A Theoretical Study of the Vibrational Dependence of the Nuclear Quadrupole Coupling Constants of some Diatomic Molecules*

E. A. C. Lucken

Département de Chimie Physique, Université de Genève, 30, quai Ernest-Ansermet,
1211 Genève 4, Switzerland

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The nuclear quadrupole coupling constant was calculated as a function of inter nuclear distance for nine quadrupolar nuclei in eight diatomic molecules by the STO 321G method. From the value of the field-gradient and its first and second derivatives the vibrational dependence of the coupling constants were calculated and shown to compare satisfactorily with experiment. The behaviour of the field-gradient as a function of inter nuclear distance can in most cases be rationalized in terms of the field-gradient that will arise for the infinitely separated atoms.

Introduction

The value of the nuclear quadrupole coupling constant, $e^2 Q q$, of a nucleus in a diatomic molecule is dependent on the vibrational state. This dependence is conventionally expressed as a power series in $(v+\frac{1}{2})$, where v is the vibrational quantum number:

$$e^2 Q q_v = e^2 Q q_0 + e^2 Q q_1 \, (v+\tfrac{1}{2}) + e^2 Q q_2 \, (v+\tfrac{1}{2})^2 + \dots \quad (1)$$

Although it has seldom, if ever, proved possible to measure the quadratic dependence with any degree of reliability, the linear term has been determined for a number of molecules. The constants q_1 and q_2 reflect the contributions of the vibrational-averaging of the field-gradient and thus are related to the dependence of the field-gradient, q, on the extension of the bond-length, $R - R_0$ $(\equiv x)$.

$$\bar{q} = q_0 + \bar{x}\left(\frac{\partial q}{\partial x}\right)_0 + \bar{x}^2\left(\frac{\partial^2 q}{\partial x^2}\right)_0 + \dots \quad (2)$$

For the harmonic oscillator we have [1]

$$\bar{x}^2 = \frac{2 B_e R_e^2}{\omega_e}\left(v+\frac{1}{2}\right). \quad (3)$$

In the limit of the harmonic oscillator $\bar{x}$ is zero, but is non-zero for the anharmonic oscillator:

$$\omega_v = \omega_e \, (v+\tfrac{1}{2}) + \chi_e \, \omega_e \, (v+\tfrac{1}{2})^2 \, . \quad (4)$$

An estimate of $\bar{x}$ is most easily obtained if a Morse potential is assumed [2]:

$$\bar{x} = \frac{3 B_e R_e}{\omega_e C}\sqrt{\chi_e \, \omega_e \, B_e}\,(v+\tfrac{1}{2}) \, . \quad (5)$$

Since both these terms are linearly dependent on $v+\frac{1}{2}$, an explicit expression for q_1 in terms of the field-gradient derivatives is thus obtained from the vibrational dependence of $\bar{x}$ and $\overline{x^2}$:

$$e^2 Q q_1 = \frac{e^2 Q B_e R_e^2}{\omega_e c}\left[\sqrt{\frac{9 \chi_e \, \omega_e \, c}{B_e R_e^2}}\left(\frac{\partial q}{\partial x}\right)_0 + \left(\frac{\partial^2 q}{\partial x^2}\right)_0\right]. \quad (6)$$

Since the field-gradient is likely to be a smoothly-varying function of x its second-derivative is likely to be much smaller than the first derivative, so that even a small degree of anharmonicity will be important.

Equation (6) thus provides a link between a variety of experimental quantities and the first and second derivatives of the field-gradients. The field gradients are not, however, experimentally available but can only be obtained as the result of a theoretical calculation of a molecular wave-function. The difficulties of calculating field-gradients are, however, well-known, and to obtain a satisfactory result usually implies the use of techniques that go beyond those that are adequate for the calculations of molecular energy of molecular geometry. A further difficulty resides in the

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Reprint requests to Prof. Dr. E. A. C. Lucken, Phys. Chem. Dept., Sciences II, University of Geneva, 30 Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland.

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fact that to derive an experimental value of a field-gradient from the quadrupole coupling constant requires a knowledge of the nuclear quadrupole moment. Since in most cases this quantity is derived from the relationship between a theoretical field-gradient and an experimental coupling constant, we are chasing our own tail.

The calculation of the field-gradient for a range of inter nuclear distances in the vicinity of R_e yields not only the value of the field-gradient at the equilibrium inter nuclear distance but also, *via* an appropriate fitting of the theoretical data to a polynomial, the values of the field-gradient derivatives at this point. These field-gradient derivatives may then be substituted in Equation (1) to yield a value for e^2Qq_1, finally giving rise to a theoretical value for the ratio of e^2Qq_1 to e^2Qq_0, which is independent of Q. In addition, the calculation of this ratio gives rise to the hope that the imperfections in the theoretical calculation of the field-gradient will cancel out.

To test this hypothesis, the field-gradients of those diatomic molecules for which the vibrational dependence of the coupling constant is known was calculated as a function of the inter nuclear distance in the neighbourhood of the experimental inter nuclear equilibrium distance by *ab initio* methods. In order to cover as wide a range of molecules as possible the calculations were performed at only the STO 31G level.

Computational Details

Calculations were performed using both the GAMESS [3] and the Gaussian 90 [4] packages with the default parameters for all atoms for a series of at least nine values of the inter nuclear distance spanning the experimental inter nuclear distance. Over the range of inter nuclear distances that were investigated the theoretical values of the field-gradients were all almost linear functions of the inter nuclear distance, with only a very slight degree of curvature. They were therefore fitted to a quadratic and, because (6) contains a number of experimental parameters, first and second derivatives of the field-gradient were calculated at the *experimental* inter nuclear distance. The difference between the minimum of the theoretical energy/distance curve and the experimental bond-length was always within the limits usually found for the STO 31G method [5].

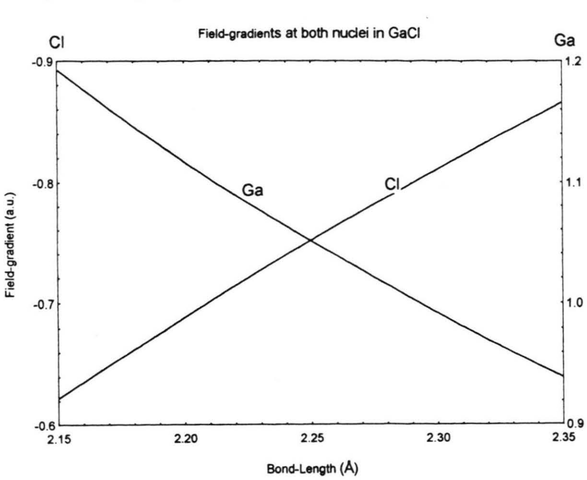

Fig. 1. The dependence of the field-gradient at the Ga and Cl sites in GaCl.

Results and Discussion

As shown in Fig. 1 for the two sites in GaCl the absolute values of the field-gradient can either increase or decrease as a function of the inter nuclear distance but in every case except that of the ^{14}N site in PN the first and second derivatives were of opposite sign. This has the consequence that the vibrational dependence usually arises from the difference between two terms of similar magnitue. The general trend of the bond-length dependence of the field-gradients can be rationalized in terms of the field-gradient that will arise when the two atoms are infinitely separated. We may illustrate this by the data for the two sites in GaCl in Figure 1. Thus for the Cl site the field gradient rises to that of the neutral Cl atom while for the Ga site the neutral atom has spherical symmetry with vacant 4p orbitals and no field-gradient. The opposite signs of the two derivatives stems from the fact that the field gradients may be expected to tend asymptotically to these limits.

Table 1 shows the equilibrium inter nuclear distances, the rotational constants, and the vibrational harmonic an anharmonic terms of (4) for eight molecules for which the quadrupole coupling data are available and which are composed of atoms lying between H and Kr in the Periodic Table. Despite the fact that Lilt falls in this category it was not included since for this molecule the valence electrons are both s-electrons and it is well-known that calculations at the STO 31G level do not give satisfactory values for the

Table 1. Rotational constants [6], bond-lengths [7] and vibrational parameters [7].

Molecule	B_e (GHz)	R (Å)	ω (cm^{-1})	$\chi\omega$(cm^{-1})
$^1H^{35}Cl$	317.557115	1.2746	2989.74	52.05
$^1H^{79}Br$	253.836185	1.413	2649.67	45.21
$^{19}F^{35}Cl$	15.483688	1.62813	793.2	9.9
$^{79}Br^{19}F$	10.66761	1.75555	671	3
$^{27}Al^{19}F$	16.56256	1.65437	814.5	8.1
$^{69}Ga^{19}F$	10.778	1.774362	623.2	3.4
$Ga^{35}Cl$	4.49373	2.20168	365	1.1
$^{31}P^{14}N$	23.57834	1.491	1337.24	6.983

Table 2. Theoretical values of the field-gradients and their first and second derivatives calculated at the experimental bond-length, at the nucleus marked with an asterisk.

Molecule	q_0 (a.u.)	$(\partial q_1/\partial x)$ (a.u. a_0^{-1})	$(\partial^2 q_1/\partial x^2)$ (a.u. a_0^{-2})	R_{min} (Å)
HCl*	−3.234	−3.2463	2.1984	1.275
HBr*	−6.547	−6.5532	6.9438	1.430
FCl*	−6.607	−1.1412	1.1645	1.689
Br*F	−12.507	−3.1991	6.8967	1.803
Al*F	0.808	−1.6490	4.8770	1.650
Ga*F	1.5406	−3.4458	12.1215	1.755
Ga*Cl	1.1144	−1.2815	3.2452	2.240
GaCl*	−0.6910	−1.2878	1.4655	2.240
PN*	1.2031	−0.7574	−2.0356	1.551

Table 3. Theoretical and experimental values of the coupling constants and their vibrational dependence. The field-gradients were converted to the coupling constants using the nuclear quadrupole moments proposed by Pykko.

Molecule	e^2Qq_1/e^2Qq_0		e^2Qq_0 (MHz)		Ref.
	Theory	Experiment	Theory	Experiment	
$H^{35}Cl$	0.0262	0.0251	−62.32	−67.6	[9]
$H^{79}Br$	0.0246	0.023	507.7	526.25	[2]
$F^{35}Cl$	0.0021	0	−127.3	−145.87	[2]
^{79}BrF	0.0012	0.0011	969.9	1086.8	[10]
^{27}AlF	−0.0151	−0.0116	−28.48	−37.75	[11]
^{69}GaF	−0.0068	−0.0102	−83.92	−107.07	[12]
$^{69}GaCl$	−0.0026	−0.0075	−60.70	−92.1	[13]
$Ga^{35}Cl$	0.0095	0.0151	−13.31	−13.3	[13]
$P^{14}N$	−0.0071	−0.0117	−5.63	−5.1718	[14]

field-gradients. For the nine quadrupolar sites in these eight molecules Table 2 shows the field gradients and their first and second derivatives at the experimental inter nuclear distance. For comparison with the experimental bond-length, Table 2 also shows the inter nuclear distances for the minima of the energy/distance curve.

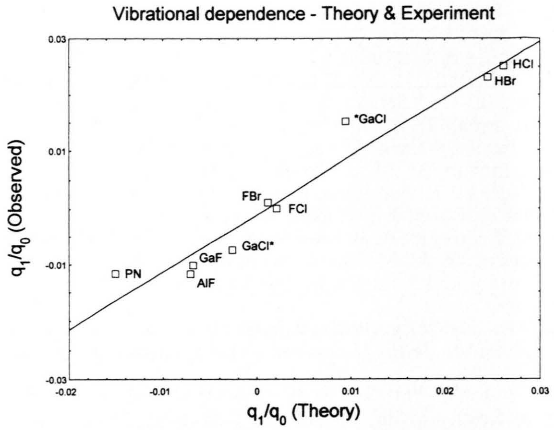

Fig. 2. The relationship between the theoretical and experimental values of the ratio of e^2Qq_1 to e^2Qq_0.

Table 3 shows the comparison between the theoretical and the experimental data, the field-gradients having been converted to coupling constants using the nuclear quadrupole moments proposed by Pykko [8]. While the agreement the theoretical and experimental coupling constants is no more than fair, as would be expected for STO 321G calculations, the agreement between theory and experiment for the ratio of e^2Qq_1 to e^2Qq_0 is much more satisfactory. This is undoubtedly due to the fact that on the one hand the values of the nuclear quadrupole moments are not required, while on the other some of the imperfections of the theoretical method cancel out when the ratio of these two terms is calculated. The least-squares fit is illustrated in Fig. 2 and given by the relationship

$$\text{Experimental value} = 1.0169 \times (\text{Theoretical value}) - 0.001027, \quad R = 0.00377 .$$

Without any constraints, this straight line does not go through the origin but if this constraint is applied, the straight-line relationship is

$$\text{Experimental value} = 0.997742 \times (\text{Theoretical value}), \quad R = 0.00368 .$$

Despite the fact that the vibrational dependence arises from the difference of two terms of similar magnitude the ratio of the coupling constant to vibrational dependence of the coupling constant may be calculated to a fair degree of accuracy with the STO 321G method.

Acknowledgements

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