Ionic Character and Hybridization in the Hydrogen Cyanide Molecule

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It is well known that the nuclear quadrupole coupling constant eQq is intimately related to the electronic structure near the nucleus of a molecule. Townes and Dailey$^{1)}$ have explained especially the ionic character and the hybridization of an atom from the analysis of the experimental values of the nuclear quadrupole constants. They have considered that the existence of a field gradient q is attributable to unbalanced electrons, i. e. p or d electrons in the valence shell.

Schatz has studied the ionic character and the hybridization of chlorine in discussing the chlorine, hydrogen chloride and methyl chloride molecules$^{2)}$, using the experimental values of the dipole moment besides the quadrupole coupling constant, and has stressed the importance of including the overlap integral for the estimation of the quadrupole coupling constant. However, his calculations of the field gradient are essentially based on the theory by Townes and Dailey$^{1)}$. Namely, he assumed the total quadrupole coupling constant dependent upon only the $3p$ and $3d$ electrons of chlorine and ignored the effects of other electrons and nuclei in the molecule.

In this paper, the ionic character and the s character of the nitrogen atom in a hydrogen cyanide molecule have been investigated by means of the theoretical evaluation of the dipole moment and the quadrupole coupling constant taking into account the effects of all the electrons and nuclei in a hydrogen cyanide molecule.

Calculation Method

Basic Wave Function. — The hydrogen cyanide molecule is a linear molecule having an NC bond distance equal to 1.156 Å and a CH bond distance equal to 1.1064 Å as determined by microwave measurements$^{3)}$. The hydrogen cyanide molecule is taken to lie along the Z axis with its nitrogen atom at the origin. The total wave function used is the following valence bond function including an ionic term ($N^- = C^+$), that is,

$$\Psi_T = A\left[\Psi_{cov} + \lambda_1 \Psi_{\sigma ion} + \lambda_2(\Psi_{\pi_x ion} + \Psi_{\pi_y ion})\right] \quad (1)$$

Where A is the normalization factor and four state functions appearing in Eq. 1 are taken as simple products of the following electron pair bond functions with the Heitler-London type:

$$\left.\begin{aligned}
\Psi_{cov} &= (NC:\sigma)^2(CH:\sigma)^2(N_2:\sigma)^2 \\
&\quad\times(NC:\pi_x)^2(NC:\pi_y)^2 \\
\Psi_{\sigma ion} &= (N_1:\sigma)^2(CH:\sigma)^2(N_2:\sigma)^2 \\
&\quad\times(NC:\pi_x)^2(NC:\pi_y)^2 \\
\Psi_{\pi_x ion} &= (NC:\sigma)^2(CH:\sigma)^2(N_2:\sigma)^2 \\
&\quad\times(N:\pi_x)^2(NC:\pi_y)^2 \\
\Psi_{\pi_y ion} &= (NC:\sigma)^2(CH:\sigma)^2(N_2:\sigma)^2 \\
&\quad\times(NC:\pi_x)^2(N:\pi_y)^2
\end{aligned}\right\} \quad (2)$$

and

$$\left.\begin{aligned}
(NC:\sigma)^2 &= A_1[n_1(i)c_2(j) + c_2(i)n_1(j)] \\
(CH:\sigma)^2 &= A_2[c_1(i)h(j) + h(i)c_1(j)] \\
(NC:\pi_x)^2 &= A_3[n_{\pi_x}(i)c_{\pi_x}(j) \\
&\qquad + c_{\pi_x}(i)n_{\pi_x}(j)] \\
(N:\pi_x)^2 &= n_{\pi_x}(i)n_{\pi_x}(j) \\
(N_1:\sigma)^2 &= n_1(i)n_1(j)
\end{aligned}\right\} \quad (3)$$

$(NC:\pi_y)^2$, $(N:\pi_y)^2$ and $(N_2:\sigma)^2$ are taken with the analogous definitions to $(NC:\pi_x)^2$, $(N:\pi_x)^2$ and $(N_1:\sigma)^2$, respectively. Therefore, in the wave function used, the higher order permutation of the electrons is neglected; that is, the orthogonarity among the electron pair bonds is assumed. The coefficients A_1, A_2 and A_3 of the electron pair bond functions are easily shown to be

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

2) P. N. Schatz, ibid., **22**, 695 (1954); **22**, 755 (1954); **22**, 1974 (1954).

3) J. W. Simmon, W. E. Anderson and W. Gordy, *Phys. Rev.*, **77**, 77 (1950).

$$\left.\begin{aligned}
&A_1=[2(1+S_{n_1c_2}{}^2)]^{-1/2}\\
&A_2=[2(1+S_{c_1h}{}^2)]^{-1/2}\\
&A_3=[2(1+S_{n_\pi c_\pi}{}^2)]^{-1/2}\\
&S_{n_1c_2}=\int n_1c_2\mathrm{d}v \qquad Sc_1h=\int c_1h\mathrm{d}v\\
&S_{n_\pi c_\pi}=\int n_\pi c_\pi\mathrm{d}v
\end{aligned}\right\}\quad(4)$$

Futhermore h, $c_{\pi x}$, $c_{\pi y}$, $n_{\pi x}$ and $n_{\pi y}$ are atomic orbitals (AO), and n_1, n_2, c_1 and c_2 are the following $s-p$ hybridized orbitals:

$$\left.\begin{aligned}
&n_1=\alpha^{1/2}(N:2s)+(1-\alpha)^{1/2}(N:2pz)\\
&n_2=(1-\alpha)^{1/2}(N:2s)-\alpha^{1/2}(N:2pz)\\
&c_1=2^{-1/2}[(C:2s)+(C:2pz)]\\
&c_2=2^{-1/2}[(C:2s)-(C:2pz)]
\end{aligned}\right\}\quad(5)$$

All the AO's except the $2p$ orbitals of nitrogen are the Slater orbitals[4] (assumed effective nuclear charge $\delta_h=1.17$, $\delta_c=1.625$ and $\delta_n=1.95$). The $2p$ orbitals of nitrogen have a great effect on the field gradient at the nitrogen nucleus. Then, the following analytic function derived from the Hartree-Fock field calculation of the ground state ${}^4S$ of the nitrogen atom[5] is used for its radial function instead of the Slater orbital,

$$\begin{aligned}R_{2p}=r\,[&1.809\exp(-1.387r)\\&+6.620\exp(-2.950r)]\end{aligned}\quad(6)$$

Dipole Moment.—The experimental value of the dipole moment of hydrogen cyanide has been known to be 3.00 D[3] and also it is given by the expression

$$\mu_T=e(\sum_{i=1}^{2}r_i-\sum_{j=1}^{10}\overline{Z_j})\quad(7)$$

$$\sum_{i=1}^{2}r_i=6.7440\ \text{Å}\quad \overline{Z_j}=\int|\Psi_T|^2Z_j\mathrm{d}v\quad(8)$$

Where e is the protonic charge (4.80288×10^{-10} esu), the first and the second term in Eq. 7 are, respectively, the contributions of the nuclei and the electrons. When the latter are calculated by the wave function given in Eq. 1, the expression is easily shown to be

$$\sum_{j=1}^{10}Z_j=M_{cov}+M_{\sigma ion}+M_{\pi ion}+M_{trans}\quad(9)$$

where

$$\left.\begin{aligned}
&M_{cov}=2\,[M(NC:\sigma)+M(CH:\sigma)\\
&\qquad+2M(NC:\pi)+M_{n_2n_2}]\\
&M_{\sigma ion}=2\lambda_1{}^2\,[M(CH:\sigma)+2M(NC:\pi)]\\
&M_{\pi ion}=4\lambda_2{}^2\,[M(NC:\sigma)+M(CH:\sigma)\\
&\qquad+M(NC:\pi)+M_{n_2n_2}]\\
&M_{trans}=4\lambda_1A_1\,[M_{n_1c_2}+2S_{n_1c_2}\{M(CH:\sigma)\\
&\quad+2M(NC:\pi)+1/2M_{n_2n_2}\}]\\
&\quad+8\lambda_2A_3\,[M_{n_\pi c_\pi}+2S_{n_\pi c_\pi}\{M(NC:\sigma)\\
&\quad+M(CH:\sigma)+M(NC:\pi)+M_{n_2n_2}\}]\\
&\quad+16\lambda_1\lambda_2A_1A_3\,[S_{n_\pi c_\pi}M_{n_1c_2}\\
&\quad+S_{n_1c_2}M_{n_\pi c_\pi}+2S_{n_1c_2}S_{n_\pi c_\pi}\\
&\quad\times\{M(CH:\sigma)+M(NC:\pi)\\
&\quad+1/2M_{n_2n_2}\}]
\end{aligned}\right\}\quad(10)$$

and the following abbreviations are adopted:

$$\left.\begin{aligned}
&M(NC:\sigma)=A_1{}^2(M_{n_1n_1}+M_{c_2c_2}\\
&\qquad+2S_{n_1c_2}M_{n_1c_2})\\
&M(CH:\sigma)=A_2{}^2(M_{c_1c_1}+M_{hh}\\
&\qquad+2S_{c_1h}M_{c_1h})\\
&M(NC:\pi)=A_3{}^2(M_{c_\pi c_\pi}+2S_{n_\pi c_\pi}M_{n_\pi c_\pi})
\end{aligned}\right\}\quad(11)$$

Also the normalization factor A is shown to be

$$\begin{aligned}A=(&1+\lambda_1{}^2+2\lambda_2{}^2+4A_1S_{n_1c_2}\lambda_1+8A_3S_{n_\pi c_\pi}\lambda_2\\&+16A_1A_3S_{n_1c_2}S_{n_\pi c_\pi}\lambda_1\lambda_2)^{-1/2}\end{aligned}\quad(12)$$

The necessary integrals of the dipole moment matrices: $M_{ab}=\int\chi_aZ\chi_b\mathrm{d}v$ and the overlap integrals: $S_{ab}=\int\chi_a\chi_b\mathrm{d}v$ are given to Table I. These values are obtained by the ordinary method[6].

Quadrupole Coupling Constant. — The experimental value of the nuclear quadrupole coupling constant has been known from the microwave datum to be -4.58 Mc.[3] On the other hand, the quadrupole coupling constant is shown to have the following expression:

$$eQq_T=eQ(q_n+q_{el})\quad(13)$$

$$q_n=0.79295e\ e\ \text{a.u.}$$

$$q_{el}=-e\int|\Psi_T|^2(3\cos^2\theta_z-1)/r^3\mathrm{d}v\quad(14)$$

Where q_T is the average value of $(\partial^2V/\partial Z^2)_{z=0}$, V being all the electrostatic potentials and Q the nuclear quadrupole moment of nitrogen ($=2\times10^{-26}\ \mathrm{cm}^2$)[1]. In Eq. 13, the

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[4] J. C. Slater, ibid., **36**, 57 (1932).

[5] D. R. Hartree and W. Hartree, *Proc. Roy. Soc.* (*London*), **A193**, 299 (1948).

[6] For example, M. Kotani et al., "Table of Molecular Integrals", Maruzen Co., Ltd., Tokyo (1955).

TABLE I. VALUES OF MOLECULAR INTEGRALS:

$$S_{ab}=\int\chi_a\chi_b\mathrm{d}v,\quad M_{ab}=\int\chi_a Z\chi_b\mathrm{d}v$$

(in Angstrom as unit)

S_{c_sh}	0.50876	M_{c_sh}	0.012501
$S_{c_\sigma h}$	0.49357	$M_{c_\sigma h}$	0.16891
$S_{n_sc_s}$	0.47011	$M_{n_sc_s}$	−0.040613
$S_{n_sc_\sigma}$	−0.49979	$M_{n_sc_\sigma}$	0.18131
$S_{n_\sigma c_s}$	0.39765	$M_{n_\sigma c_s}$	0.13353
$S_{n_\sigma c_\sigma}$	−0.30254	$M_{n_\sigma c_\sigma}$	−0.026792
$S_{n_\pi c_\pi}$	0.29880	$M_{n_\pi c_\pi}$	−0.020225
		$M_{c_sc_\sigma}$	0.47003
		$M_{n_\sigma n_s}$	0.39169

The following abbreviated notations for AO's are used; $h=(H{:}1s)$, $c_s=(C{:}2s)$, $c_\sigma=(C{:}2pz)$, $c_\pi=(C{:}2px$ or $2py)$, $n_s=(N{:}2s)$, $n_\sigma=(N{:}2pz)$ and $n_\pi=(N{:}2px$ or $2py)$. The one-center and the two-center integrals are respectively evaluated with the nucleus in question and the center of internuclear distance as the origin.

first and the second term on the right are, respectively, the contributions of the nuclei except the nitrogen nucleus and the electrons to the field gradient q_T. q_{el} is calculated by Eq. 1 as follows:

$$\begin{aligned}q_{el}=&2[q(NC:\sigma)+q(CH:\sigma)\\&+2q(NC:\pi)+q_{n_2n_2}]\\&+2\lambda_1^2[q(CH:\sigma)+2q(NC:\pi)+2q_{n_1n_1}]\\&+4\lambda_2^2[q(NC:\sigma)+q(CH:\sigma)+q(NC:\pi)\\&+q_{n_2n_2}+q_{n_\pi n_\pi}]\\&+4A_1\lambda_1[q_{n_1c_2}+2S_{n_1c_2}\{q(CH:\sigma)\\&+2q_{n_\pi c_\pi}+3/2\,q_{n_1n_1}\}]\\&+8A_3\lambda_2[q_{n_\pi c_\pi}+2S_{n_\pi c_\pi}\{q(NC:\sigma)\\&+q(CH:\sigma)+q_{n_2n_2}+q_{n_\pi c_\pi}+1/2\,q_{n_\pi n_\pi}\}]\\&+16A_1A_3\lambda_1\lambda_2[S_{n_\pi c_\pi}q_{n_1c_2}+S_{n_1c_2}q_{n_\pi c_\pi}\\&+2S_{n_1c_2}S_{n_\pi c_\pi}\{q(CH:\sigma)\\&+q(NC:\pi)+3/2\,q_{n_1n_1}+1/2\,q_{n_\pi n_\pi}\}]\end{aligned}\tag{15}$$

Here the following abbreviations are adopted:

$$\left.\begin{aligned}q(NC:\sigma)&=A_1^2(q_{n_1n_1}+q_{c_2c_2}\\&\qquad+2S_{n_1c_2}q_{n_1c_1})\\q(CH:\sigma)&=A_2^2(q_{c_1c_1}+q_{hh}+2S_{c_1h}q_{c_1h})\\q(NC:\pi)&=A_3^2(q_{n_\pi n_\pi}+q_{c_\pi c_\pi}\\&\qquad+2S_{n_\pi c_\pi}q_{n_\pi c_\pi})\end{aligned}\right\}\tag{16}$$

All $q_{ab}=-eq_{ab}'=-e\int\chi_a(3\cos^2\theta_z-1)/r^3\chi_b\mathrm{d}v$ are calculated by using the methods of Barnett and Coulson[7]. These values are given in Table II.

TABLE II. VALUES OF FIELD GRADIENT INTEGRALS:

$$q_{ab}'=\int\chi_a(3\cos^2\theta_z-1)/r^3\chi_b\mathrm{d}v\ \text{(in atomic unit)}$$

$q_{n_\sigma n_\sigma}'$	2.36606	$q_{c_sc_s}'$	0.098460
$q_{n_\pi n_\pi}'$	−1.18303	$q_{c_sc_\sigma}'$	−0.048937
$q_{n_sc_s}'$	0.030116	$q_{c_\sigma c_\sigma}'$	0.133908
$q_{n_sc_\sigma}'$	−0.045963	$q_{c_\pi c_\pi}'$	0.080736
$q_{n_\sigma c_s}'$	0.102260	q_{hh}'	0.011326
$q_{n_\sigma c_\sigma}'$	−0.160130	q_{c_sh}'	0.027928
$q_{n_\pi c_\pi}'$	−0.012108	$q_{c_\sigma h}'$	0.035842

The three-center integrals q_{c_sh}' and $q_{c_\sigma h}'$ are evaluated by Ruedenberg-Mulliken's approximation[8];

$$\int\chi_a 1/r_c^3\chi_b\mathrm{d}v\approx1/2\,S_{ab}\left(\int|\chi_a|^2 1/r_c^3\mathrm{d}v+\int|\chi_b|^2 1/r_c^3\mathrm{d}v\right)$$

Results and Discussion

The parameters to be determined are the ionic characters λ_1, λ_2 and the $s-p$ hybridization of nitrogen α. Now, in use of Eqs. 7 and 13, the relation of λ_1 and λ_2

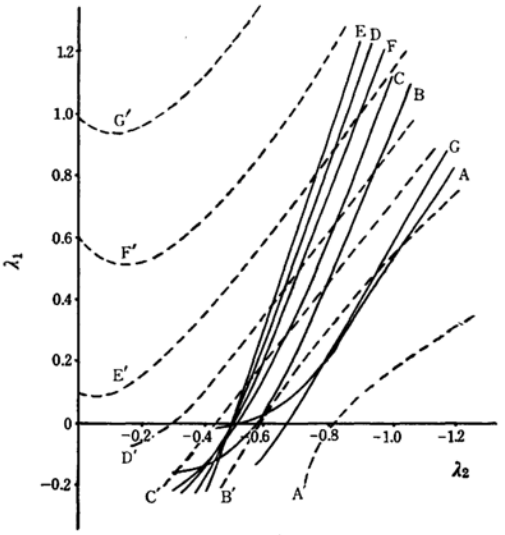

Fig. 1. The relationship between λ_1 and λ_2, being chosen in all cases to give the experimental values. α is taken as a parameter. The full and dotted lines are respectively the curves of the dipole moment and the quadrupole coupling constant.

A: $\alpha=0.2$ A′: $\alpha=0.20$
B: $\alpha=0.3$ B′: $\alpha=0.30$
C: $\alpha=0.4$ C′: $\alpha=0.35$
D: $\alpha=0.5$ D′: $\alpha=0.40$
E: $\alpha=0.6$ E′: $\alpha=0.45$
F: $\alpha=0.7$ F′: $\alpha=0.50$
G: $\alpha=0.8$ G′: $\alpha=0.60$

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[7] M. P. Barnett and C. A. Coulson, *Trans. Roy. Soc.* (*London*), **243**, 221 (1951).

[8] R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949); K. Ruedenberg, *J. Chem. Phys.*, **19**, 1433 (1951).

which are taken to coincide with the experimental values is shown in Fig. 1, in which the hybridization α is taken as a parameter. From Fig. 1, it is seen that the dipole moment is not much affected by the s character between $\alpha=0.3$ and 0.7, but it depends on the ionicity as a considerable extent. This will explain the well-known fact that there is a possibility to take up the ionic character as a measure of the dipole moment[9]. On the other hand, the eQq curves are intensely dependent upon the s character, too. The α, λ_1 and λ_2 values are not determined simultaneously, but it will be clear from Fig. 1 that the region of allowed α value is between about 0.3 and 0.5. Now, it is possible to calculate the NC bond moment under the same scheme as above. The NC bond moments for the reasonable set of α, λ_1 and λ_2 obtained from Fig. 1 are as follows:

α	λ_1	λ_2	NC bond moment
0.50	1.81	−1.16	2.57 D
0.45	1.04	−0.94	3.38 D
0.40	0.61	−0.80	1.61 D
0.35	0.35	−0.72	1.59 D
0.30	0.04	−0.60	1.42 D

The NC bond moment has been estimated to be about 3.5 D by Smyth[10]. If his estimation is correct, a reasonable set of three parameters would be taken to be $\alpha=0.45$, $\lambda_1=1.04$ and $\lambda_2=-0.94$. Then, the experimental value of total molecular dipole moment of the hydrogen cyanide molecule 3.0 D can be explained to be 3.4 D (N^-C^+ bond moment) plus −0.4 D (C^+H^- bond moment). The value −0.4 D for the C^+H^- bond moment may be acceptable taking into account the inclusion of the atomic dipole term by Coulson[11].

From the eQq data, Townes and Dailey[1] and separately Dailey[12] have estimated the structure of HCN as follows:

	Structure		Assumed s character	Assumed eQq per p electron**	
	Covalent	Ionic			
	90%	10%	25%	−24 Mc.	Townes &
or	90%	10%	50%	−10 Mc.	Dailey
	90%	10%	45%	—	Dailey

In both estimates, obviously some arbitrariness exists in the determination of the parameters because of several having been obtained from only one experiment value. On the other hand, Pauling[13] has presumed that the ionicity of the NC bond would probably have about 57% from the experimental values of the dipole moment of alkyl cyanides. The relative weights of structures are expressed in the following two ways; the one is due to the definition that the weights of the covalent and two ionic parts are given in the ratio $1:\lambda_1^2:2\lambda_2^2$ by Coulson[14] (I), and the other includes a transitional structure as well as covalent and ionic by Syrkin and Dyatkina[15] (II). Then, the following results are obtained from the present calculation:

Structure		Weight of structure, % By I	By II
Covalent	(A)	26.0	10.2
σ ionic	(B)	28.1	11.2
π_x & π_y ionic	(C)	45.9	18.1
Transitional	(A)—(B)		21.3
〃	(A)—(C)		19.3
〃	(B)—(C)		20.0

Following the definition by Coulson, the present result with 74% as the ionic structure seems rather to support Pauling's conclusion. Here it is interesting to note that in a triple bond NC, each structure with the σ or π polarized bond has nearly equal weight, notwithstanding the fact that σ bond has larger overlap (∼0.7) and, on the other hand, π bond smaller overlap (∼0.3). However, it is probably impossible in the present calculation to state anything about the relationship between the degree of the overlap of each bond in the multiple bond and the polarization of the bond or the mobilities of electron in bond.

Fig. 2 shows the curves of the quadrupole coupling constants calculated, taking into account only p electrons of nitrogen and all the charges for the field gradient at the nitrogen nucleus with $\alpha=0.45$. Now, being taken to fix λ_1 and λ_2 values, the eQq values taking into account the contribution of all the charges are always larger than ones for only p electrons. This difference probably depends upon whether or not the charge distribution in the overlap

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[9] L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N. Y. (1940), p. 46.

[10] C. P. Smyth, *J. Am. Chem. Soc.*, **60**, 183 (1938).

[11] C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).

[12] B. P. Dailey, *J. Phys. Chem.*, **57**, 490 (1953).

** Using Eq. 6, the authors obtain −11.12 Mc. for *eQq* per *2pz* electron; Y. Kato et al., This Bulletin, **32**, 527 (1959).

[13] See Ref. 9, p. 75.

[14] C. A. Coulson, "Valence", Oxford Univ. Press, London (1952), p. 123.

[15] Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond". Butterworths Scientific Publications, London (1950), p. 205.

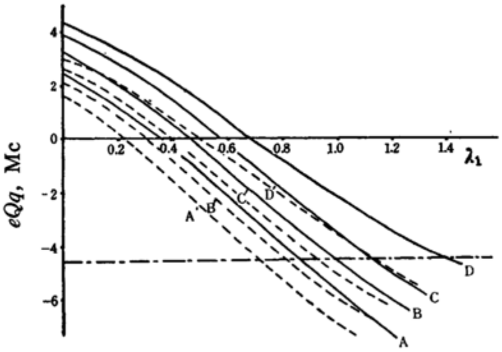

Fig. 2. Quadrupole coupling constant of HCN as a function of λ_1. λ_2 is taken as a parameter and α is fixed to 0.45. The horizontal chain line is the experimental value. The full and dotted lines are respectively the curves under the consideration of all the charge and only p electrons for the field gradient at the nitrogen nucleus.

A & A': $\lambda_2=-0.8$
B & B': $\lambda_2=-0.9$
C & C': $\lambda_2=-1.0$
D & D': $\lambda_2=-1.1$

region is taken into account in evaluating the field gradient. Gordy[16] has argued that the overlap effects should be ignored and has pointed out the merits of his simple relation between the ionicity and quadrupole coupling constant in which the s character is neglected entirely. Certainly the field gradient is proportional to $1/r^3$, but at the same time to the charge density. Therefore, it should be naturally required for the evaluation of the nuclear quadrupole coupling constant to take into account not only the redistribution of the charge near the nucleus due to the formation of the chemical bond, but also the distribution of the charge in bonding region because of its larger density.

In this point, the present results will support Schatz's calculation of eQq including the overlap effects.

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[16] W. Gordy, *J. Chem. Phys.*, **19**, 792 (1951); W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy", John Wiley & Sons, Inc., New York (1953), p. 272.