Dipole Moments and Nuclear Quadrupole Coupling Constants of Alkyl Halides

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The relation between nuclear quadrupole coupling constants of molecules and the nature of chemical bonds has been discussed by Townes and Dailey⁽¹⁾. Miyagawa⁽²⁾ pointed out a parallelism between the nuclear quadrupole coupling constant and the apparent C—Cl bond moment of various chlorides.

It has been known that the dipole moment of alkyl halide increases with the increasing number of carbon atoms. The data are listed in Table I. This fact has hitherto been interpreted by an inductive effect⁽³⁾, which, however, has not always given a satisfactory interpretation to it. At the same time, the values of nuclear quadrupole coupling constants of these molecules in the solid state decrease zigzag with the increasing number of carbon

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

[2] I. Miyagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 1061 (1954).

[3] K. Higashi, *J. Chem. Soc. Japan* (*Nippon Kagaku Kaisi*). **57**, 1006 (1936); L. G. Groves and S. Sugden, *J. Chem. Soc.*, **1937**, 158.

TABLE I

DIPOLE MOMENTS* OF ALKYL HALIDE (DEBYE UNITS)

CH_3Cl	1.869[a]	CH_3Br	1.797[a]	CH_3I	1.647[a]
C_2H_5Cl	1.98[b]	C_2H_5Br	1.99[c]	C_2H_5I	1.93[c]
	2.00[c]		2.01[d]		1.87[d]
n-C_3H_7Cl	2.04[e]	n-C_3H_7Br	2.01[c]	n-C_3H_7I	1.97[c]
			2.15[d]		2.01[d]
n-C_4H_9Cl	2.11[d]	n-C_4H_9Br	2.15[d]	n-C_4H_9I	2.08[d]
	2.04[f]				
tert-C_4H_9Cl	2.13[g]				

* The observed values in the gaseous state.

a) W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy", John Wiley and Sons, Inc., New York, N. Y., (1953), p. 361.

b) J. C. Jelatis, *Tech. Rep.*, **7**, O. N. R. Contract N5 ori—78 T. O. I. Lab. Ins. Res., Mass. Inst. Tech. (1947).

c) P. C. Mahanti, *Phil. Mag.*, (7) **20**, 274 (1935).

d) L. G. Groves and S. Sugden, *J. Chem. Soc.*, **1937**, 158.

e) R. Sanger, O. Steiger and K. Gachter, *Helv. Phys. Acta*, **5**, 200 (1932).

f) C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **3**, 347 (1935).

g) R. H. Wiswall and C. P. Smyth, ibid., **9**, 356 (1941).

TABLE II

NUCLEAR QUADRUPOLE COUPLING CONSTANTS OF ALKYL HALIDE (Mc)

Alkyl chloride (^{35}Cl)[a]		Alkyl bromide (^{79}Br)[b]		Alkyl iodide (^{127}I)[b]	
CH_3Cl	68.40	CH_3Br	528.9	CH_3I	1753
C_2H_5Cl	66.0	C_2H_5Br	497.0	C_2H_5I	1647
n-C_3H_7Cl	66.4	n-C_3H_7Br	503.0	n-C_3H_7I	1672
n-C_4H_9Cl	—	n-C_4H_9Br	499.9	n-C_4H_9I	1660
tert-C_4H_9Cl	62.3				

a) See foot-note a) appendix under Table I.

b) S. Kojima, K. Tsukada, S. Ogawa and A. Shimauchi, *J. Chem. Phys.*, **21**, 1415(1953).

atoms as shown in Table II. To throw light on these facts, the correlation among the electronic properties of the carbon-halogen bonds in alkyl halide molecules and the nuclear quadrupole coupling constants and the dipole moments of the molcules has been studied. A valence bond theory is developed to get the dependences of dipole moments and of nuclear quadrupole coupling constants on the ionicity of the carbon-halogen bond. The method used here is similar to that developed by Baughan, Evans and Polanyl[4].

Calculation and Results

The bonding wave function for a C—X (X=halogen) bond of an alkyl halide molecule can be constructed as follows:

$$\psi_{bCX} = (2+2S^2_{CX}+4\lambda S_{CX}+\lambda^2)^{-1/2} [\psi_X(1)\psi_C(2)+\psi_X(2)\psi_C(1) + \lambda\psi_X(1)\psi_X(2)] \qquad (1)$$

where

$$\psi_X = a\psi_{ns}+b\psi_{np}$$
$$\psi_C = 1/2\psi_{2s}+\sqrt{3}/2\,\psi_{2p} \qquad (2)$$

n=3, 4 and 5 for Cl, Br and I, respectively, and S_{CX} is the overlap integral defined by

$$S_{CX} = \int \psi_X(1)\psi_C(1)d\tau_{(1)}$$

The non-bonding hybrid orbital of the halogen atom is given by

$$\psi_{nb} = c\psi_{ns}+d\psi_{np}$$

From the orthogonality and normalization conditions for ψ_X and ψ_{nb}, we have

$$\left.\begin{aligned} a^2+b^2 &= 1 \\ c^2+d^2 &= 1 \\ ac+bd &= 0 \end{aligned}\right\} \qquad (3)$$

The C—H bonds in methyl halide molecules are assumed to be pure covalent bonds, so that the wave functions for the bonds can be described as

$$\psi_{bCH} = (2+2S^2_{CH})^{-1/2} \times [\psi_C(1)\psi_H(2)+\psi_C(2)\psi_H(1)] \qquad (4)$$

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[4] E. C. Baughan, M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1941).

where

$$S_{\mathrm{CH}} = \int \psi_{\mathrm{C}}(1)\psi_{\mathrm{H}}(1)\mathrm{d}\tau_{(1)}$$

ψ_{H} is the 1*s* orbital of hydrogen atom, and ψ_{C} is assumed to be the tetrahedral hybrid orbital given by Eq. 2.

On the assumption of the orthogonality relationship between $\psi_{b\mathrm{CX}}$ and $\psi_{b\mathrm{CH}}$ the dipole moment of methyl halide is given by

$$\vec{\mu} = 3\vec{\mu}_{\mathrm{CH}} + \vec{\mu}_{b\mathrm{CX}} + \vec{\mu}_{nb}$$

where

$$\vec{\mu}_{\mathrm{CH}} = e(2\overline{Z}_{\mathrm{CH}} - R_{\mathrm{CH}})$$
$$\vec{\mu}_{b\mathrm{CX}} = e(2\overline{Z}_{\mathrm{CX}} - R_{\mathrm{CX}})$$
$$\vec{\mu}_{nb} = 2e\overline{Z}_{nb}$$

e is the electronic charge; R_{CH} and R_{CX} are the C—H and the C—X bond distances, respectively; the z-axis is taken along each bond direction with the carbon atom at the origin; $\overline{Z}_{\mathrm{CH}}$, $\overline{Z}_{\mathrm{CX}}$ and $\overline{Z}_{nb}$ are the average values of the z coordinates of the bonding electrons for the C—H and C—X bonds, and the non-bonding electrons of the halogen atom, respectively. The explicit expressions for $\overline{Z}_{\mathrm{CH}}$, $\overline{Z}_{\mathrm{CX}}$ and $\overline{Z}_{nb}$ are well known, so that they are not described here.

A nuclear quadrupole coupling constant is usually expressed by eQq, where e is the electronic charge, Q is the nuclear quadrupole moment and q is the electric field gradient at the nucleus of the coupled atom with reference to the charge symmetric axis z, that is

$$q = e\sum_i \int \psi_i^*[(3\cos^2\theta_i - 1)/r_i^3]\psi_i \mathrm{d}\tau_i$$

where the subscript i refers to the i-th electron, ψ_i is the wave function of the i-th one, r_i is the distance from the nucleus of the coupled atom, and θ_i is the angle between the r direction and the z axis. In the present work, only the valence electrons of the halogen atom are taken into account; the contributions from the others in the molecule are ignored, because the electrons on other atoms are too far away and the inner-shell clouds of the halogen atom have the symmetry to make the contribution to q insignificant. In this approximation, we obtain

$$q = 2q_{b\mathrm{CX}} + 2q_{np_x} + 2q_{np_y} + 2q_{nb} \qquad (5)$$

where

$$q_{\psi} = e\int \psi^*[(3\cos^2\theta - 1)/r^3]\psi \mathrm{d}\tau$$

Now since q equals to naught for a completely filled p-shell, it can be easily be seen that

$$q_{np_x} = q_{np_y} = -\frac{1}{2}q_{np_z} \qquad (6)$$

In consideration of Eqs. 3, 5 and 6, q is expressed as

$$q = [-b^2(1+2S^2{}_{\mathrm{CX}}+2\lambda S_{\mathrm{CX}})q_{np_z}+2(S_{\mathrm{CX}}+\lambda)$$
$$\times q_{\mathrm{CX}}-q_{\mathrm{C}}]/(1+S^2{}_{\mathrm{CX}}+2\lambda S_{\mathrm{CX}}+\lambda^2/2)$$

where

$$q_{\mathrm{CX}} = e\int \psi_{\mathrm{C}}[(3\cos^2\theta-1)/r^3]\psi_{\mathrm{X}}\mathrm{d}\tau$$

In this case, q_{C} is very small compared with other terms, so the halogen quadrupole coupling constant may be written as

$$eQq = [-b^2(1+2S^2{}_{\mathrm{CX}}+2\lambda S_{\mathrm{CX}})eQq_{np_z}$$
$$+2(S_{\mathrm{CX}}+\lambda)eQq_{\mathrm{CX}}]/(1+S^2{}_{\mathrm{CX}}$$
$$+2\lambda S_{\mathrm{CX}}+\lambda^2/2)$$

The atomic orbitals used in the calculation are the following hydrogen-like ones in which the screening constants were determined by Pauling and Sherman[5]: Cl(Z_{3s}=8.3, Z_{3p}=6.5), Br(Z_{4s}=11.3, Z_{4p}=8.8), I(Z_{5s}=14.5, Z_{5p}=11.7), C(Z_{2s}=3.96, Z_{2p}=3.09), H(Z_{1s}=1.00). The bond distances are taken to be R_{CH}=1.10 Å, R_{CCl}=1.78 Å, R_{CBr}=1.94 Å, and R_{CI}=2.14 Å throughout the series of these alkyl halides.

The q_{np_z} values calculated by use of these atomic orbitals, are shown in Table III. The results are in poor agreement with the accurate values. This means that such a theoretical procedure does not give satisfactory results because of the inaccuracy of the wave functions, especially in the part closer to the nucleus. In this work, therefore, the values of eQq_{np_z} are taken from the experimental quadrupole coupling constants of atomic halogen;

TABLE III

q_{np_z} values

	$q_{\mathrm{calc.}}$ (10^{15}e.s.u.)	$q_{\mathrm{obs.}}$* (10^{15}e.s.u.)
$q_{3p_z}^{\mathrm{Cl}}$	6.06	9.59
$q_{4p_z}^{\mathrm{Br}}$	6.34	15.9
$q_{5p_z}^{\mathrm{I}}$	7.63	~45

* These values were obtained by using the experimental quadrupole coupling constants[6] of atomic halogen and the quadrupole moments[a] of the halogen nucleus.

a) See foot-note a) appendix under Table I.

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[5] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

$eQq^{\mathrm{Cl}}_{3p_z}=109.74\mathrm{Mc}$,[6] $eQq^{\mathrm{Br}}_{4p_z}=-769.62\mathrm{Mc}$[6] and $eQq^{\mathrm{I}}_{5p_z}=2292.44\mathrm{Mc}$,[6] respectively.

The exchange term eQq_{CX} is evaluated by means of Löwdin's approximation[7] in which eQq_{C} is disregarded. In this procedure, μ and eQq are represented as the functions of λ and b^2, so that these values are determined by the experimental values of μ and eQq for methyl halide. For this purpose, the experimental values* for these gaseous molecules ($eQq_{\mathrm{CH_3Cl}}=-75.3\mathrm{Mc}$[3], $eQq_{\mathrm{CH_3Br}}=577.3\mathrm{Mc}$[3] and $eQq_{\mathrm{CH_3I}}=-1934\mathrm{Mc}$[3]) are used. The values of λ and b^2 so obtained are given in Table IV.

TABLE IV

	CH_3Cl	CH_3Br	CH_3I
λ	1.0209	0.9134	0.6056
b^2	0.9749	0.9661	0.9456
$\mu_{b\mathrm{CX}}(\mathrm{C^+X^-})$ (a.u.)	1.0321	0.7544	0.3107
μ_{nb}(a.u.)	0.6035	0.8516	1.2359

The determination of λ for the R—X bonds in alkyl halides (R=ethyl, *n*-propyl, *n*-butyl, *tert*-butyl) other than methyl halide is made by using the following process.

We obtain the following relation for the R—X bond from Eq. 1

$$\lambda^2/(2+2S^2_{\mathrm{CX}}) = R_{ic}/(H_{ii}-E) \qquad (7)$$

where R_{ic} is the ionic-convalent resonance energy for the R—X bond, H_{ii} is the energy of the pure ionic structure R^+X^-, and E is the dissociation energy of the R—X bond.

Based on the assumption that the value of the factor b^2 is the same as that in methyl halide in the series of R-X bonds, the same value of overlap integral S_{CX} can be used for all R—X bonds. Thus, from Eq. 7, the value of λ can be determined if the values for R_{ic}, H_{ii} and E are known. The method is similar to that of Baughan, Evans and Polanyi[4]. They made an interesting application of the theory of ionic-covalent resonance to their correlation of changes in dipole moment and to bond energy along the series of alkyl derivatives R—X, in which R is methyl, ethyl, *n*-propyl or *tert*-butyl. They drew attention to the following trends along these series.

(1) The R—H bond energy decreases markedly.

(2) The R—X (X≠H) bond energy decreases less rapidly than the R—H bond energy.

(3) The dipole moment of the C—I bond increases parallel to the decrease in the R—I bond energy.

The data for the bond energy E(R—X) are shown in Table V. The interpretation has been given that the decrease in E(R—H) was attributed solely to the increasing resonance energy in alkyl radicals R_r, because the C—H bond was considered to be approximately a pure covalent bond. Hence

$$E(\mathrm{R—H}) = E(\mathrm{CH_3—H}) - R_r \qquad (8)$$

TABLE V

E(R-X) values*

R	E(C-H)[a]	E(C-Cl)[b]	E(C-Br)[a]	E(C-I)[b]
methyl	102.5	80.5	68.5	54.0
ethyl	97.5	79.4	67.0	52.0
n-propyl	95.0	77.4	64.5	50.0
n-butyl	94.0	—	63.5	49.0
tert-butyl	86.0	74.7	—	—

* All the E values are given in kcal. mole^{-1}.

a) E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943).

b) J. S. Roberts and H. A. Skinner, ibid., **45**, 339 (1959).

In the case of R—X bonds (X≠H), the ionic-covalent resonance energy in the R—X molecule increases along the series, due to the increased stability of the R^+X^- ion pair. Accordingly, there is the radical resonance energy R_r, which, as with R—H bonds, tends to decrease the bond energy, and there is an increase in ionic-covalent resonance energy R_{ic}, in the molecules, tending to increase the bonding energy. That is

$$E(\mathrm{R—X}) = E(\mathrm{CH_3—X}) - R_r + \Delta R_{ic} \qquad (9)$$

where

$$\Delta R_{ic} = R_{ic}(\mathrm{R—X}) - R_{ic}(\mathrm{CH_3—X}) \qquad (10)$$

The E(R—X) values in Table V are used in the present calculation and the R_r values are obtained by Eq. 8. By use of Eqs. 9 and 10, the R_{ic}(R—X) values can be evaluated, when we know the R_{ic}(CH$_3$—X) values. These values are obtained from Eq. 7, using the λ, S_{CX} and H_{ii}(CH$_3$—X) values. The H_{ii}(CH$_3$—X) values are evaluated by using the Born-Meyer formula[8]

$$H_{ii} = e^2[-1/R_{\mathrm{CX}} + \rho/R_i^2 \times \exp\{(R_i - R_{\mathrm{CX}})/\rho\}] + I_{\mathrm{C}} - E_{\mathrm{X}}$$

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[6] H. Robinson, H. G. Dehmelt and W. Gordy, *J. Chem. Phys.*, **22**, 511 (1954).

[7] P. O. Löwdin, ibid., **21**, 374 (1953).

[*] The dipole moment values used here are taken from those in Table I.

[8] M. Born and J. E. Meyer, *Z. Physik.*, **75**, 1 (1932); E. Warhurst, *Trans. Faraday Soc.*, **45**, 461 (1949).

TABLE VI

Molecules	λ	μ_{bCCl} (a.u.)	$\Delta\mu_{bCCl}$ (D)	$\Delta\mu_{obs.}$* (D)	$\lvert eQq\rvert$ (Mc)	$\Delta eQq_{calc.}$ (Mc)	$\Delta eQq_{obs.}$ (Mc)
CH_3Cl	1.021	1.032	0	0	75.3	0	0
C_2H_5Cl	1.076	1.067	0.09	0.11 0.13	73.7	1.6	2.4
n-C_3H_7Cl	1.098	1.081	0.12	0.17	73.0	2.3	2.0
t-C_4H_9Cl	1.205	1.146	0.29	0.26	70.1	5.2	6.1

Molecules	λ	μ_{bCBr} (a.u.)	$\Delta\mu_{bCBr}$ (D)	$\Delta\mu_{obs.}$* (D)	$\lvert eQq\rvert$ (Mc)	$\Delta eQq_{calc.}$ (Mc)	$\Delta eQq_{obs.}$ (Mc)
CH_3Br	0.913	0.754	0	0	577.3	0	0
C_2H_5Br	0.971	0.797	0.11	0.19 0.21	564.7	12.6	31.9
n-C_3H_7Br	0.990	0.811	0.14	0.19 0.33	560.5	16.8	25.9
n-C_4H_9Br	0.998	0.817	0.16	0.33	558.8	18.5	29.0

Molecules	λ	μ_{bCI} (a.u.)	$\Delta\mu_{bCI}$ (D)	$\Delta\mu_{obs.}$* (D)	$\lvert eQq\rvert$ (Mc)	$\Delta eQq_{calc.}$ (Mc)	$\Delta eQq_{obs.}$ (Mc)
CH_3I	0.606	0.311	0	0	1934	0	0
C_2H_5I	0.666	0.365	0.14	0.22 0.28	1889	45	106
n-C_3H_7I	0.686	0.382	0.18	0.36 0.32	1875	59	81
n-C_4H_9I	0.692	0.387	0.19	0.43	1870	64	93

* These values are obtained from the data in Tables I and II.

where e is the electronic charge, ρ is given the value $\rho = 0.345$ Å,[8] R_i is the equilibrium distance of R^+X^- ion pair, I_C is the ionization potential of carbon atom and E_X is the electron affinity of the halogen atom. The values of the quantities employed here are R_i(C—Cl) = 2.17 Å[9], R_i(C—Br) = 2.30 Å[9], R_i(C—I) = 2.48 Å[9], $I_C = 11.42$ eV[10], $E_{Cl} = 3.82$ eV[10], $E_{Br} = 3.69$ eV[10] and $E_I = 3.55$ eV[10].

The H_{ii} values for R^+X^- ion pair are evaluated from $H_{ii}(CH_3—X)$ according to the following assumption by Baughan, Evans and Polanyi.

$$H_{ii}(\mathrm{R—X}) \approx H_{ii}(\mathrm{CH_3—X}) - R_r$$

Thus, using Eq. 7, we can calculate the λ values for the R—X bonds. The values of λ obtained and those of μ_{bCX} and eQq consequently obtained are shown in Table VI.

The variations of dipole moments and quadrupole coupling constants along the series of these molecules are interesting for us, so the quantities $\Delta\mu$, $\Delta\mu_{bCX}$ and ΔeQq defined as follows are introduced for comparisons between the observed values and the calculated ones.

$$\Delta\mu = \mu(\mathrm{R—X}) - \mu(\mathrm{CH_3—X})$$

$$\Delta\mu_{bCX} = \mu_{bCX}(\mathrm{R — X}) - \mu_{bCX}(\mathrm{CH_3—X})$$

$$\Delta eQq = eQq(\mathrm{R — X}) - eQq(\mathrm{CH_3—X})$$

These values are listed in Table VI.

Discussion and Conclusion

In this calculation, the exchange terms eQq_{CX} are evaluated by Löwdin's approximation. Both Mulliken's approximation[11] and the neglect of the exchange terms have not always been sufficient for determining of b^2 and λ for all methyl halides. Usually these terms[1] have been evaluated as about a few percent or less of eQq_{np_z}. The values of these terms calculated here, however, are 19 percent of eQq_{3p_z} for the C—Cl bond, 14 percent of eQq_{4p_z} for the C—Br bond and 9 percent of eQq_{5p_z} for the C—I bond, respectively.

The b^2 values obtained here are greater than the values[1] estimated hitherto for Cl,

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[9] E. C. Baughan and M. Polanyi, ibid., **37**, 648 (1941).

[10] H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

[11] R. S. Mulliken, *J. chim. phys.*, **46**, 500, 521 (1949).

less than those[1] for bromine and iodine though their accurate values have not yet been known. These greater values indicate the small amount of *s* character in the halogen bonding orbitals. It should be noted, however, that the so-called atomic dipole is considerably great, as seen in Table IV.

The magnitude of μ of alkyl halide depends to a great extent on those of $\mu_{b\mathrm{CX}}$ and μ_{nb}, though it is not determined by them alone. It is seen from the results in Table VI that the variations of the C—X bond moments $\Delta\mu_{b\mathrm{CX}}$ give a considerable contribution to those of molecule $\Delta\mu$. Furthermore, these results can be improved by taking account of the increasing *s* character in the halogen bonding orbitals along the series of these molecules, which means the elimination of the assumption that b^2 is constant along the series of these molecules, because it results in the increasing values of $\Delta(\mu_{b\mathrm{CX}}+\mu_{nb})$* and of ΔeQq. They show that the variations of dipole moments along the series of these molecules should be interpreted by those of $\mu_{b\mathrm{CX}}$ or $(\mu_{b\mathrm{CX}}+\mu_{nb})$ instead of by an inductive effect.

The variations of dipole moments $\Delta\mu$ of the corresponding alkyl halides listed in Table VI increase in the sequence R—Cl, R—Br and R—I. This fact is not interpreted by an inductive effect. The present results suggest a qualitative explanation for this.

From these results, we can expect the values of eQq to decrease smoothly with the increasing carbon number. On the other hand, these values in the solid state fall zigzag as described above. This correlation is similar to the relations between the boiling points and the melting points of these molecules. It may be, therefore, reasonable that the zigzag of the eQq values in the solid state comes from the same reason as the one on which the irregularity between the melting points and the number of carbon is based.

In view of the present calculations, it seems highly probable that the eQq values of these molecules in the gaseous state will decrease smoothly with the increasing carbon number, though those in the solid state decrease zigzag with the increasing carbon number and that the ionic character of the C—X bonds in alkyl halide molecules increase with the increasing carbon number.

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* The quantity is given the same definition as $\Delta\mu_{b\mathrm{CX}}$ and so on.