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Dependence of Quadrupole Coupling Constant on the Vibrational State in ICN Molecule

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The microwave spectrum of the hyperfine components of the $J=1\leftarrow 0$ and $J=2\leftarrow 1$ rotational transitions of ICN molecule has been measured and the dependence of quadrupole coupling constant on the vibrational state was found. The values of $(eqQ)_I$ for each vibrational state are as follows:

Vibrational States	$(eqQ)_I$ in Mc/sec	
	from the frequencies of the $J=1\leftarrow 0$ transition	from the frequencies of the $J=2\leftarrow 1$ transition
(0, 0, 0)	-2418.8 ± 0.5	-2420.1 ± 0.3
(1, 0, 0)	-2426.8 ± 0.7	-2425.1 ± 0.5
(0, 2, 0)	-2403.3 ± 0.8	-2403.1 ± 0.5

The difference in the $(eqQ)_I$ value for the (0, 2, 0) state from that for the (0, 0, 0) state, previously explained by Javan for the (0, 1, 0) state, was confirmed, though the numerical values are slightly different from his. The change of $(eqQ)_I$ due to the excitation of the stretching vibration was also found and was explained in terms of the change of the double bond character of I-C bond.

§ 1. Introduction

The dependence of quadrupole coupling constant on the vibrational states of the molecule has been described by several authors.¹⁾⁻⁵⁾ Tetenbaum pointed out the change of $(eqQ)_{Br}$ of BrCN molecule when the bending vibration

was excited.²⁾ Javan remeasured the lines of the $J=4\leftarrow 3$ rotational transition of ICN molecule and confirmed the change of $(eqQ)_I$.⁶⁾ He explained it taking into account the change of q , the gradient of the electric field along the nuclear axis produced by the electrons.

Though both of them did not refer to the change of the quadrupole coupling constant due to the excitation of the stretching vibra-

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tion, this change seems to be possible, because the stretching vibration tends to elongate the bond and thus decreases the double bond character of I-C bond, which results in the increase of $(eqQ)_I$. This work has been carried out with the aim of investigating these changes.

§ 2. Experiments and Results

The hyperfine components of the $J=1\leftarrow 0$ and $J=2\leftarrow 1$ rotational transitions of ICN molecule have been measured with the Stark modulation spectrometer of four meters in length. The frequencies have been obtained by extrapolating the observed frequencies at various Stark fields to those at zero field. The measured frequencies with the calculated ones are shown in Table Ia and II a. For

Table Ia.

Frequencies of the hyperfine components of the $J=1\leftarrow 0$ rotational transition for $IC^{12}N$ in Mc/sec.

		(0, 0, 0) lines	
F_i	F_f	observed	calculated
5/2	7/2	6577.06	6577.81
		6577.95	
5/2	5/2	6070.66	6071.33
		6071.61	
5/2	3/2	6799.79	6799.77
		(1, 0, 0) lines	
F_i	F_f	observed	calculated
5/2	7/2	6559.63	6559.56
5/2	5/2	6051.36	6051.41
5/2	3/2	6782.16	6782.28
		(0, 2, 0) lines	
F_i	F_f	observed	calculated
5/2	7/2	6610.24	6610.00
5/2	5/2	6106.71	6106.75
5/2	3/2	6830.47	6830.50

Table Ib.

Values of $(eqQ)_I$ and rotational constant B for $IC^{12}N$ derived from the frequencies of the $J=1\leftarrow 0$ transition

Vibrational state	$(eqQ)_I$ in Mc/sec	B in Mc/sec
(0, 0, 0)	-2418.8 ± 0.5	3225.77 ± 0.1
(1, 0, 0)	-2426.8 ± 0.7	3216.42 ± 0.1
(0, 2, 0)	-2403.3 ± 0.8	3242.30 ± 0.1

almost all lines, probable errors were less than 0.05 Mc/sec. The largest probable error amounted to 0.5 Mc/sec for the weakest lines.

I. Hyperfine components of the $J=1\rightarrow 0$ rotational transition.

Three hyperfine components due to the nuclear quadrupole moment of I^{127} were observed for each vibrational state, (0, 0, 0), (1, 0, 0), and (0, 2, 0). Since the initial state is $I=0$, (0, 1, 0) lines are not allowed. Because of the nuclear quadrupole moment of N^{14} , the lines are further split. This effect was taken into consideration in the analysis of the frequencies using the method proposed by Bardeen and Townes with -3.8 Mc/sec for $(eqQ)_N$ of ICN molecule.⁷⁾ The lines of the excited vibrational states were so weak that the splitting due to the nitrogen quadrupole moment could not be measured. The values of $(eqQ)_I$ and the rotational constants B derived from the measured frequencies and used in the calculation are listed in Table Ib.

II. Hyperfine components of the $J=2\leftarrow 1$ rotational transition.

According to the selection rule $\Delta F = \pm 1, 0$,

Table II a.

Frequencies of the hyperfine components of the $J=2\leftarrow 1$ rotational transition for $IC^{12}N$ in Mc/sec

		(0, 0, 0) lines	
F_i	F_f	observed	calculated
7/2	9/2	12956.38	12956.08
		12489.27	
7/2	7/2	12489.88	12489.35
		12622.19	
7/2	5/2	12996.93	12996.09
		12996.50	
5/2	7/2	12994.98	12996.09
		13129.36	
5/2	5/2	13129.68	13129.35
		13465.77	
5/2	3/2	13465.77	13465.73
3/2	5/2	12400.35	12400.54
		12401.33	
3/2	3/2	12737.22	12736.92
3/2	1/2	13048.33	13048.42
		(1, 0, 0) lines	
F_i	F_f	observed	calculated
7/2	7/2	12451.36	12451.37
5/2	7/2	12959.17	12959.17
5/2	3/2	13429.80	13429.80
3/2	3/2	12699.69	12699.46
3/2	1/2	13011.34	13011.63
		(0, 2, 0) lines	
F_i	F_f	observed	calculated
7/2	9/2	13021.92	13021.88
7/2	7/2	12558.38	12558.42
5/2	5/2	13193.32	13193.80
5/2	3/2	13527.88	13527.95

Table II b.

Values of $(eqQ)_I$ and rotational constant B for $IC^{12}N$ derived from the frequencies of the $J=2\leftarrow 1$ transition

Vibrational state	$(eqQ)_I$ in Mc/sec	B in Mc/sec
(0, 0, 0)	-2420.1 ± 0.3	3225.56 ± 0.05
(1, 0, 0)	-2425.1 ± 0.5	3216.28 ± 0.04
(0, 2, 0)	-2403.1 ± 0.5	3242.11 ± 0.05

nine hyperfine components should be observed for each vibrational state, (0, 0, 0), (1, 0, 0), (0, 2, 0), (0, 1, 0), and (1, 1, 0), where the last two allow I -doublets. Because of complexity of the Stark pattern of these I -doublets and their inadequacy for the purpose of this work, only strong lines belonging to the (0, 0, 0), (1, 0, 0), and (0, 2, 0) vibrational states have been measured. Many strong I -doublets with large Stark shift made it very difficult to measure accurately the lines which overlap with them, and some lines were abandoned for this reason. The values of $(eqQ)_I$ and rotational constants B derived from these frequencies and used in the calculation are listed in Table II b.

§ 3. Discussions

The changes of $(eqQ)_I$ due to the excitation of the bending vibration were 15.5 Mc/sec and 17.0 Mc/sec for the $J=1\leftarrow 0$ and $J=2\leftarrow 1$ transitions, respectively. Javan⁵⁾ measured (0, 1, 0) lines and obtained 9.45 Mc/sec for the change, which corresponds to 18.90 Mc/sec of our case, because of the fact that the mean square amplitude is proportional to the vibrational quantum number. The gradient of the electric field when the bending vibration is excited is given by the formula, $q=(1-3/2\bar{\theta}^2)q_0$ ⁵⁾ where q_0 is the value of q for the ground vibrational state and $\bar{\theta}^2$ is the mean square amplitude of the deflection angle of I-C bond from its equilibrium direction when the bending vibration is excited. Using the above formula with the mean square amplitude calculated from the vibrational spectrum, the change of $(eqQ)_I$ is calculated to be 12.6 Mc/sec. The rest of the change seems to be due to the fact that the valence electrons do not follow the motion of I and C nuclei.

The changes of $(eqQ)_I$ due to the excitation of the stretching vibration are 8.0 Mc/sec and 5.0 Mc/sec for the $J=1\leftarrow 0$ and $J=2\leftarrow 1$ trans-

itions, respectively. Though there is rather large discrepancy between these values, the change of $(eqQ)_I$ is beyond the experimental error. This change may be explained by considering the change of the weight of the two resonating structures,⁶⁾ $I-C\equiv N$ and $I^+=C=N^-$. The magnitude of q of the double bond structure is half as large as that of the single bond structure. When the stretching vibration is excited, the bond is elongated owing to the anharmonicity of the potential energy and thus the double bond character of I-C bond is decreased. This consideration explains the increase in the magnitude of $(eqQ)_I$ in agreement with the experiment. The order of magnitude of this kind of change is estimated using Pauling's relation between the bond length and the double bond character. The change of the rotational constant B due to the excitation of the stretching vibration is assumed to be due to the proportional stretching of I-C bond and C-N bond, approximating the bond length of I-C bond in (1, 0, 0) state as $r_0 = r_0 (B_0/B_v)^{1/2}$, where r_0 is the bond length of I-C bond in the ground vibrational state and B_0 and B_v are rotational constants of the ground and excited vibrational states, respectively. Substituting the values in Table I b and II b with $r_0 = 1.995 \text{ \AA}$ ⁸⁾, it gives $r_0 = 1.998 \text{ \AA}$. The double bond character x of I-C bond for ICN molecule calculated from the observed value of $(eqQ)_I$ is 0.13⁹⁾. From Pauling's relation,⁹⁾

$$R = [R_1(1-x) + 3R_2x] / [(1-x) + 3x],$$

the variation of x due to the change of the bond length δR is calculated to be

$$\delta x = x(2x+1)\delta R / (R-R_1),$$

where R_1 is the I-C bond length when pure single bond is assumed. Substituting $x=0.13$, $R=1.995 \text{ \AA}$, $R_1=2.10 \text{ \AA}$, and $\delta R = r_0 - r_0 = 0.003 \text{ \AA}$, this formula gives the change of the double bond character due to the stretching of the I-C bond as $\delta x = -0.0047$. Though the value of 2.10 \AA for R_1 is not quite definite, the difference as large as 0.01 \AA in R_1 does not affect the first figure of δx . The gradient of the electric field is given by the formula,

$$q(x) = [-(1-s+d)(1-x) - (1/2-s+d)(1+\varepsilon)x]q_{\delta 10},^{10)}$$

where $q_{\delta 10}$ is the value of q for iodine atom, and s and d indicate the fraction of s and d

hybridization, respectively. Because of the positive ionization of the I atom in the $I^+=C=N^-$ structure, which pulls the electron closer to the nucleus, the factor $1+\varepsilon$ is multiplied to the second term. This is differentiated to give the variation of q due to the change of the double bond character x as

$$\delta q = [1/2 - \varepsilon(1/2 - s + d)]q_{s10}\delta x.$$

For the case of I-C bond $s-d$ and ε can safely be estimated to be 0.15 and 0.15, respectively. With these values and the above mentioned value of δx , it is shown that

$$q(1, 0, 0)/q(0, 0, 0) = 1.0026$$

which is in fair agreement with the following experimental values

$$q(1, 0, 0)/q(0, 0, 0) = \begin{cases} 1.0033 & (J=1\leftarrow 0) \\ 1.0021 & (J=2\leftarrow 1). \end{cases}$$

Major part of the discrepancy between the two values seems to be due to the experimental error, which arises chiefly from the weakness of the lines and the splittings due to the nuclear quadrupole moment of N^{14} . The value derived from the lines of the $J=2\leftarrow 1$ transition seems to be more reliable than that from the $J=1\leftarrow 0$ transition, because more appropriate lines could be adopted for analysis in the former case than the latter.

§ 4. Isotope Lines

The spectrum of the hyperfine components of the $J=1\leftarrow 0$ rotational transition for $IC^{13}N$ molecule in the (0, 0, 0) state was observed. The measured frequencies are shown in Table III. The hyperfine components of the $J=2\leftarrow 1$ transition of $IC^{13}N$ molecule could not be measured, being hidden by the complicated I -

doubling lines of $IC^{12}N$.

Table III.

Frequencies of the hyperfine components of the $J=1\leftarrow 0$ rotational transition for $IC^{13}N$ in Mc/sec

		(0, 0, 0) lines
F_i	F_f	
5/2	7/2	6480.72
5/2	5/2	5974.43
5/2	3/2	6703.25

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