

kinetic-theory value of about  $1 \times 10^{-7}$  sec and with the characteristic time for rotational redistribution  $\simeq 3 \times 10^{-7}$  given by Radford and Broida.<sup>9</sup> This agreement indicates that a large percentage of the collisions result in changes in the rotational state of the molecule.

### CONCLUSION

The measured spectrum agrees with the number of lines predicted and reveals a rather large hyperfine splitting in the  $B^2\Sigma$  state of CN and a relatively small spin splitting. The result is a rather unusual fine and hyperfine structure in the  $K'=4$  rotational level,  $v=0$ ,  $B^2\Sigma$  state of the CN molecule.

Linewidth measurements as a function of pressure show a linear dependence of linewidth on pressure. The collision diameter, calculated from the slope of the linewidth-versus-pressure curve, is in reasonable agreement with the kinetic-theory value.

The results presented have demonstrated that energy levels which cannot be observed by regular optical spectroscopy methods can be found by using a microwave pumping technique. Such techniques are useful only in cases where significant population differences are present. The population increase of about 30% in the individual levels caused by the microwave pumping may have some application for laser action.

The feasibility of this technique applied to excited states of molecules has provided the basis for future work devoted toward other rotational perturbations in CN as well as in other molecules.

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## Hyperfine Structure of the $B^2\Sigma^+$ State of CN\*

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Hyperfine-structure energy formulas are developed for  $^2\Sigma$  states of diatomic molecules and are used to analyze some of the results of the microwave-optical experiment on the CN molecule described in the preceding paper. For the excited  $B^2\Sigma^+$  state the following hyperfine structure constants are derived:  $|\Psi^2(0)| = (10.2 \pm 0.2) \times 10^{24} \text{ cm}^{-3}$ ,  $\langle (3 \cos^2\chi - 1)/r^3 \rangle_{\text{av}} = (7 \pm 2) \times 10^{24} \text{ cm}^{-3}$ , and  $eQq = (-5 \pm 5) \text{ MHz}$ . These results are found to be consistent with the valence bond structure  $:C \equiv N:$ , in which the unpaired electron occupies the  $\sigma$ -bond orbital of the molecule.

### INTRODUCTION

EXPLOITING a novel microwave-optical technique, Evenson, Dunn, and Broida<sup>1</sup> have recently determined the hyperfine structure of two rotational levels of the CN molecule, one of which is a spin doublet level of the excited electronic state  $B^2\Sigma^+$ . This is the first precise measurement of magnetic hyperfine structure in a  $^2\Sigma$  molecular state, and the results, shown in Table I, fit none of the standard energy formulas<sup>2</sup> In particular, the familiar Interval Rule, which states that the separation between hyperfine structure levels with angular momentum numbers  $F$  and  $F-1$  should be proportional to the value of  $F$ , is obviously disobeyed. The reason for this becomes evident when one observes that the separations between levels of different  $F$  in Table I are as large as the separations between levels of different  $J$ ;

that is, the hyperfine structure is comparable in size with the fine structure. This situation, which may be expected to be typical of  $^2\Sigma$  molecular states, corresponds to a thoroughly mixed vector coupling scheme, midway between the limiting cases called  $b_{\beta J}$  and  $b_{\beta S}$

TABLE I. Hyperfine structure—fine structure intervals in the  $B^2\Sigma^+$ ,  $v=0$ ,  $K=4$  spin doublet level of CN. All entries in MHz.

$J, F^a$	Measured interval <sup>b</sup>	Calculated interval <sup>c</sup>
	$\Delta\nu(J, F \rightarrow J, F-1)$	
$\frac{9}{2}, \frac{11}{2}$	139.2	137
$\frac{9}{2}, \frac{9}{2}$	160.8	157
$\frac{7}{2}, \frac{9}{2}$	-113.6	-117
$\frac{7}{2}, \frac{7}{2}$	-383.7	-386
	$\Delta\nu(J, F \rightarrow J-1, F-1)$	
$\frac{9}{2}, \frac{7}{2}$	244.4	243

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<sup>1</sup> K. M. Evenson, J. L. Dunn, and H. P. Broida, preceding paper, Phys. Rev. **136**, A1566 (1964). See also, R. L. Barger, H. P. Broida, A. J. Estin, and H. E. Radford, Phys. Rev. Letters **9**, 345 (1962).

<sup>2</sup> C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), Chap. 8.

<sup>a</sup> The  $J$  values listed are those of the case  $b_{\beta J}$  levels which connect with the actual intermediate coupling levels via an adiabatic transformation.

<sup>b</sup> Taken from Table II of Ref. 1 (preceding paper). Experimental uncertainties are  $\pm 0.5 \text{ MHz}$ .

<sup>c</sup> Calculated from Eqs. (5), (8), and (9), using the values  $\delta=497$ ,  $b=467$ ,  $c=60$ ,  $eQq=-5$ , all in MHz.

by Townes and Schawlow.<sup>2</sup> Since  $\mathbf{J}$  (the total angular momentum but for nuclear spin) is not conserved by such an intermediate coupling scheme, the magnetic hyperfine structure interaction cannot be cast into the usual  $\mathbf{I} \cdot \mathbf{J}$  form, the form which leads to, among other things, the Interval Rule.

Intermediate coupling cases do not often succumb to general energy calculations, yielding formulas applicable to any molecule, but the  ${}^2\Sigma$  case is an example of one that does. Such formulas are derived here from the basic hyperfine structure theory of Frosch and Foley,<sup>3</sup> and are applied to the special case of CN in its  $B {}^2\Sigma^+$  state.

#### UNPERTURBED CASE

By "unperturbed" is meant the absence of rotational perturbations between the  ${}^2\Sigma$  level of interest and other levels, belonging to different electronic states of the same molecule, which may happen to lie nearby. Although they play an important role in the microwave-optical technique of the CN experiment,<sup>4</sup> and must also be considered in a detailed analysis of the CN hyperfine structure, such perturbations affect at most only a few of the many energy levels of a  ${}^2\Sigma$  state, and they will be disregarded for the moment.

The hyperfine structure of CN, and other  ${}^2\Sigma$  molecules with a single magnetic nucleus, arises almost entirely from the interaction of the nuclear magnetic moment with the spin magnetic moment of the molecule's single unpaired electron. Smaller contributions come from the nuclear electric-quadrupole interaction and, smaller yet, from the interaction of the nuclear magnetic moment with the residual orbital magnetic moment of the unpaired electron. This small orbital interaction shows up clearly in  ${}^4\Sigma$  states, where it has no competition from other magnetic interactions, but it is insignificant in comparison with the strong spin interaction in  ${}^2\Sigma$  states, and will be neglected here. The relevant parts of the hyperfine structure Hamiltonian (given in full detail by Frosch and Foley<sup>3</sup>) are then

$$H_{\text{hfs}} = b(\mathbf{I} \cdot \mathbf{S}) + cI_z S_z + eQq[3I_z^2 - I(I+1)]/4I(2I-1), \quad (1)$$

where

$$\begin{aligned} b &= (16\pi/3)g_I\mu_0\mu_N\Psi^2(0) - g_I\mu_0\mu_N\langle(3\cos^2\chi - 1)/r^3\rangle_{\text{av}}, \\ c &= 3g_I\mu_0\mu_N\langle(3\cos^2\chi - 1)/r^3\rangle_{\text{av}}, \\ q &= \sum_i e_i \langle(3\cos^2\chi_i - 1)/r_i^3\rangle_{\text{av}}, \end{aligned}$$

and  $I_z$  and  $S_z$  are the components of nuclear and electronic spin along the internuclear axis. The averages in the constants  $b$  and  $c$  are taken over the motion of the unpaired electron, while that in  $q$  is taken over the charge distribution of the entire molecule;  $\mathbf{r}$  is the radius vector with origin at the magnetic nucleus and  $\chi$  is the angle included between  $\mathbf{r}$  and the molecular axis. The

<sup>3</sup> R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952).

<sup>4</sup> H. E. Radford and H. P. Broida, Phys. Rev. **128**, 231 (1962).

symbol  $Q$  is the electric quadrupole moment of the nucleus, as defined by Bardeen and Townes,<sup>5</sup> while  $\Psi^2(0)$ , which measures the strength of the relativistic part of the magnetic interaction, is the probability of finding the unpaired electron at the magnetic nucleus.

The hyperfine structure energies may be found as a function of the unknown constants  $b$ ,  $c$ , and  $q$  by diagonalizing the matrix of the hyperfine structure Hamiltonian in a chosen angular-momentum representation. For  ${}^2\Sigma$  states, a convenient representation is that of case  $b_{\beta J}$ , the various functions of which are labeled by the sharp quantum numbers  $\Lambda$ ,  $K$ ,  $S$ ,  $J$ ,  $I$ ,  $F$ , and  $m_F$ . The matrix of the approximate Hamiltonian (1) in this representation is diagonal in  $\Lambda$ ,  $S$ ,  $I$ ,  $F$ , and  $m_F$ , but off-diagonal by two units in  $K$  and  $J$ ; i.e., the nonvanishing matrix elements of (1) have the form  $\langle KJ | H_{\text{hfs}} | K'J' \rangle$  where  $K' - K = 0, \pm 1, \pm 2$ , and  $J' - J = 0, \pm 1, \pm 2$ , subject to the limitation  $K' + S \geq J' \geq K' - S$ . In most cases, however, the hyperfine structure energies will be much smaller than the rotational energy separations of different  $K$  levels, and a good approximation may be had by diagonalizing the matrix for a single value of  $K$ . In a  ${}^2\Sigma$  state, with  $J = K \pm \frac{1}{2}$ , this matrix has the following elements (taken from the paper of Frosch and Foley,<sup>3</sup> after some necessary matrix multiplications):

$$\begin{aligned} \langle KJ = K - \frac{1}{2} | H_{\text{hfs}} | KJ = K - \frac{1}{2} \rangle &= \left( -b + \frac{c}{2K-1} \right) \\ &\times \frac{C}{2(2K+1)} + W_Q, \quad (2) \end{aligned}$$

$$\begin{aligned} \langle KJ = K + \frac{1}{2} | H_{\text{hfs}} | KJ = K + \frac{1}{2} \rangle &= \left( b + \frac{c}{2K+3} \right) \\ &\times \frac{C}{2(2K+1)} + W_Q, \quad (3) \end{aligned}$$

$$\begin{aligned} \langle KJ = K \pm \frac{1}{2} | H_{\text{hfs}} | KJ = K \mp \frac{1}{2} \rangle &= \frac{E}{2(2K+1)} \\ &\times \left[ b + \frac{c}{2} + \frac{3eQqD}{2I(2I-1)(2K-1)(2K+3)} \right], \quad (4) \end{aligned}$$

where

$$\begin{aligned} W_Q &= -eQq[3C(C+1)/2 - I(I+1)J(J+1)] \\ &\quad / 8I(2I-1)J(J+1), \\ C &= F(F+1) - I(I+1) - J(J+1), \\ D &= F(F+1) - I(I+1) - (K - \frac{1}{2})(K + \frac{3}{2}), \\ E &= [F + K - I + \frac{1}{2}](F + I - K + \frac{1}{2}) \\ &\quad \times (F + K + I + \frac{3}{2})(K + I - F + \frac{1}{2})^{1/2}. \end{aligned}$$

<sup>5</sup> J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

The matrix element (4), which is off diagonal in  $J$ , acts to uncouple the electron spin from the molecular rotation, and is responsible for deviations from the Interval Rule. (The diagonal quadrupole interaction  $W_Q$  also contributes to these deviations, but this is ordinarily a small effect.) The degree to which the spin is uncoupled depends on the original fine structure separation of the two levels  $J=K+\frac{1}{2}$  and  $J=K-\frac{1}{2}$ , the so-called spin doublet interval  $\delta$ . When  $\delta$  is large in comparison with the hyperfine-structure constant  $b$ , as for example in high rotational levels of light molecules, the spin uncoupling will be small and the Interval Rule will hold approximately; when, as in the present case,  $\delta$  is comparable with  $b$ , severe spin uncoupling and departures from the Interval Rule can be expected. The chief

sources of fine structure in  $^2\Sigma$  states are the second-order spin-orbit interaction and the direct spin-rotation interaction, both of which are exceedingly difficult to calculate. At the cost of introducing one more adjustable parameter, the fine structure can, however, be accounted for by simply adding a  $\delta$  to the diagonal matrix element (2). By making the sign as well as the magnitude of  $\delta$  adjustable, one may include the possibility of inverted fine structure. Conservation of angular momentum requires all fine structure interactions to be diagonal in  $J$ , and so the off-diagonal element (4) is unaffected.

Since the energy matrix is  $2 \times 2$  (for each set of values  $K, F$ ), the corresponding secular equation is quadratic and has exact analytic solutions. These are:

$$W(IKF) - W_0(K) = \frac{\delta}{2} - \frac{b}{4} + \frac{cD}{(2K-1)(2K+3)} + \frac{eQq[\frac{3}{4}D(D+1) - (K-\frac{1}{2})(K+\frac{3}{2})(I-\frac{1}{2})(I+\frac{3}{2})]}{2I(2I-1)(2K-1)(2K+3)} \\ \pm \frac{1}{2} \left\{ \Delta^2 + \frac{2b\Delta}{2K+1} [F(F+1) - I(I+1) - (K+\frac{1}{2})^2] + \frac{\Gamma(2b+\Gamma)E^2}{(2K+1)^2} + b^2(I+\frac{1}{2})^2 \right\}^{1/2}, \quad (5)$$

where

$$\Delta = \delta - \frac{2c[F(F+1) - I(I+1)]}{(2K-1)(2K+1)(2K+3)} - \frac{3}{16} \frac{eQq}{I(2I-1)} \left\{ K + \frac{1}{2} - \frac{8[F(F+1) - I(I+1)][F(F+1) - I(I+1) + 1]}{(2K-1)(2K+1)(2K+3)} \right\}, \\ \Gamma = \frac{c}{2} + \frac{3eQqD}{2I(2I-1)(2K-1)(2K+3)},$$

and  $D$  and  $E$  are defined above. This formula gives the energies of all the fine structure-hyperfine structure levels,  $2(2I+1)$  in number,<sup>6</sup> of any unperturbed rotational level of a  $^2\Sigma$  state. These energies are measured relative to  $W_0(K)$ , the energy of the original, unsplit spin doublet. Values of  $F$  range in unit steps from  $K+I+\frac{1}{2}$  to  $K-I-\frac{1}{2}$ . For all but these two extreme values of  $F$  there are two energy levels, given by the  $+$  and  $-$  signs before the radical in (5). If the spin uncoupling is small ( $b \ll \delta$ ), these two levels correspond to the two  $J$  values  $J=K \pm \frac{1}{2}$ , but this identification breaks down when the spin uncoupling is appreciable, since  $J$  is then no longer a good quantum number. For the extreme values of  $F$ , however,  $J$  is always a good quantum number and Eq. (5) simplifies to give (except for the added  $\delta$ ) just the two diagonal energy expressions (2) and (3).

#### PERTURBED CASE

The energy formula (5) can be fitted reasonably well, within a few tens of megahertz, to the level separations of Table I, but for a better fit it is necessary to take account of the rotational perturbation which is known to exist between the  $K=4$  spin doublet levels of the

$B^2\Sigma^+$ ,  $v=0$  state of CN, the particular levels of interest here, and the  $J=\frac{7}{2}$   $\Lambda$ -type doublet levels of the  $A^2\Pi_{3/2}$ ,  $v=10$  state of the same molecule. Denoting the unperturbed case (b) wave functions by  $|v \Lambda K J\rangle$ , one can write the perturbed wave functions of the  $K=4$  spin doublet, in the absence of hyperfine structure, as

$$\psi(J=K+\frac{1}{2}) = |0 0 K K+\frac{1}{2}\rangle, \quad (6)$$

$$\psi(J=K-\frac{1}{2}) = (1-\rho^2)^{1/2} |0 0 K K-\frac{1}{2}\rangle \\ + \rho(\frac{1}{2}+m)^{1/2} |1 0 1 K-1 K-\frac{1}{2}\rangle \\ + \rho(\frac{1}{2}-m)^{1/2} |1 0 1 K K-\frac{1}{2}\rangle, \quad (7)$$

in which  $\rho$  is the "mixing parameter" of the rotational perturbation<sup>4</sup> and  $m$  is a parameter which specifies the vector coupling of the admixed  $^2\Pi_{3/2}$  state, the state represented by the last two terms of the function (7).<sup>7</sup> For the special case considered here the numerical value of  $\rho^2$  is 0.14,<sup>8</sup> whence it is clear that the  $J=\frac{7}{2}$  level of the spin doublet has to a considerable degree the properties of the perturbing  $^2\Pi_{3/2}$  level, including its electronic orbital angular momentum. For an accurate cal-

<sup>6</sup> In the few cases where  $I \geq K$ , the number of levels is  $2(2K+1)$ .

<sup>7</sup> G. C. Dousmanis, T. M. Sanders, Jr., and C. H. Townes, Phys. Rev. **100**, 1735 (1955). Corrections to the case (b) functions (43) of this reference have been made by J. J. Gallagher and C. M. Johnson [Phys. Rev. **103**, 1727 (1956)] and are incorporated above.

<sup>8</sup> N. H. Kiess and H. P. Broida, J. Mol. Spectry. **7**, 194 (1961).

ulation of hyperfine structure, therefore, the complete Hamiltonian of Frosch and Foley, including orbital interactions, would have to be used; the result however, would contain more unknown parameters than could be evaluated from the existing data. Pending the outcome of further hyperfine structure measurements on CN, a more profitable course is to correct only for the largest effect of the rotational perturbation, which is the diminishment of the normal  ${}^2\Sigma$  hyperfine structure by the amplitude factor  $(1-\rho^2)^{1/2}$  in Eq. (7). In this way one avoids introducing any more unknown parameters, but has to neglect terms diagonal in  $J$  of the type  $\rho^2({}^2\Pi_{3/2} \times |H_{\text{hfs}}|^2\Pi_{3/2})$  and  $2\rho(1-\rho^2)^{1/2}({}^2\Sigma, v=0) |H_{\text{hfs}}|^2\Pi_{3/2}$ ,  $v=10$ ), as well as, off diagonal in  $J$ , the term  $\rho({}^2\Sigma, v=0, J=\frac{3}{2} |H_{\text{hfs}}|^2\Pi_{3/2}, v=10, J=\frac{7}{2})$ . Fortunately, these terms are not large: the first, because of the smallness of the  ${}^2\Pi_{3/2}$  hyperfine structure<sup>1</sup> is approximately 1 MHz in size; the latter two, because of the smallness of the vibrational overlap integral,<sup>4</sup> should not exceed 1 or 2 MHz. Within expected errors of at most a few megahertz, then, the perturbed hyperfine structure of the  $K=4$  doublet should be given by the calculation of the preceding section, provided the factor  $(1-\rho^2)$  is applied to the diagonal matrix element (3) and the factor  $(1-\rho^2)^{1/2}$  to the off-diagonal element (4). The results of the energy calculation are the same as before except for an additive correction term

$$-\frac{1}{2}\rho^2\alpha \quad (8)$$

outside the radical in Eq. (5) and another additive correction term

$$-\rho^2\{\mp 2\alpha[\Delta + b[F(F+1) - I(I+1) - (K + \frac{1}{2})^2]/(2K+1)] - \rho^2\alpha^2 + 4\beta^2\} \quad (9)$$

inside the radical of Eq. (5). Because it is easy to do, these results have been generalized to apply to any perturbed spin doublet of a  ${}^2\Sigma$  state. The appropriate diagonal matrix element is represented by  $\alpha$ ; this stands for the diagonal element (2) if the level  $J=K-\frac{1}{2}$  is perturbed and for the diagonal element (3) if the level  $J=K+\frac{1}{2}$  is perturbed. The ambiguous sign before  $2\alpha$  in (9) is to be taken  $-$  or  $+$  according to whether the perturbed level is, respectively,  $J=K-\frac{1}{2}$  or  $J=K+\frac{1}{2}$ . The symbol  $\beta$  stands for the off-diagonal matrix element (4).

Incomplete as they are, the corrections (8) and (9) do manage to account for nearly all of the departures of the perturbed CN hyperfine structure from the energy formula (5). Within an rms deviation of 3 MHz between the predicted and the measured level separations (both of which are shown in Table I) the experimental results of Evenson, Dunn, and Broida can be fitted by assigning the following numerical values:

$$\begin{aligned} \delta &= 497 \pm 10 \text{ MHz}, \\ b &= 467 \pm 10 \text{ MHz}, \\ c &= 60 \pm 15 \text{ MHz}, \\ eQq &= -5 \pm 5 \text{ MHz}, \end{aligned}$$

where the uncertainties are estimates based on the sensitivity of the predicted level separations to small changes in the parameters, as well as on the known inadequacies of the corrections (8) and (9). Since five level separations are available for the determination of four parameters, the fact that a fit is possible verifies reasonably well the quantum mechanical algebra that led to the energy formula (5).

#### ELECTRONIC STRUCTURE OF CN

The hyperfine structure parameters  $b$  and  $c$ , when combined with the nitrogen nuclear magnetic moment<sup>9</sup>  $\mu = +0.40369 \pm 0.00004 \mu_N$ , yield the following values for the molecular constants defined under Eq. (1):

$$\begin{aligned} \langle (3 \cos^2\chi - 1)/r^3 \rangle_{av} &= (7 \pm 2) \times 10^{24} \text{ cm}^{-3}, \\ |\Psi^2(0)| &= (10.2 \pm 0.2) \times 10^{24} \text{ cm}^{-3}. \end{aligned}$$

These results are perhaps best regarded as tests for Hartree-type molecular wave functions, but, in the absence of such functions for CN, they may be discussed in the simpler and more qualitative language of the valence bond model. In this language one may ask "Where is the unpaired electron?" and hope to get a definite answer from the measured hyperfine structure. The answer in the case of the NO molecule, for example, is that the electron occupies a  $\pi$ -bond orbital, spending 65% of its time close to the nitrogen nucleus and 35% of its time close to the oxygen nucleus.<sup>10</sup> Such results do not, of course, obviate the need for accurate molecular wave functions, but they do serve to correlate some of the diverse properties of molecules, and also may help to guide the course of subsequent wave function calculations.

The most stable valence-bond structure of CN is undoubtedly the triply bonded structure  $\cdot\text{C}\equiv\text{N}\cdot$ , in which the unpaired electron occupies a hybrid orbital of the carbon atom. For a  $\Sigma$  state this is a nonbonding  $\sigma$  orbital, extending mostly away from the nitrogen nucleus, and its hyperfine structure interaction with the nitrogen nucleus will be small—a rough estimate yields interaction constants a few megahertz in size. This structure, therefore, certainly does not fit the  $B\,{}^2\Sigma^+$  state of CN, although it probably suffices for the ground  $X\,{}^2\Sigma^+$  state.

Of valence bond structures which place the unpaired electron nearer the nitrogen nucleus, the most likely is the structure  $:\text{C}\equiv\text{N}\cdot$ , formed by taking one of the paired electrons of the triple bond structure out of its  $\sigma$ -bond orbital and placing it in the nonbonding  $\sigma$  orbital of the carbon nucleus. The alternative structure  $\cdot\text{C}\equiv\text{N}$  is probably unimportant; it runs counter to electronegativity principles by placing a positive formal charge on the more electronegative atom, and also runs counter to experimental indications that CN has a small

<sup>9</sup> W. G. Proctor and F. C. Yu, Phys. Rev. **77**, 716 (1950); **81**, 20 (1951).

<sup>10</sup> G. C. Doumanis, Phys. Rev. **97**, 967 (1955).

electric dipole moment.<sup>1</sup> The  $:C\equiv N:$  structure is more reasonable in these respects and satisfies, furthermore, the intuitive demand that an excited configuration embody some clearly defined excitation process; in this case it is the rupture of a covalent bond caused by moving an electron from the middle of the molecule to the far side of the carbon nucleus. Whether or not this excited configuration is in fact the  $B^2\Sigma^+$  state may be decided by appeal to its expected hyperfine structure, an estimate of which follows.

The strength and angular dependence of the hyperfine structure interaction depends chiefly on the orbital wave function near the nitrogen nucleus. Townes and Dailey's<sup>11</sup> analysis of quadrupole interactions in several nitrogen-containing molecules shows that this wave function for a  $\sigma$  bond can be represented rather well as a linear combination of  $2s$  and  $2p_z$  orbitals of the nitrogen atom, mixed in roughly equal proportions ("s character" of between 25 and 50%). Accordingly, an unpaired electron in a  $\sigma$ -bond orbital could show values of  $\Psi^2(0)$  and  $\langle(3\cos^2\chi-1)/r^3\rangle_{av}$  up to half as large as those characteristic of, respectively, a  $2s$  and a  $2p_z$  electron in a free nitrogen atom. This estimate is subject to a normalization correction for the distortion of the wave function toward the other nucleus, a correction which in the similar molecule NO reduces the hyperfine structure interaction by about 35%. If one assumes, for lack of better information, the same distortion in CN, a reasonable *a priori* estimate of the size of the hyperfine structure constants might be 30% of their free-atom values. Comparing the measured values of  $\Psi^2(0)$  and

$\langle(3\cos^2\chi-1)/r^3\rangle_{av}$  for CN with the free-atom values  $34\times 10^{24}\text{cm}^{-3}$  and  $18\times 10^{24}\text{cm}^{-3}$ , calculated by Dousmanis,<sup>10</sup> one sees that this 30% estimate is rather good; the actual percentages are, respectively, 33% and  $(39\pm 11)\%$ , the latter figure reflecting the rather large experimental uncertainty in the hyperfine structure constant  $c$ .

The hyperfine-structure measurements thus lend strong support to the postulated electronic structure  $:C\equiv N:$ , and the argument can now be inverted to get a better description of the  $\sigma$ -bond orbital. It is possible to determine simultaneously the  $s$  character of the orbital in the vicinity of the nitrogen nucleus and also the distortion of the orbital toward the carbon nucleus, i.e., the fractional contribution of atomic carbon orbitals to the total wave function. Neglecting the small hyperfine structure interaction of the electron with the nitrogen nucleus while it is in the relatively distant carbon orbitals, one finds 45% as the  $s$  character of the nitrogen orbital and 30% as the contribution of atomic carbon orbitals. Finally, this "wave function" may be tested by using it to predict the electric quadrupole coupling constant according to the method of Townes and Dailey,<sup>11</sup> a method which is discussed further for the case of NO by Lin, Hijikata, and Sakamoto.<sup>12</sup> The predicted coupling constant based on the value of  $\langle(3\cos^2\chi-1)/r^3\rangle_{av}$  calculated by Dousmanis and the nuclear quadrupole moment<sup>13</sup>  $Q=1.6\times 10^{-26}\text{cm}^2$ , is  $eQq=-3.5$  MHz, in essential (but noncritical) agreement with the experimental value of  $-5\pm 5$  MHz.

<sup>11</sup> C. H. Townes and B. P. Dailey, Jr., J. Chem. Phys. **17**, 782 (1949).

<sup>12</sup> C. C. Lin, K. Hijikata, and M. Sakamoto, J. Chem. Phys. **33**, 878 (1960).

<sup>13</sup> C. C. Lin, Phys. Rev. **119**, 1027 (1960).