

## Effects of the Bending Mode of Vibration on the Hyperfine Structure of ICN†

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The bending mode of vibration in ICN introduces an asymmetry in the electric field gradient at the iodine nucleus. From an observed variation in the  $l$ -type doublet splittings of various hyperfine components for the  $v_2=1$  state, the asymmetry parameter is determined as  $\eta=0.0087$ . It is found that the measured splittings can be accounted for fully by including second-order perturbation terms arising from field asymmetry. The ratio  $(eqQ)_{v=0}/(eqQ)_{v_2=1}$  is measured as 1.0039. This ratio and the observed value of  $\eta$  are discussed in terms of the molecular bending and I-C bonding electrons.

### INTRODUCTION

PURE rotational transitions in the linear molecule ICN show a rather large hyperfine structure due to the electric quadrupole interaction of the iodine nucleus. In the first excited state of the bending mode of vibration,  $v_2=1$ , each component of the hyperfine pattern appears as a doublet. This doubling is caused by a removal of degeneracy in the  $l=\pm 1$  state where  $l$  is the quantum number of the internal angular momentum due to vibration. Removal of degeneracy is to a large extent caused by the well-known  $l$ -type doubling effect which originates from a rotation-vibration interaction. In a given rotational transition, the contribution from this source to the doublet splitting, being independent of the hyperfine interaction, is equal for all components of the pattern.

A further contribution to the doublet splitting may arise from the quadrupole hyperfine interaction as a result of an asymmetry in the average of the gradient of the electric field at the nucleus. Such an effect causes a variation of the doublet splitting in various components of the hyperfine structure. A preliminary report on the observation of the effect has already appeared in the form of a short abstract.<sup>1</sup> In this paper a more detailed discussion is presented with some further interpretation of the observed hyperfine structure.

### FIELD ASYMMETRY

The effect of the asymmetry in the electric field gradient in a linear molecule can be treated in a way similar to that of a slightly asymmetric rotor.<sup>2,3</sup> The asymmetry arises from the bending mode of vibration. The matrix element of the quadrupole hyperfine interaction energy between the  $l=+1$  and  $l=-1$  states is

$$\langle J, l=\pm 1, F | H_Q | J, l=\mp 1, F \rangle = -\frac{1}{2} \eta eqQ f(J, F),$$

where  $f(J, F)$  is the Casimir function as tabulated by

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<sup>1</sup> A. Javan and C. H. Townes, Phys. Rev. **86**, 608 (1952).

<sup>2</sup> C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York).

<sup>3</sup> G. Knight and B. T. Feld, Massachusetts Institute of Technology Research Laboratory of Electronics, Report No. 123, 1949 (unpublished).

Townes and Bardeen<sup>4</sup> and where

$$\eta = \frac{\langle \partial^2 V / \partial y^2 \rangle - \langle \partial^2 V / \partial x^2 \rangle}{q}, \quad q = \left\langle \frac{\partial^2 V}{\partial z^2} \right\rangle.$$

The  $(x, y, z)$  system of axes is a right-handed system with the  $z$  direction along the axis of the molecule and the  $y$  direction in the plane of the bent molecule. It should be noted that the  $z$  direction is uniquely determined with respect to the bent molecule by the linear momentum and Eckart's condition.<sup>5</sup> In terms of an asymmetric molecule, the  $x$ ,  $y$ , and  $z$  axes can be thought to represent, within a good approximation, the three principal axes of inertia with the  $x$  axis corresponding to the largest moment of inertia and the  $z$  axis the smallest. The averages in the expression for  $\eta$  have to be taken over electronic as well as vibrational motions.

Inclusion of the above term in the doublet splitting,  $\Delta\nu$ , of the rotational transition  $J+1 \leftarrow J$  gives, for  $F_f \leftarrow F_i$

$$\Delta\nu = 2q_i(J+1) + \eta eqQ [f(J+1, F_f) - f(J, F_i)], \quad (1)$$

where the first term is due to the  $l$ -type doubling effect and  $q_i$  is the  $l$ -doubling constant.

Earlier observation<sup>6</sup> on the hyperfine structure of ICN for the state  $v_2=1$  failed to detect the presence of a field asymmetry,  $\eta$ , at the nucleus of iodine. The reason was that in the few hyperfine components of the  $J=4 \leftarrow 3$ ,  $v_2=1$ , studied by these investigators, the factors multiplying  $\eta eqQ$  in expression (1) for  $\Delta\nu$  were particularly small so that the contributions from this source were masked by their experimental errors. An examination of the hyperfine structure for the same rotational transition reveals that there are some components in the pattern whose doublet splittings show rather large variations. A few of these components were chosen for study and determination of the constants of the spectrum.

The presence of an electric quadrupole interaction due to the nitrogen nucleus introduces coupling of the nitrogen spin to the rotation of the molecule. However,

<sup>4</sup> J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

<sup>5</sup> C. Eckart, Phys. Rev. **47**, 552 (1935); see also reference 2.

<sup>6</sup> Townes, Holden, and Merritt, Phys. Rev. **74**, 1113 (1948).

since the quadrupole coupling constant of this nucleus is about 800 times smaller than that of the iodine, it causes only slight splittings in the hyperfine pattern. In cases where the nitrogen quadrupole coupling could be resolved, it was found that the nitrogen structures in both members of a given doublet were identical. This indicates that the effect of an asymmetry in the electric field gradient at the nitrogen nucleus is smaller than the experimental errors. Thus the quantity  $\Delta\nu$  is independent of the coupling of the nitrogen nucleus and can be designated by the final and initial values of  $F_1$ , where  $F_1$  is the quantum number corresponding to the resultant angular momentum of  $J$  and the iodine spin. Table I contains a list of the measured  $\Delta\nu$  and corresponding theoretical values given by (1). The constants  $q_I$  and  $\eta eqQ$  are  $q_I = 2.643$  Mc/sec;  $\eta eqQ = 21.00$  Mc/sec. Small discrepancies in the  $F_1 = 7/2 \leftarrow 5/2$  and  $F_1 = 5/2 \leftarrow 3/2$  transitions, noted in the last column of Table I, are due to a second-order effect involving the field asymmetry which will be discussed shortly.

Resolution of the nitrogen quadrupole splitting makes it possible to measure the coupling constant  $eqQ$  of iodine to good accuracy and to determine its variation with the vibrational quantum number  $v_2$ . Table II contains a list of the absolute frequencies of the measured hyperfine components in the ground vibrational state and the higher frequency components of the  $l$ -doublets,  $l_2$ , in the first excited state of the bending mode. Since the nitrogen coupling constant is small, the quantum number  $F_1$  remains approximately a good quantum number. The designation of the states can be made by the values of  $F_1$  and  $F$  where  $F$  is the quantum number of the total angular momentum resulting from addition of the angular momentum corresponding to  $F_1$  and the nitrogen spin. However, in the rotational state  $J=3$  there is an accidental degeneracy between the levels  $F_1 = 9/2$  and  $F_1 = 7/2$ . The perturbation due to the nitrogen coupling causes a considerable admixture of these two states. This fact prevents use of the  $F_1$  quantum number to designate the state of the molecule for these two levels. In Table II these states are denoted by the total angular momentum  $F$  in parentheses followed by subscripts 1 and 2.  $(F)_1$  is taken to have lower energy than  $(F)_2$ . The theoretical frequencies listed in Table II are calculated by using a first and second order effects due to the quadrupole coupling of

TABLE I. Splittings of some of the hyperfine components in the  $J=4 \leftarrow 3$ ,  $v_2=1$  transition.

$F_{1f} \leftarrow F_{1i}$	Measured	Theoretical (first order)	Difference
$11/2 \leftarrow 11/2$	$24.715 \pm 0.020$	24.715	0
$\left. \begin{matrix} 7/2 \leftarrow 9/2 \\ 7/2 \leftarrow 7/2 \end{matrix} \right\}$	$19.840 \pm 0.035$	19.840	0
$5/2 \leftarrow 7/2$	$17.511 \pm 0.020$	17.549	0.038
$3/2 \leftarrow 5/2$	$17.310 \pm 0.020$	17.260	-0.050

TABLE II. Observed frequencies of certain hyperfine components of the ground and  $v_2=1$  excited state of ICN. Only the higher-frequency components ( $l_2$ ) of the  $l$ -type doublets are listed, since the lower-frequency components ( $l_1$ ) can be obtained from these and Table I.

$F_{1f} \leftarrow F_{1i}$	$F_f \leftarrow F_i$	Observed	Calculated
$v_2=1, l_2:$			
$11/2 \leftarrow 11/2$	$\left. \begin{matrix} 13/2 \leftarrow 13/2 \\ 11/2 \leftarrow 11/2 \\ 9/2 \leftarrow 9/2 \end{matrix} \right\}$	25567.571	25567.58
	$5/2 \leftarrow (7/2)_1$	26216.380	216.44
	$7/2 \leftarrow (9/2)_1$	26216.771	216.79
	$5/2 \leftarrow (7/2)_2$	26217.428	217.49
	$\left. \begin{matrix} 3/2 \leftarrow 5/2 \\ 3/2 \leftarrow 3/2 \end{matrix} \right\}$	26265.548	26265.59
$3/2 \leftarrow 5/2$	$\left. \begin{matrix} 5/2 \leftarrow 5/2 \\ 5/2 \leftarrow 7/2 \end{matrix} \right\}$	26265.210	26265.19
	$1/2 \leftarrow 3/2$	26265.610	26265.64
$v=0$			
$11/2 \leftarrow 11/2$	$\left. \begin{matrix} 13/2 \leftarrow 13/2 \\ 9/2 \leftarrow 9/2 \end{matrix} \right\}$	25393.517	25393.48
	$11/2 \leftarrow 11/2$	25393.776	25393.75
	$5/2 \leftarrow 7/1$	26217.022	
	$3/2 \leftarrow 5/2$	26248.971	26249.05

the iodine nucleus. The following coupling constants are determined: For iodine  $eqQ = -2420.3 \pm 0.2$  Mc/sec in the  $v=0$  state,  $eqQ = -2410.85 \pm 0.2$  Mc/sec in the  $v_2=1$  state giving a ratio  $(eqQ)_{v=0}/(eqQ)_{v_2=1} = 1.0039 \pm 0.0001$ . For nitrogen  $eqQ = -3.8$  Mc/sec.

Using the value of  $eqQ$  obtained here for iodine in the  $v_2=1$  state, the asymmetry parameter is found to be  $\eta = 0.0087$ . The lines reported in reference 6 agree well with the above constants. It should be pointed out that the presence of the terms in  $\eta$  does not effect the center of a doublet. The asymmetry  $\eta eqQ$  can conveniently be eliminated in obtaining  $eqQ$  by treating the center of the doublets in the hyperfine structure as in the case of no field asymmetry.

#### EFFECTS OF SECOND-ORDER IN THE FIELD ASYMMETRY

As is pointed out in reference 6, the second-order corrections for the quadrupole coupling of the iodine nucleus is quite appreciable in the ICN molecule. In the absence of a field asymmetry the correction is of the order  $(eqQ)^2/B \times 10^{-3}$  Mc/sec. This term arises from matrix elements of the quadrupole interaction between states  $\langle J; l; F_1 |$  and  $\langle J \pm 1, \pm 2; l; F_1 |$ . The inclusion of a field asymmetry gives rise to new matrix elements between states  $\langle J; l; F_1 |$  and  $\langle J \pm 1, \pm 2; l \pm 2; F_1 |$ . Since these elements are off-diagonal in the quantum number  $l$  they effect only the doublet splittings. Therefore, the centers of the doublets are independent of  $\eta$  even to a second-order calculation. The second-order contribution to the splitting from the field asymmetry alone is of the order  $[\eta^2 (eqQ)^2/B] \times 10^{-3}$  Mc/sec and, because of the smallness of  $\eta$ , is negligible. However, the presence of a

second-order correction due to the cross terms in elements diagonal and off diagonal in  $l$  introduces a correction of the order  $[\eta(eqQ)^2/B] \times 10^{-3}$  which is large enough to account for a small deviation of the observed  $\Delta\nu$  from the first-order expression mentioned earlier.

The part of the matrix element  $\langle J; l; F_1 | H_Q | J \pm 1, \pm 2; l \pm 2; F_1 \rangle$  which depends essentially on the overall rotation of the molecule can conveniently be factored out.<sup>7</sup> The factor depending on the rotation is

$$\langle J; l; M_J = J | \nabla E_{zz} | J \pm 1, \pm 2, l \pm 2; M_J = J \rangle.$$

The similarity of the treatment of the quadrupole interaction with that of an asymmetrical top rotor was mentioned earlier. In the latter case the quantum number  $K$  takes the place of  $l$ , and we shall use  $K$  instead of  $l$  below. The formula given here can be applied to a second-order calculation in the case of an asymmetric rotor or for a symmetric top molecule with the interacting nucleus located off the symmetry axis.

The above matrix element can be evaluated either by a direct integration over the rotational wave function or the use of Racah's coefficients. The following expressions are obtained:

$$\begin{aligned} & \langle J, K, J | \nabla E_{zz} | J+1, K-2, J \rangle \\ &= \frac{-\eta eqQ}{2(J+2)(J+1)} \\ & \quad \times \left[ \frac{(J-K+1)(J-K+2)(J-K+3)(J+K)}{2J+3} \right]^{\frac{1}{2}}, \\ & \langle J, K, J | \nabla E_{zz} | J+1, K+2, J \rangle \\ &= \frac{+\eta eqQ [J+K+3]}{2(J+2)(J+1)} \\ & \quad \times \left[ \frac{(J+K+2)(J+K+1)(J-K)}{(2J+3)(J+K+3)} \right]^{\frac{1}{2}}, \\ & \langle J, K, J | \nabla E_{zz} | J+2, K-2, J \rangle \\ &= \frac{-\eta eqQ}{2(J+2)(2J+3)} \\ & \quad \times \left[ \frac{(J-K+1)(J-K+2)(J-K+3)(J-K+4)}{(J+1)(2J+5)} \right]^{\frac{1}{2}}, \\ & \langle J, K, J | \nabla E_{zz} | J+2, K+2, J \rangle \\ &= \frac{-\eta eqQ [(J+K)^2 + 7(J+K) + 12]}{2(2J+3)(J+2)} \\ & \quad \times \left[ \frac{(J+K+1)(J+K+2)}{(J+1)(2J+5)(J+K+3)(J+K+4)} \right]^{\frac{1}{2}}. \end{aligned}$$

<sup>7</sup> J. K. Bragg, Phys. Rev. 74, 533 (1948).

The factors multiplying these expressions to give the total matrix elements can be found in reference 7. The correction to the splitting of the  $(J, F_1, K = \pm 1)$  energy level is

$$\delta E = 2 \sum_{J, K'} \frac{\langle J, K = +1, F_1 | H_Q | J', K', F_1 \rangle \times \langle J', K', F_1 | H_Q | J, K = -1, F_1 \rangle}{E_J - E_{J'}}.$$

An evaluation of this quantity for the doublets listed in Table I gives a correction of  $-58$  kc/sec for the transition  $3/2 \leftarrow 5/2$ ,  $36$  kc/sec for  $5/2 \leftarrow 7/2$ , and only about  $10$  kc/sec for the rest of the transitions.

Thus, the discrepancies listed in Table I is fully accounted for by this second-order effect and we can conclude that the inclusion of the asymmetry parameter  $\eta$  at the nucleus of iodine alone is sufficient to account for the observed variations of the doublet splittings in the hyperfine structure of ICN.

#### CALCULATION OF $\eta$ AND VIBRATIONAL DEPENDENCE OF $eqQ$

Let us first ignore the effect of the molecular bending on the electronic structure of the molecule. When the molecule is bent, the axis of symmetry for the cylindrical charge distribution around the iodine nucleus no longer coincides with the principal axis  $z$  of inertia of the molecule. This introduces an asymmetry into the gradient of the electric field in the coordinate system corresponding to the principal axes of inertia which depends on the degree to which the molecule is bent. Hence the asymmetry must be averaged over the vibrational state to give the quantity  $\eta$  of Eq. (1). The tensor for the electric field gradient is diagonal when expressed in a system of axes  $(x', y', z')$  with  $z'$  in the direction of the axis of cylindrical charge distribution. In this system of axes, the tensor depends on only one parameter because of the relations:

$$\left\langle \frac{\partial^2 V}{\partial x'^2} \right\rangle = \left\langle \frac{\partial^2 V}{\partial y'^2} \right\rangle = -\frac{1}{2} \left\langle \frac{\partial^2 V}{\partial z'^2} \right\rangle.$$

A transformation of this tensor to the principal axes of inertia of the molecule,  $(x, y, z)$ , gives the following relations:

$$\begin{aligned} \left\langle \frac{\partial^2 V}{\partial y^2} \right\rangle - \left\langle \frac{\partial^2 V}{\partial x^2} \right\rangle &= \frac{3}{2} q' \langle \sin^2 \theta \rangle, \\ \left\langle \frac{\partial^2 V}{\partial z^2} \right\rangle &= q' \left( 1 - \frac{3}{2} \langle \sin^2 \theta \rangle \right), \end{aligned} \quad (2)$$

where  $\theta$  is the angle between  $z$  and  $z'$  and where  $q'$  is the average of  $\partial^2 V / \partial z'^2$  over electronic wave function.

From the observed value of  $\eta = 0.0087$  and the above equations, one obtains  $\langle \sin^2 \theta \rangle = 0.0058$ .

Under the assumption that the axis of symmetry for

the charge distribution is in coincidence with I—C direction, one may calculate  $\eta$  directly as follows:

The angle  $\theta$  between the I—C direction and the  $z$  axis can be expressed in terms of the distance  $r$  of the carbon nucleus from the line through I and N. Using the known interatomic distances of ICN and the conservation of the linear momentum, and Eckart's condition one obtains for small values of  $\theta$ ,  $\theta = 0.385r$ . In this relation,  $\theta$  is in radians if  $r$  is expressed in angstrom. Since the angle  $\theta$  remains small in the course of vibration, the value of the angle can be substituted for  $\sin\theta$ . Thus, for the evaluation of  $\langle \sin^2\theta \rangle$  it is necessary to estimate the average of  $r^2$ .

The vibrational wave function in the  $v$ th excited state of the bending mode of oscillation with internal angular momentum  $l$  is

$$\psi_{v,l} = N e^{i l \chi} \exp(-\rho^2/2) \rho^{l|l} L_{\frac{1}{2}(v+|l|)}^{l|l}(\rho^2),$$

where  $L_{\frac{1}{2}(v+|l|)}^{l|l}$  is the associated Laguerre polynomial and where  $\chi$  and  $\rho$  are defined by the normalized doubly degenerate normal coordinates of oscillation,  $Q_1$  and  $Q_2$ , as:

$$Q_1 = \rho \cos\chi, \quad Q_2 = \rho \sin\chi.$$

The quantity  $\rho$  in terms of the distance  $r$  takes the form  $\alpha r$  with the proportionality constant  $\alpha$  given by  $2\pi(\mu\nu/h)^{\frac{1}{2}}$  where  $\nu$  is the normal frequency of the bending mode of vibration and where the quantity  $\mu$ , the reduced mass, is given by

$$\mu = \frac{m_2(m_1+m_2+m_3)I^e}{m_1m_3(l_{1,3})^2 \left( \left[ \frac{m_2}{m_1}(l_{2,3})^2/(l_{1,3})^2 \right] + \left[ \frac{m_2}{m_3}(l_{1,2})^2/(l_{1,3})^2 \right] + 1 \right)}.$$

In this equation,  $I^e$  is the equilibrium moment of inertia of the molecule; the indices 1, 2, and 3 refer to the three nuclei with subscript 2 standing for the middle nucleus; the  $m_i$ 's are the nuclear masses and  $l_{i,j}$ 's the internuclear distances. For ICN, one obtains  $\mu = 8.858$ . The angle  $\chi$  in the above wave function is the inclination of the plane of the bent molecule with respect to a fixed plane passing through the  $Z$  axis.

Evaluation of the average of  $r^2$  over this wave function gives

$$\langle v_2 = 1, |l| = 1 | r^2 | v_2 = 1, |l| = 1 \rangle = 2/\alpha^2,$$

yielding  $\eta = 0.0051$ .

This calculated value is only 60% of the value 0.0087 obtained from the experimental results. Such a discrepancy is considerably outside of experimental error and indicates clearly that the assumption of the I—C direction taken as the axis for a cylindrical charge distribution is not justified.

For an explanation of this discrepancy, we propose the following two effects:

1. An increase in the value of  $\eta$  over the above calculated value can be expected if one introduces the notion of a "bent bond" in the iodine-carbon bonding electrons. For such a bond, the axis of the charge distribution around the iodine nucleus deviates from the I—C direction, hence resulting in such increase.

2. The electron bond configuration in the ICN molecule is known to involve the two structures I—C $\equiv$ N and I $^+$ =C=N $^-$ , with about 13% importance for the second resonating structure. If one ignores the effect of bending on the electronic configuration, a cylindrically symmetric charge distribution for the iodine-carbon bonding electron is required and therefore the  $\pi$  orbitals in the second resonating structure necessarily will consist of 50%  $\pi_x$  and 50%  $\pi_y$  orbitals. The presence of the bending mode of vibration, however, introduces a non-equivalence in the orbitals in the plane of bending and perpendicular to this plane, hence  $\pi_x$  and  $\pi_y$  orbitals may take an unequal population thus destroying the cylindrical symmetry of the charge distribution. This effect also can result in an increase of the value of  $\eta$ .

Unfortunately, our experimental data cannot determine separately the extent to which each of these effects occur. In order to show the meanings of our measured quantities in terms of the above considerations, first let us treat the case where the electron distribution around the iodine nucleus remains cylindrically symmetric, but a bent bond is introduced in the I—C bond as a result of molecular bending:

The quantity  $\langle \sin^2\theta \rangle = 0.0058$  evaluated above from the measured value of  $\eta$  corresponds to the angle  $\theta_1$  between the axis of symmetry for the electric charge distribution and the axis of the molecule. The corresponding average for the angle  $\theta_2$  formed by the I—C direction can be calculated from  $\langle r^2 \rangle$  as 0.0034. The difference between these two values indicates that under the assumption of a cylindrically symmetric charge distribution a bent bond necessarily occurs as a result of the bending mode of vibration. To a good approximation  $\theta_1$  can be taken as a linear function of the normal coordinates of the bending mode. This results in a proportionality between  $\theta_1$  and  $\theta_2$  with the proportionality constant  $(\langle \theta_1^2 \rangle / \langle \theta_2^2 \rangle)^{\frac{1}{2}} = 1.30$ . The value of  $q = \langle \partial^2 V / \partial z^2 \rangle$  according to the Eq. (2) depends on  $\langle \sin^2\theta \rangle$ . This dependence accounts for the observed variation in the coupling constant  $eqQ$  with the vibrational quantum number  $v_2$ . From (2) one obtains:

$$(eqQ)_{v_2=0} / (eqQ)_{v_2=1} = \frac{q'_{v_2=0} \left( 1 - \frac{3}{2} \langle \sin^2\theta_1 \rangle_{v_2=0} \right)}{q'_{v_2=1} \left( 1 - \frac{3}{2} \langle \sin^2\theta_1 \rangle_{v_2=1} \right)}. \quad (3)$$

$\langle \sin^2\theta_1 \rangle$  can be estimated by observing the fact that  $\theta_1$  is linearly related to  $\theta_2$  and the average of  $\theta_2^2$  over the zero point vibration is half as large as that for the  $v_2 = 1$  state. Therefore

$$\langle \theta_1^2 \rangle_{v_2=0} = \frac{1}{2} \langle \theta_1^2 \rangle_{v_2=1},$$

which gives

$$(1 - \frac{3}{2}\langle \sin^2\theta_1 \rangle_{v=0}) / (1 - \frac{3}{2}\langle \sin^2\theta_1 \rangle_{v_2=1}) = 1.0040.$$

From this ratio and the observed ratio

$$[(eqQ)_{v=0} / (eqQ)_{v_2=1}] = 1.0039 \pm 0.0001,$$

one obtains for  $q'_{v=0}/q'_{v_2=1}$  a value of very nearly unity.

Let us consider next the 2nd effect where an unequal population in the  $\pi_x$  and  $\pi_y$  orbitals in the absence of a bent bond causes the increase in  $\eta$ :

In this case due to the fact that  $\langle \partial^2 V / \partial x'^2 \rangle \neq \langle \partial^2 V / \partial y'^2 \rangle$ , Eqs. (2) are modified and take the form:

$$\langle \partial^2 V / \partial y'^2 \rangle - \langle \partial^2 V / \partial x'^2 \rangle = \frac{1}{2}q'[3\langle \sin^2\theta \rangle + \eta'(2 - \langle \sin^2\theta \rangle)],$$

$$\langle \partial^2 V / \partial z'^2 \rangle = \frac{1}{2}q'[2 - 3\langle \sin^2\theta \rangle + \eta'\langle \sin^2\theta \rangle],$$

where

$$\eta' = \left( \left\langle \frac{\partial^2 V}{\partial y'^2} \right\rangle - \left\langle \frac{\partial^2 V}{\partial x'^2} \right\rangle \right) / \left\langle \frac{\partial^2 V}{\partial z'^2} \right\rangle,$$

and where  $\theta$  is the angle between the  $z'$  direction and the axis  $z$  of the molecule with  $z'$  in the I-C direction and  $y'$  in the plane of bending. Ignoring the small quantity  $\eta'\langle \sin^2\theta \rangle$ , we obtain  $\eta = (3/2)\langle \sin^2\theta \rangle + \eta'$ .

The calculated value of  $\langle \sin^2\theta \rangle$  and our measured  $\eta$  yields  $\eta' = 0.0035$ .

In terms of the molecular orbitals  $\eta'$  can be interpreted as follows:

The  $\sigma$  bond is cylindrically symmetric and does not contribute to  $\eta'$ . In the resonant structure  $I^+ = C = N^-$ , the wave function for the  $\pi$  electron in terms of  $p_x$  and  $p_y$  orbitals has the form  $\psi = \chi^{\frac{1}{2}}p_x + (1-\chi)^{\frac{1}{2}}p_y$ . It can be shown that such wave function gives  $\eta' = 3(1-2\chi)$ . Since this structure has an importance of about 13%, the expected value of  $\eta'$  is  $0.39(1-2\chi)$  giving  $\chi = 0.49$ . This means that a 2% decrease in the  $p_x$  orbitals for the perpendicular bond at the iodine nucleus can account for the observed value of  $\eta$ .

For the ratio of the quadrupole coupling constant in the ground vibrational state and the first excited state of the bending mode, the Eq. (3) still holds where  $\theta_1$  should be taken as the angle formed by the I-C direction and the axis  $z$  of the molecule. The average of the square of this angle in the ground and the  $v_2=1$  state discussed above yields for  $q'_{v=0}/q'_{v_2=1}$  a value again very nearly unity.

The fact that a bent bond can occur together with a nonequivalent  $p_x$  and  $p_y$  orbitals in the resonant structure  $I^+ = C = N^-$  implies that the amount of bending and the change in the population of the  $p_x$  and  $p_y$  orbitals calculated above are the upper limits for these effects. However, in the calculation of the change in the electric field gradient along the axis with the quantum number  $v_2$ , either of the above two assumptions yields an

undetectable change. The observed variation of the coupling constant  $eqQ$  with the quantum number  $v_2$  in ICN, therefore, is mostly a kinematical effect due to the dependence of this quantity on  $\langle \sin^2\theta \rangle$ .

One should bear in mind that a dependence of  $eqQ$  on  $\langle \sin^2\theta \rangle$  is not peculiar to linear molecules. For instance, the perpendicular modes of oscillation in the symmetrical top molecules, such as in  $XYZ_3$  molecules, introduces a similar dependence of the coupling constant. In general, a larger variation in  $eqQ$  may be expected in these types of oscillation compared to the parallel modes of vibration for which the system of principal axes of the electric field gradient tensor undergoes no rotation with respect to the principal axes of inertia of the molecule.

#### ASYMMETRY PARAMETER $\eta$ , AND VIBRATIONAL DEPENDENCE OF $eqQ$ IN BrCN

The rotational transition  $J=6 \leftarrow 5$  in the first excited state of the bending mode of vibration in BrCN has been measured by Tetenbaum.<sup>8</sup> A variation in the  $l$ -doublet splittings of various hyperfine transitions was observed by him. However, he did not attempt to analyze his data on the basis of an asymmetry in the electric field gradient. From the data in Table III of his paper, one obtains a value of  $\eta = 0.0095 \pm 0.0010$  for either of the two isotopic species in Br. Specifically, this value is calculated from the two transitions  $9/2 \leftarrow 9/2$  and  $13/2 \leftarrow 13/2$ , which show the largest variations in their splittings. The agreement of formula (1) of the present paper with the splittings of the rest of the hyperfine transitions of BrCN is satisfactory and to within the reported experimental errors.

Considerations similar to those for ICN above show that for BrCN the asymmetry may be produced by a bent bond with the ratio  $\theta_1/\theta_2 = 1.25$  or by a small amount of asymmetry in the double-bond structure  $Br^+ = C = N^-$  during bending.

The ratio of the quadrupole coupling constants  $eqQ$  in the ground and the first excited state of the bending mode of oscillation in BrCN is about the same in both isotopic species of Br and is  $(eqQ)_{v=0} / (eqQ)_{v_2=1} = 1.004 \pm 0.001$ . For a bent bond one obtains, along the lines discussed for ICN,  $q'_{v=0}/q'_{v_2=1} = 0.999 \pm 0.001$  where as in the absence of a bent bond one obtains  $q'_{v=0}/q'_{v_2=1} = 1.001 \pm 0.001$ .

These results are in consistence with the above observation on the ICN molecule.

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<sup>8</sup> S. J. Tetenbaum, Phys. Rev. **86**, 440 (1952).