO)
Wright Air Development Center
Wright-Patterson Air Force Base, Ohio

2 Commanding General (WCLR)
Wright Air Development Center
Wright-Patterson Air Force Base, Ohio

1 Commanding General (WCLRR)
Wright Air Development Center
Wright-Patterson Air Force Base, Ohio

2 Technical Library
Commanding General
Wright Air Development Center
Wright-Patterson Air Force Base, Ohio

1 Commanding General (RCREC-4C)
Rome Air Development Center
Griffiss Air Force Base
Rome, New York

1 Commanding General (RCR)
Rome Air Development Center
Griffiss Air Force Base
Rome, New York

- 2 Commanding General (RCRW)
Rome Air Development Center
Griffiss Air Force Base
Rome, New York
- 6 Commanding General (CRR)
Air Force Cambridge Research Center
230 Albany Street
Cambridge 39, Massachusetts
- 1 Commanding General
Technical Library
Air Force Cambridge Research Center
230 Albany Street
Cambridge 39, Massachusetts
- 2 Director
Air University Library
Maxwell Air Force Base, Alabama
- 1 Commander
Patrick Air Force Base
Cocoa, Florida
- 2 Chief, Western Division
Air Research and Development Command
P. O. Box 2035
Pasadena, California
- 1 Chief, European Office
Air Research and Development Command
Shell Building
60 Rue Ravenstein
Brussels, Belgium
- 1 U. S. Coast Guard (EEE)
1300 E Street, N. W.
Washington, D. C.
- 1 Assistant Secretary of Defense
(Research and Development)
Research and Development Board
Department of Defense
Washington 25, D. C.
- 5 Armed Services Technical Information Agency
Document Service Center
Knott Building
Dayton 2, Ohio

- 1 Director
Division 14, Librarian
National Bureau of Standards
Connecticut Avenue and Van Ness St., N. W.
- 1 Director
Division 14, Librarian
National Bureau of Standards
Connecticut Avenue and Van Ness St., N. W.
- 1 Office of Technical Services
Department of Commerce
Washington 25, D. C.
- 1 Commanding Officer and Director
U. S. Underwater Sound Laboratory
New London, Connecticut
- 1 Federal Telecommunications Laboratories, Inc.
Technical Library
500 Washington Avenue
Nutley, New Jersey
- 1 Librarian
Radio Corporation of America
RCA Laboratories
Princeton, New Jersey
- 1 Sperry Gyroscope Company
Engineering Librarian
Great Neck, L. I., New York
- 1 Watson Laboratories
Library
Red Bank, New Jersey
- 1 Professor E. Weber
Polytechnic Institute of Brooklyn
99 Livingston Street
Brooklyn 2, New York
- 1 University of California
Department of Electrical Engineering
Berkeley, California
- 1 Dr. E. T. Booth
Hudson Laboratories
145 Palisade Street
Dobbs Ferry, New York
- 1 Cornell University
Department of Electrical Engineering
Ithaca, New York

- 1 University of Illinois
Department of Electrical Engineering
Urbana, Illinois
- 1 Johns Hopkins University
Applied Physics Laboratory
Silver Spring, Maryland
- 1 Professor A. von Hippel
Massachusetts Institute of Technology
Research Laboratory for Insulation Research
Cambridge, Massachusetts
- 1 Director
Lincoln Laboratory
Massachusetts Institute of Technology
Cambridge 39, Massachusetts
- 1 Signal Corps Liaison Office
Massachusetts Institute of Technology
Cambridge 39, Massachusetts
- 1 Mr. Hewitt
Massachusetts Institute of Technology
Document Room
Research Laboratory of Electronics
Cambridge, Massachusetts
- 1 Stanford University
Electronics Research Laboratory
Stanford, California
- 1 Professor A. W. Straiton
University of Texas
Department of Electrical Engineering
Austin 12, Texas
- 1 Yale University
Department of Electrical Engineering
New Haven, Connecticut
- 1 Mr. James F. Trosch, Administrative Aide
Columbia Radiation Laboratory
Columbia University
538 West 120th Street
New York 27, N. Y.
- 1 Dr. J. V. N. Granger
Stanford Research Institute
Stanford, California