$$
\begin{aligned}
{}_1I_{vv'} &= \int U_m{}^s\, x\, U_{m'}{}^s\, dx \\
{}_2I_{vv'} &= \int U_m{}^s\, x^2\, U_{m'}{}^s\, dx = 2\,{}_1I_{vv'} \cdot t_2 \\
{}_3I_{vv'} &= \int U_m{}^s\, x^3\, U_{m'}{}^s\, dx = 3\,{}_1I_{vv'} \cdot t_3
\end{aligned}
$$

Thus

$$f_{vv'} = = -(M_1/\beta)\,{}_1I_{vv'}\left[1 - 2\left(\frac{M_2}{\beta M_1} + \frac{3M_3 \ln k}{\beta^2 M_1}\right)(t_2 - \ln k) + \frac{3M_3}{\beta^2 M_2}(t_3 - (\ln k)^2)\right] \quad (5)$$

The three functions ${}_1I_{vv'}$, $(t_2 - \ln k)$ and $(t_3 - (\ln k)^2)$ are defined below and are those listed in Table III. The parameter $k = 1/xe$ is the anharmonicity constant for the molecule.

$$
\begin{aligned}
{}_1I_{vv'} &= \frac{1}{(v'-v)(k-v'-v-1)} \times \left[\frac{v'!\,(k-v'-1)!(k-2v-1)(k-2v'-1)}{v!(k-v-1)!}\right]^{1/2} \\
&= \beta r_e S_1{}^{vv'} \qquad (6)
\end{aligned}
$$

where S_1 is given by equation 50, reference 7.

$$
\begin{aligned}
(t_2 - \ln k) &= \psi\,(k - v - v' - 1) - \ln k + \sum_{j=0}^{j=v'-v-2} \frac{1}{1+j} \\
&\quad - \sum_{K=0}^{K=v-1} \frac{K!\,(k-2v-1+K)!}{(v'-v+1+K)!(k-v-v'+K)!} \times \sum_{i=0}^{i=K} \frac{(v'-v+i)!(k-v'-v-1+i)!}{i!(k-2v-1+i)!} \\
&= \frac{1}{r_e}\cdot\frac{S_{II}}{S_I} \qquad (7)
\end{aligned}
$$

where S_{II} is defined by eq. 51 in reference 7. For all practical purposes, although simple formulas for it exist, the double sum may be approximated by

$$\Sigma\,\Sigma = v/(v'-v+1)(k-v'-v) \equiv vA_{vv'}$$

and this has been done in Table III.

$$
\begin{aligned}
t_3 - (\ln k)^2 &= \psi^2(k-v'-v-1) + \psi'(k-v'-v-1) - (\ln k)^2 \\
&\quad + 2\sum_{i=0}^{i=v'-v-2} \frac{1}{1+i}\left(\psi(k-v'-v-1) + \sum_{j=0}^{=v'-v-3-i} \frac{1}{2+i+j}\right) \\
&\quad + 2\left(1 - \psi\,(k-v'-v-1) - \sum_{i=0}^{i=v'-v-2} \frac{1}{1+i}\right)vA_{vv'} \qquad (8)
\end{aligned}
$$

where a similar approximation has been made and a quadruple sum of the order of $vA_{vv'}{}^2$ has been dropped. In these equations $\psi(\alpha)$ is the logarithmic derivative of the gamma function, for which $\psi(\alpha) = (\alpha - 1)!$ if α is an integer. $\psi'(\alpha) = d\psi/d\alpha$.

The dipole constants then are determined from the formula

$$\pm\left[\frac{(I/\nu^4)_a}{(I/\nu^4)_b}\right]^{1/2} = \frac{(f_{vv'})_a}{(f_{vv''})_b} \qquad (9)$$

in which only the parameters given in Table IV occur (a and b are two bands originating in the same upper level).

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

Iodine Nuclear Quadrupole Resonance Spectrum of Boron Triiodide[1]

BY W. G. LAURITA AND W. S. KOSKI

RECEIVED JANUARY 8, 1959

The iodine nuclear quadrupole resonance spectrum of boron triiodide has been studied. The frequencies of the $^1/_2 \rightarrow {}^3/_2$ and the $^3/_2 \rightarrow {}^5/_2$ transitions were measured as 212.6 and 340.1 Mc./sec., respectively. Each of the resonances was a doublet with a separation of 25 kc./sec. for the lower frequency transition and an approximate intensity ratio of 1 to 4. The quadrupole coupling constant (eQq) was found to be 1176 Mc./sec. and the asymmetry parameter was 0.456. The large asymmetry parameter was interpreted as due to π-bond character of the boron-iodine bond. The experimental data are discussed in terms of significance to the electronic structure of the molecule. The number of iodine resonances in boron triiodide was found to be the same as the number of resonances found in other boron trihalides for corresponding transitions. This suggests that the crystal structure of BI_3 is the same as BBr_3 and BCl_3 which are known.

Introduction

Nuclei such as I^{127}, which have an asymmetrical distribution of charge, possess a quadrupole moment. Such nuclei interact with the electrons and other nuclei in a molecule or a crystal to produce a variation in the electrostatic energy of the system with nuclear orientation. Transitions between these orientational energy levels give rise to hyperfine structure in the rotational spectra of molecules and to the so-called pure nuclear quadrupole spectra in solids. The energy of the electrostatic interaction between the asymmetric nuclei and the electric field of the molecule or crystal depends on the nuclear quadrupole moment (Q), on the nuclear spin (I) and on the second derivative of the potential relative to the appropriate axes. The z-axis is considered to be the bond axis and $q_{zz} = \partial^2 V/\partial z^2$, $q_{yy} = \partial^2 V/\partial y^2$ and $q_{xx} = \partial^2 V/\partial x^2$. The experimental data permit an evaluation of eQq_{zz}, the quadrupole coupling constant in which e is the proton charge and an asymmetry parameter (η).

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}}$$

These two quantities are intimately related to the distribution of electronic charge in the molecule and have been interpreted in a semi-empirical fashion in terms of electronic structure of molecules.

---

[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)-1526. Reproduction in whole or in part is permitted for any purpose of the United States Government.

In addition, the number of resonances that are observed is dependent on the crystal environment in which the nucleus in question finds itself. Consequently, such measurements can at times give crystallographic information. This paper deals with the experimental measurement of eQq_{zz} and η and their relationship to the nature of the chemical binding in BI_3. Comparison also is made with the corresponding parameters in the other boron trihalides.

Experimental

The spectrometer used is of the self-quenched superregenerative type using Zeeman modulation. Two 955 tubes are employed in push-pull. It has a range from 100 to 400 Mc./sec. and is tuned through this range by means of a shorting bar on the Lecher wires which serve as a tank circuit. The resonance signal is modulated by subjecting the sample to a magnetic field which is turned on and off periodically. This is accomplished by means of a square-wave generator capable of delivering about an ampere of current to a five ohm coil. When the sample is placed along the axis of this solenoid, the field produced is sufficient to periodically reduce the intensity of the resonance signal. The square-wave generator is triggered by a 210 c./s. signal which also serves as a reference signal for the phase-sensitive detector. The output of the tuned amplifier and phase-sensitive detector is recorded by an Esterline–Angus recorder. Quadrupole resonance signals from BI_3 were measured at Dry Ice temperature. Frequency measurements were made with the Gertsh model FM-3 frequency meter.

Results and Discussion

Since our spectrum arises from the interaction of the electric quadrupole moment of the nucleus with an asymmetric electric field which surrounds the nucleus, it is a function of the state of electrons outside of closed shells. We have used the Townes and Dailey method for analyzing the data[2] and additional information about double-bond character was obtained from the asymmetry parameter using Bersohn's procedure.[3]

The expression for the energy levels includes both the quadrupole coupling constant eQq/h and the asymmetry parameter, and since the iodine spectrum consists of two lines, it is possible to determine both of these. A coupling constant of 1176 Mc./sec. and an asymmetry parameter of 0.456 were read directly from a "Table of Eigenvalues for Pure Quadrupole Spectra" by R. Livingston and H. Zeldes.

Since the quadrupole moment Q for a particular nucleus is constant, the value of the coupling constant is determined by $\partial^2 V/\partial z^2$ where V is the potential due to the surrounding field and z is in the direction of the internuclear distance. For halide atoms the field gradient at the site of the nucleus is due to a lack of one electron in the p shell (one unbalanced p electron). The coupling constants for halide atoms have been calculated to be[4] 110 Mc./sec. for Cl^{35}, 770 Mc/sec. for Br^{71} and 2230 Mc./sec. for I^{127}.

The measured coupling constant for a molecule may then be compared to the coupling constant for an atom. If the coupling constant for an atom remained unchanged when placed in a compound, we could conclude that its electric environment remained unperturbed and that in both cases it lacks one electron in the p shell.

The field gradient at a halogen nucleus in a molecule is determined, then, by the number of unbalanced electrons in the p_z orbital. Townes and Dailey have estimated that sp hybridization occurs to the extent of 15% if the electronegativity of the atom to which the halogen is bonded is 0.25 unit less than the electronegativity of the halogen. This would tend to promote 15% of an electron into the p_z orbital, thus reducing the number of unbalanced p_z electrons by that amount; this assumption is made for all of the boron halides. In addition, there is the effect of double-bond formation which extracts electrons from an orbital orthogonal to the p_z direction. From the consideration that $q_{xx} + q_{yy} + q_{zz} = 0$ at the nucleus and that the structure of a pure double bond lacks a p_x electron, the field gradient in the z-direction for this structure is equivalent to a field gradient produced by the addition of one-half of an electron to the p_z orbital. That is, if the field gradient in the z- and y-directions produced by the lack of one electron in the x-direction are equal then $q_{zz} = -{}^1/_2\, q_{xx}$. For the double-bond structure, therefore, the number of unbalanced p_z electrons is $(1 - s - {}^1/_2)$ where $s = 0.15$. Townes and Dailey have multiplied this figure by 1.25 to account for the closer approach of the electrons to the nucleus due to a positive charge on the halogen. The ionic structure produces a completely filled shell so that the contribution of this structure is zero.

If we describe the bond as a combination of the three structures which have been mentioned. we may calculate the contribution of each of these structures to the total coupling constant for the molecule. The covalent structure contributes $0.85(1 - \pi - \mathrm{I})eQq/h_{\mathrm{at}}$; the double-bond structure contributes $0.44\ \pi eQq/h_{\mathrm{at}}$; and the ionic structure contributes nothing. Therefore

$$f = 0.85 - 0.85I - 0.41\pi \tag{1}$$

where f is the ratio of the coupling constants for the molecule and the atom and π is the fraction of double bond character.

By a method suggested by Goldstein and Bragg[5] and applied by Bersohn,[3] the double-bond character may be obtained directly from the asymmetry parameter. For a nucleus with spin ${}^3/_2$

$$\pi = \frac{4\eta\nu_{{}^1/_2 - {}^3/_2}}{3eQq_{\mathrm{at}}} \tag{2}$$

and for a nucleus with spin ${}^5/_2$

$$\pi = \frac{80\eta\nu_{{}^1/_2 - {}^3/_2}}{3eQq_{\mathrm{at}}(6 + 35\eta^2/9)} \tag{3}$$

In this case ν is the lower observed frequency. The derivation is based upon the assumption that the difference in population of the p_x and p_y orbitals is a direct measure of the double-bond character. It is only applicable to bonds which do not have threefold or greater symmetry about the bond direction, because η equals zero for all such bonds. In principle, therefore, one should be able to describe the chemical bonds for the BX_3 molecules by means of the known quantities eQq and η.

---

(2) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

(3) R. Bersohn, *ibid.*, **22**, 2078 (1954).

(4) V. Jaccarino and J. G. King, *Phys. Rev.*, **83**, 471 (1953).

(5) J. H. Goldstein and J. K. Bragg, *ibid.*, **75**, 1453 (1949).

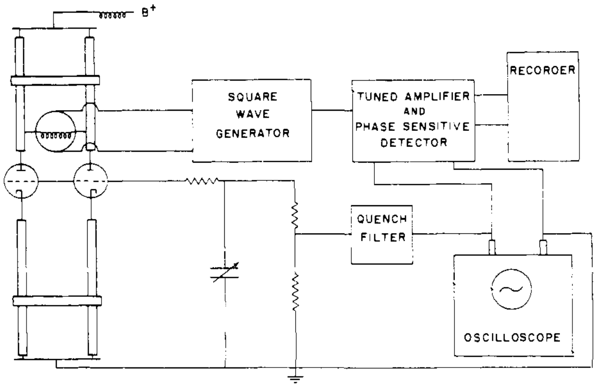
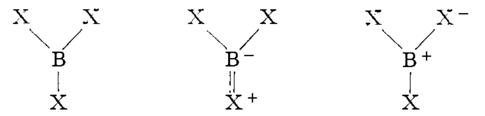


Fig. 1.—Block diagram of the self quenched superregenerative, Zeeman modulated spectrometer used in this investigation.

From eq. 1 and 3, the B–I bond in BI_3 was found to be 52% covalent, 16% double bond and 32% ionic. From Chiba's measurements[6] of BCl_3 and BBr_3 resonances, we find in the same manner that the B–Br bond is 47% covalent, 12% double bond and 41% ionic. The asymmetry parameter was not determined for the trichloride but Chiba (by assuming 50% ionic character) found 6% double-bond character and 44% covalent character.

If one is satisfied with the assumptions inherent in the Townes–Dailey treatment of quadrupole coupling data, one concludes that BI_3 can be best represented by the indicated contributions from the structures



Conclusions such as these have to be taken with reservations since a number of aspects of the interpretation of quadrupole spectra are poorly understood. However, it will be appreciated that there is much potentially valuable information on electronic structure of molecules available from quadrupole-coupling data which will become increasingly more available to us as the theoretical understanding of the effects develop.

The double-bond character in the boron trihalides can be discussed in terms of a simple molecular orbital model described by Coulson[7] and applied by Bersohn[3] in the determination of double bond character of carbon–chlorine bonds. This model assumes interaction of pπ-orbitals in a field arising from nuclei, non-bonding electrons and bonding orbitals.

In the particular case of the boron trihalides there are four pπ-orbitals which may interact. The degree to which this interaction reduces the electron density of the halogen pπ-orbitals is assumed to be a measure of the double bond character. Limiting the treatment to these orbitals one may write

$$\psi = \frac{c_1}{\sqrt{3}}({}_1\varphi_x + {}_2\varphi_x + {}_3\varphi_x) + c_2\varphi_B$$

where φ designates the pπ-orbital indicated by the subscript. Making the usual approximations one obtains a value for c_2

$$c_2 = \frac{3/\sqrt{3}\, c_1\beta_{Bx}}{\alpha_{xx} - \alpha_{BB}}$$

where

$$\beta_{Bx} = \int \varphi_x H \varphi_B \, d\tau \qquad \alpha_{xx} = \int \varphi_x H \varphi_x \, d\tau$$

Following Bersohn this expression may be simplified by introducing an approximation for the coulomb integrals and noting that $c_1^2 + c_2^2 = 1$; then since c_2^2 is proportional to the double bond character (π)

$$\pi = \frac{k\beta^2_{Bx}(1 - c_2^2)}{(X_B - X_x)^2} \tag{4}$$

where k is a constant as far as a discussion of the family of boron trihalides is concerned, X is the electronegativity. This rough model indicates that the amount of double bond character in BX_3 is proportional to β^2_{BX}. This integral would be expected to decrease as the difference in size of the two atoms in the B–X bond increases. An inverse dependence on the square of the electronegativity difference of the two atoms is indicated. In the series BCl_3, BBr_3 and BI_3 the quadrupole coupling measurements indicate a systematic increase in π-bond character suggesting that the electronegativity effect outweighs the effect of the integral β^2_{BX}.

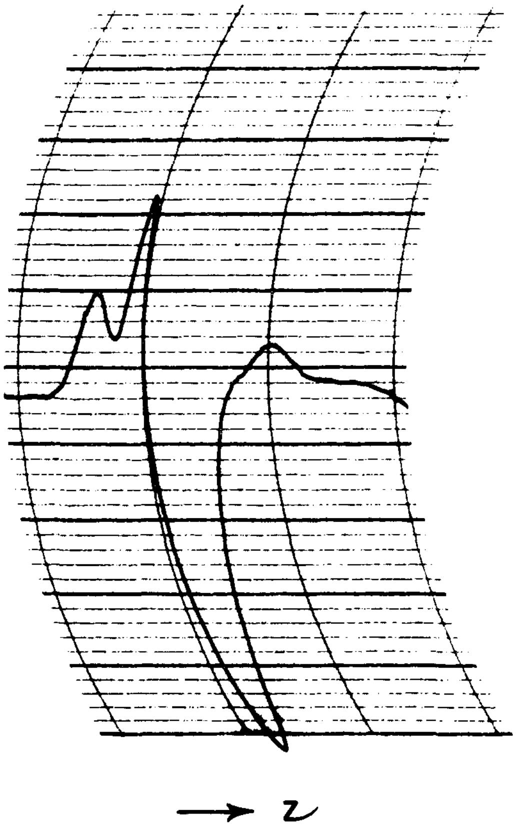


Fig. 2.—A typical iodine resonance obtained for BI_3. The $\nu_{1/2} \rightarrow {}_{3/2}$ transition occurred at 212.6 Mc./sec. The doublet separation was 25 ± 5 kc./sec. The $\nu_{3/2} \rightarrow {}_{5/2}$ transition was measured at 340.1 Mc./sec.

An additional aspect of this problem which may

---

(6) T. Chiba, *J. Phys. Soc. Japan*, **13**, 860 (1958).

(7) C. A. Coulson, "Valence," Oxford Press, London, 1952.

be worth noting is the apparent discrepancy that occurs when one compares the fraction double bond character with the corresponding value obtained from Pauling's equation[8] using covalent radii of the atoms involved. The discrepancy can be partially removed by combining the Pauling equation with an equation suggested by Schomaker and Stevenson[9] which attempts to account for shortening of a bond due to a difference in electronegativities of the atoms involved. This correction has been reviewed critically by Wells.[10] If one considers the possible simultaneous effect on bond length of the ionic and double bond characters and combines the Pauling and Schomaker equations one then obtains an expression

$$R = R_1 - \frac{(R_1 - R_2)3\pi}{(2\pi + 1)} - 0.09(X_X - X_B) \qquad (5)$$

where R = observed bond distance, R_1 = sum of covalent radii[8] and R_2 = sum of double bond radii.[8] If this expression is now used to get the π-bond character from observed bond distances the agreement with quadrupole data is reasonable. For example the fraction double bond character from bond distances[8,11,12] is 0.05, 0.16 and 0.20 whereas the quadrupole data give 0.06, 0.12 and 0.16 for BCl_3, BBr_3 and BI_3, respectively. Of course, equations such as (5) should be taken with considerable reservation. However, we felt that it was of interest to point out that if a sufficient number of effects are taken into consideration the conclusions drawn from observed bond distances are not necessarily in conflict with quadrupole data.

In addition, one can make some qualitative comments on the crystal structure of BI_3 relative to the other boron trihalides whose structures are known. It has been determined that the resonance in BI_3 consists of a doublet with an intensity ratio of one to four. The doublet separation is 25.5 ± kc./sec. in the lower frequency transition. In the other trihalides this doublet has been attributed to a boron isotope effect. The magnitude of the splitting and the intensity ratio obtained for the BI_3 case suggests that the same interpretation can be given for the splitting as in BCl_3 and BBr_3. Furthermore, since the resonance in BI_3 is the same except for absolute magnitude of the frequency and splitting, it can be concluded that its crystal structure is very probably the same as that of BBr_3 which is known. All of the iodines are in equivalent positions and the molecule is planar.

The authors are indebted to Dr. Frank J. Adrian for a very informative discussion on the molecular orbital aspects of these compounds.

BALTIMORE, MARYLAND

---

[8] L. Pauling, "Nature of Chemical Bond," Cornell University Press, Ithaca, New York, 1948.

[9] V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

[10] A. F. Wells, *J. Chem. Soc.*, 55 (1949).

[11] P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

[12] M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 195 (1957).

[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES CORPORATION]

Further Comments on the Polymorphism of Nb_2O_5. The High Temperature Metastable Phase ϵ

BY ARNOLD REISMAN AND FREDERIC HOLTZBERG

RECEIVED NOVEMBER 18, 1958

Experimental evidence is presented which indicates the existence of a high temperature metastable phase of Nb_2O_5, ϵ. Attempts at correlating the available information with the proposed stability diagram of Shafer and Roy were unsuccessful, and their interpretation is analyzed.

Introduction

In 1957,[1] the authors published an article describing the polymorphic behavior of Nb_2O. During an investigation of the system Nb_2O_5–Ta_2O_5, anomalies in the cooling behavior of Nb_2O_5 rich melts indicated the existence of a new high temperature polymorph of the pentoxide. Since the effect on the equilibrium diagram Nb_2O_5–Ta_2O_5 would depend on whether this new phase was enantiomorphic or not, a separate study of its thermal properties was undertaken, and the results indicate that the new phase, ϵ, is metastable, relative to α. Recently,[2] Shafer and Roy postulated the existence of a new Nb_2O_5 phase, I (high), stable in the temperature interval 1285° to the melting point and also proposed that the β-phase has a definite interval of stability. Since the existence of the (I high) form was not substantiated in the present investigation and since the arguments presented in support of a stable β-region are not self consistent, the stability diagram was reevaluated.

Experimental Procedure

The DTA equipment has been described previously.[1,3] Heating and cooling experiments were conducted in the appropriate apparati using a gain of 5 to 10 μv./inch and a temperature variation of 2–3°/minute. High purity Nb_2O_5 containing <0.2% Ta_2O_5 as the major contaminant was dried in platinum at 1100° for 24 hr. prior to use. The diffraction pattern of the ignited oxide corresponded to that of the α-form,[1] and gave an experimental density[4] of 4.548 ± 0.002 g./cm.^{3} at 25°, in good agreement with the X-ray density of 4.52 g./cm.^{3} at the same temperature.[1] The freezing point of the pentoxide was found to be 1491 ± 2°.

---

[1] F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, THIS JOURNAL, **79**, 2039 (1957).

[2] M. W. Shafer and R. Roy, *Z. Krist.*, **110**, 241 (1958).

[3] A. Reisman, F. Holtzberg and E. Banks, THIS JOURNAL, **80**, 37 (1958).

[4] A. Reisman, F. Holtzberg, M. Berkenblit and M. Berry, *ibid.*, **78**, 4514 (1956).