Quadrupolar spin relaxation due to electric field gradients induced by vibrations and collisions

by H. JÖRG OSTEN

Academy of Sciences of the GDR, Central Institute of Physical Chemistry,
1199 Berlin, Rudower Chaussee 6, German Democratic Republic

and CYNTHIA J. JAMESON

Department of Chemistry, University of Illinois at Chicago,
Chicago, Illinois 60680, U.S.A.

The spin relaxation of quadrupolar nuclei in highly symmetric electronic environments via vibrationally-induced electric field gradients is considered. A model is presented for tetrahedral molecules which yields a nuclear quadrupole coupling constant for ^{189}Os in an excited vibrational state of OsO_4 which is in reasonable agreement with experimentally observed values. The nuclear quadrupole coupling constants for the central nucleus in excited E and F_2 vibrational states of $GeCl_4$, $GeBr_4$, RuO_4, OsO_4 molecules as well as the MO_4^{n-} ions ($M = $ V, Cr, Mn, Mo, Tc, Re) are calculated using this model. These coupling constants lead to quadrupolar relaxation rates which are orders of magnitude too small compared to experiment. Alternate mechanisms, collisional-deformation by long-range van der Waals interactions and fields induced by octopole moments, are proposed. A binary collision model is used in which the fluctuating electric fields associated with London dispersion forces during a collision create electric field gradients at the quadrupolar nucleus. Parallel development of vibrational and intermolecular effects on nuclear shielding with vibrational and collisional-deformation-induced electric field gradients is shown. The latter mechanism and the octopole-induced fields are capable of giving relaxation rates of the right order of magnitude.

1. INTRODUCTION

The nuclear spin relaxation of nuclei with spin $> \frac{1}{2}$ is generally attributed to the interaction of the nuclear electric quadrupole moment with the electric field gradient at the nuclear site, modulated by molecular collisions which occur at a rate of the order of $10^{12} \, s^{-1}$ in liquids. For nuclear sites having other than cubic symmetry, there is an intrinsic (static) electric field gradient tensor whose components are given by

$$q_{\alpha\beta} = \partial E_\alpha / \partial x_\beta, \tag{1}$$

where E is the electric field at the nuclear spin due to the electronic environment. These components are made time-dependent by collisions, both reorientation and magnitude changes contributing to relaxation [1]. Where a static electric field

gradient exists this mechanism for nuclear spin relaxation is usually found to dominate all others, unless the nuclear electric quadrupole moment is very small.

In nuclear sites which have T_d or O_h symmetry, there is no static electric field gradient. However, even in these cases the relaxation time of the nucleus is still found to be shorter than might be expected if other than the quadrupolar mechanism is responsible for relaxation. For example, the relaxation time of the quadrupolar ^{189}Os nucleus in OsO_4 is $230\,\mu s$ whereas for the spin $\frac{1}{2}$ ^{187}Os nucleus in exactly the same environment it is orders of magnitude longer ($\sim 5\,s$) [2]. There are several models which attempt to account for relaxation by the quadrupolar mechanism in spherically symmetric, tetrahedral, or octahedral nuclear sites [3–6]. All are based on the creation of an instantaneous electric field gradient which averages to zero but which has a non-vanishing mean square.

Briefly, the contributions to the instantaneous electric field gradient come from the following:

(a) Electrostatic contributions which are important for electrolyte solutions are: (1) the distortion of the noble gas core at the nuclear site due to electrostatic charges or multipoles in the first coordination sphere; (2) the distortion of the noble gas core due to electrostatic charges or multipoles in the second coordination sphere and farther out; and (3) the direct electrostatic contribution to the electric field gradient at the nuclear site due to all the surrounding charges and multipoles.

(b) When the point charge multipoles are replaced by electron clouds there are additional *electronic contributions*. Collision between a solvent molecule and the probe molecule leads to a distortion of the electronic distribution at the nuclear site due to long-range (van der Waals) and short-range (repulsive) interactions. The same distortion of electronic distribution which leads to a decrease in nuclear magnetic shielding with increasing gas density leads to electric field gradients at the nuclear site. There are two effects: One is the general expansion of the electron cloud of the probe molecule due to attraction to the nuclei of the solvent molecule. Second is a deviation from spherical symmetry which leads to a paramagnetic shielding contribution and also an electric field gradient. Deverell [7] has modelled the short-range part by using a sum of squares of overlap integrals, the same type of approach used by Adrian to model the short-range contributions to ^{129}Xe deshielding with density in xenon gas [8]. Hertz has also included a short-range contribution in his model and shown that it leads to the same form as Deverell's model in the limiting case [3].

(c) A vibrational contribution arises when an asymmetric vibration (E or F_2 symmetry for a T_d nuclear site, or E_g or F_{2g} symmetry for an O_h site) is excited. The $v = 1$ state has a non-vanishing electric field gradient. This is considered an important contribution in the relaxation of ^{189}Os in OsO_4, $^{99,101}Ru$ in RuO_4, [6, 9] as well as ^{73}Ge in $GeCl_4$ and $GeBr_4$, [10] and $M = {}^{35,37}Cl$, $^{79,81}Br$, $^{50,51}V$, ^{53}Cr, ^{55}Mn, $^{95,97}Mo$, ^{99}Tc, ^{187}Re, in MO_4^{n-} ions in D_2O [9]. This mechanism has even been invoked in relaxation of M^{+n} ions in aqueous solution by considering the vibrations of the H_2O molecules which form a tetrahedral or octahedral first coordination sphere [4].

All these models (except Brown and Colpa [6]) have adjustable constants which make it possible to explain the *entire* relaxation rate by a 'reasonable' choice of parameters. Thus, the electrostatic contributions alone have been used

to explain relaxation rates of $^7Li^+$, $^{23}Na^+$, $^{39}K^+$, $^{85}Rb^+$, $^{133}Cs^+$, $^{27}Al^{3+}$, $^{69}Ga^{3+}$, $^{35}Cl^-$, $^{81}Br^-$, $^{127}I^-$, in dilute aqueous solutions [3], and $^7Li^+$ and $^{133}Cs^+$ relaxation in supercooled aqueous solutions or in viscous liquids such as glycerol [11, 12]. The short-range repulsive contributions alone have been used to account for relaxation rates of halide ions in solutions of various alkali halides [5, 7], and the vibrations of H_2O molecules around ions have been used to account for relaxation rates in aqueous solutions of Al^{3+} and Ga^{3+} salts, Na^+, Br^- and I^- ions, and ^{59}Co in octahedral Co(III) complexes [4, 13].

These models each have counterparts in the interpretation of solvent effects and vibrational effects on nuclear shielding. The theoretical approaches used in accounting for effects on nuclear shielding can be applied to quadrupolar relaxation in highly symmetric nuclear environments. It is from this vantage point that we consider the problem of vibrationally-induced quadrupolar relaxation. We consider only tight-binding systems such as $GeCl_4$, $GeBr_4$, OsO_4, RuO_4, MO_4^{n-}, with emphasis on neutral species, since we are not specifically interested in the electrostatic effects which are well treated by the theory of Hertz [3].

There are some interesting experimental evidence which have been proposed as supporting the vibrational mechanism of quadrupolar relaxation.

(*a*) The relaxation rates of a series of molecules of the type MO_4^{n-} in D_2O solution and the neutral RuO_4 in CCl_4 solution have been characterized in a nice set of experiments by Tarasov *et al.* [9]. This set of molecules is specially suited for investigation for the following reasons: Because ^{16}O has no spin, the intramolecular dipole–dipole or scalar coupling mechanism for *M* relaxation is absent. The central atom has a highly symmetrical electronic environment, so the shielding anisotropy mechanism is probably not important. Only quadrupolar, spin–rotation, and intermolecular dipole–dipole interaction need to be considered. Tarasov *et al.* studied relaxation times and their temperature dependence in pairs of nuclei $^{35, 37}Cl$, $^{50, 51}V$, $^{99, 101}Ru$, $^{79, 81}Br$, and $^{95, 97}Mo$. The ratios of $1/T_1$ for $^{35}Cl/^{37}Cl$ in ClO_4^- and $^{79}Br/^{81}Br$ in BrO_4^- are essentially indistinguishable from the ratios expected on the basis of the nuclear quadrupole moments. The ratio of $Q^2(2I + 3)/(2I - 1)I^2$ is 4.54 for $^{50}V/^{51}V$. Observed relaxation rates in VO_4^- have ratios around 3·34, which could be within experimental errors in the quadrupole moments. For MoO_4^{2-} the ratios are also close to that which could be expected using the nuclear quadrupole moments [14]. Especially intriguing is the temperature dependence of the $^{101}Ru/^{99}Ru$ ratio of relaxation rates in the system RuO_4 in CCl_4 solution, in which there is no possibility for electrostatic contributions. Tarasov and coworkers' experiments on the MO_4^{n-} systems indicate a change in the temperature dependence ($1/T_1$ curves show minima when plotted against temperature). The curvature is explained by the authors on the basis of two competing quadrupolar mechanisms with different *T* dependences, one with $\exp(-hc\omega/kT)$ and the other with $\exp(E_{act}/kT)$, the vibrational and electrostatic or collisional deformation mechanisms respectively. The latter are associated with correlation times exhibiting Arrhenius type behaviour.

(*b*) *T*-dependent relaxation studies of all 3 nuclei in $Co(CN)_6^{3-}$ by Chacko and Bryant give interesting results [15]. The ^{59}Co relaxation rate in $Co(CN)_6^{-3}$ decreases with an increase in temperature (as expected from Arrhenius-type behaviour), but the rate of decrease is a factor of 2 smaller than that of ^{13}C in the same molecule. Furthermore, the changes in correlation time upon ion-pair for-

mation which are deduced from changes in the ^{13}C and ^{15}N relaxation rates are not reflected in ^{59}Co relaxation rates upon ion-pair formation. These experiments provide a challenge to the Hertz model which considers the outer solvation sphere mainly responsible for relaxation. According to the Hertz model $1/T_1$ can be affected systematically by placing counterions of high charge outside the first coordination sphere of the ^{59}Co. However, Chacko and Bryant estimate that this accounts for only $\leqslant 30$ per cent of the change in the electric field gradient at the Co nucleus. The ^{59}Co relaxation rates are interpreted by invoking an additional mechanism other than the electrostatic model (such as vibrational) operating in ^{59}Co relaxation.

There are unequivocal pieces of evidence for vibrationally-induced electric field gradients. One is the electric quadrupole coupling which is observed as hyperfine structure in the excited rovibrational states of the totally symmetric electronic state of $^{189}OsO_4$, for example [16, 17]. Other related evidence is the variation of intrinsic quadrupole coupling constants with vibrational state for the halogen nuclei in $CH_3{}^{35}Cl$ and $CH_3{}^{79}Br$ [18], the isotope effect on the nuclear quadrupole coupling constants in H/D/T—Cl, Br, I molecules [19], and the temperature-dependent quadrupole coupling constants observed in gas-phase nuclear quadrupole resonance spectroscopy [20, 21]. All can be attributed to vibrational effects on electric field gradients at the nuclear site. The relaxation evidence provided by Tarasov et al. for ^{73}Ge in $GeCl_4$ and $GeBr_4$, RuO_4 in CCl_4 and for MO_4^{n-} in D_2O solution constitutes the most direct evidence cited for vibrationally-induced quadrupolar relaxation. In this paper we examine the nature of this evidence.

In Tarasov's discussion of the data, only a single vibrational mode is considered to be responsible and the temperature dependence is attributed to a factor $\exp\,(-hc\omega/kT)$ which takes into account the vibrational population of the lowest frequency fundamental level. A quantitative treatment of vibrationally-induced electronic field gradients is in order, which includes all efg-active vibrational modes (E and $2F_2$ in a T_d molecule). We devise a straightforward way of determining first and second derivatives of the efg with respect to displacement coordinates, without having to do a full vibration–electronic coupling calculation for the molecule. In this paper we deduce $(\partial q_{\alpha\beta}/\partial S)$ and $(\partial^2 q_{\alpha\beta}/\partial S^2)$ numerically from efg components generated from point charge displacements, where S is a symmetry coordinate belonging to E or F_2. We have used an anharmonic force field for each of the MO_4 neutrals and ions. We verify (numerically) the symmetry relations between cubic force constants and between derivatives of the efg components. We obtain reasonably good agreement with experimental ^{189}Os efg values for the $961\,cm^{-1}$ vibrational excited state in $^{189}OsO_4$ with this method. We discover periodic trends in the reduced intramolecular quadrupolar relaxation rate due to vibration of MO_4^{n-} type systems, with $M = V$, Cr, Mn, Mo, Tc, Ru, Re, Os. In addition, we offer an alternate calculation of the vibrationally-induced quadrupolar relaxation rates and the expected temperature dependence of $1/T_1$ by this mechanism. This is the first time that a quantitative treatment of vibrationally-induced quadrupolar relaxation rates and the expected temperature dependence has been presented. Finally, we present a model for collisional-deformation-induced electric field gradients and examine the temperature dependence and magnitudes of the rates observed by Tarasov et al. with the aid of these models.

2. METHOD

The interaction of a nuclear quadrupole moment Q with an electric field gradient at the position of the nucleus can be written in terms of vector components of the nuclear spin operator I as follows:

$$W = -(1/6) \sum_{\alpha, \beta} [eQ/I(2I - 1)][(3/2)(I_\alpha I_\beta + I_\beta I_\alpha) - \delta_{\alpha\beta} I^2]q_{\alpha\beta}, \qquad (2)$$

where α, β run over molecule-fixed axes x, y, z. The components of the electric field gradient at the nuclear site for a non-degenerate electronic state can be expressed as an expansion in terms of the vibrational coordinates Q_i

$$q_{\alpha\beta} = (q_{\alpha\beta})_e + \sum_i (\partial q_{\alpha\beta}/\partial Q_i)_e Q_i + \tfrac{1}{2} \sum_{i,j} (\partial^2 q_{\alpha\beta}/\partial Q_i \, \partial Q_j)_e Q_i Q_j + \dots. \qquad (3)$$

For the systems which we are considering here, $(q_{\alpha\beta})_e$, the electric field gradient at the static or equilibrium configuration is zero.

In order to calculate relaxation rates, we proceed as follows: First we write the electric field gradient components as an expansion in symmetry internal coordinates

$$q_{\alpha\beta} = (q_{\alpha\beta})_e + \sum_t (\partial q_{\alpha\beta}/\partial S_t)_e S_t + \tfrac{1}{2} \sum_{r,t} (\partial^2 q_{\alpha\beta}/\partial S_r \, \partial S_t)_e S_r S_t + \dots. \qquad (4)$$

An approximation is made by assuming a linear transformation between internal coordinates and cartesian displacement coordinates. The appropriate symmetry

Table 1. Constants used in the calculations: Q are in $10^{-28}\,m^2$, r_e and a in Å.

Nucleus	I	Q [38]	γ†	Molecule	r_e	Ref.	a
^{73}Ge	9/2	−0·2	10	GeCl$_4$	2·08	[39]	1·44
				GeBr$_4$	2·297	[39]	1·27
^{35}Cl	3/2	−0·0789	50	ClO$_4^-$	1·435	[40]	2·89
^{81}Br	3/2	0·28	100	BrO$_4^-$	1·78	[39]	1·21
^{50}V	6	0·21	10	VO$_4^{3-}$	1·717	[41]	1·52
^{51}V	7/2	−0·052					
^{53}Cr	3/2	0·03	10	CrO$_4^=$	1·66	[42]	1·86
^{55}Mn	5/2	0·55	10	MnO$_4^-$	1·59	[39]	2·46
^{95}Mo	5/2	0·12	30	MoO$_4^=$	1·81	[43]	1·49
^{99}Tc	9/2	0·3	30	TcO$_4^-$	1·715	[44]	2·14
^{99}Ru	5/2	0·076	30	RuO$_4$	1·706	[45]	2·34
^{101}Ru	5/2	0·44					
^{187}Re	5/2	2·6	130	ReO$_4^-$	1·723	[46]	1·46
^{189}Os	3/2	0·8	130	OsO$_4$	1·712	[47]	1·53

† These values of γ are estimates, on the basis of the following values for the closest closed shell ions [23]: $\gamma(Ge)$ from $\gamma(Ga^{3+}) = 9\cdot5$; $\gamma(Cl)$ from $\gamma(Cl^-) = 56\cdot6$; $\gamma(Br)$ from $\gamma(Br^-) = 123, 100$; $\gamma(V, Cr, Mn)$ from $\gamma(Mn^{2+}) = 11\cdot37, 6\cdot81$; $\gamma(Mo, Tc, Ru)$ from $\gamma(Ag^+) = 34\cdot9, 22.11$; $\gamma(Re, Os)$ from $\gamma(Cs^+) = 102\cdot5, 110$, $\gamma(Xe) = 157$ [48], $\gamma(I^-) = 138, 175$, $\gamma(Yb^{3+}) = 79$.

coordinates for the E and F_2 vibrations in terms of cartesian displacement coordinates are

$$S_{2a} = (1/2\sqrt{6})\{-\Delta x_1 + \Delta y_1 + 2\,\Delta z_2 + \Delta x_2 - \Delta y_2 + 2\,\Delta z_2 - \Delta x_3$$
$$- \Delta y_3 - 2\,\Delta z_3 + \Delta x_4 + \Delta y_4 - 2\,\Delta z_4\},$$

$$S_{2b} = (1/2\sqrt{2})\{\Delta x_1 + \Delta y_1 - \Delta x_2 - \Delta y_2 + \Delta x_3 - \Delta y_3 - \Delta x_4 + \Delta y_4\},$$

$$S_{3x} = (1/2\sqrt{3})\{\Delta x_1 - \Delta y_1 + \Delta z_1 + \Delta x_2 - \Delta y_2 - \Delta z_2 + \Delta x_3 + \Delta y_3$$
$$- \Delta z_3 + \Delta x_4 + \Delta y_4 + \Delta z_4\},$$

$$S_{3y} = (1/2\sqrt{3})\{-\Delta x_1 + \Delta y_1 - \Delta z_1 - \Delta x_2 + \Delta y_2 + \Delta z_2 + \Delta x_3 + \Delta y_3$$
$$- \Delta z_3 + \Delta x_4 + \Delta y_4 + \Delta z_4\},$$

$$S_{3z} = (1/2\sqrt{3})\{-\Delta x_1 + \Delta y_1 - \Delta z_1 + \Delta x_2 - \Delta y_2 - \Delta z_2 + \Delta x_3 + \Delta y_3$$
$$- \Delta z_3 - \Delta x_4 - \Delta y_4 - \Delta z_4\},$$

$$S_{4x} = (1/2\sqrt{6})\{2\,\Delta x_1 + \Delta y_1 - \Delta z_1 + 2\,\Delta x_2 + \Delta y_2 + \Delta z_2 + 2\,\Delta x_3$$
$$- \Delta y_3 + \Delta z_3 + 2\,\Delta x_4 - \Delta y_4 - \Delta z_4\},$$

$$S_{4y} = (1/2\sqrt{6})\{\Delta x_1 + 2\,\Delta y_1 + \Delta z_1 + \Delta x_2 + 2\,\Delta y_2 - \Delta z_2 - \Delta x_3$$
$$+ 2\,\Delta y_3 + \Delta z_3 - \Delta x_4 + 2\,\Delta y_4 - \Delta z_4\},$$

$$S_{4z} = (1/2\sqrt{6})\{-\Delta x_1 + \Delta y_1 + 2\,\Delta z_1 + \Delta x_2 - \Delta y_2 + 2\,\Delta z_2 + \Delta x_3$$
$$+ \Delta y_3 + 2\,\Delta z_3 - \Delta x_4 - \Delta y_4 + 2\,\Delta z_4\}. \tag{5}$$

As a first order approximation we assume a point charge model where the point charges are located at the position of the oxygen nuclei. *Ab initio* calculations yield net atomic charges equal to -0.67 and -0.57 for O and $+0.67$ and $+1.29$ for the central atom in CrO_4^{2-} and MnO_4^{-} ions respectively [21]. Other values for atomic charge of O in MnO_4^{-} are -0.36 by CNDO/VESCF with CI and -0.41 by a scattered wave calculation [22]. Calculated atomic charges on the oxygen atom in various other MO_4^{n-} ions are comparable. Although there may be periodic trends in the atomic charges in MO_4^{n-}, we use -0.5 for all since systematic calculations on all MO_4^{n-} ions using the same method are not available. If we displace these charges according to the definition of the symmetry coordinates in equation (5) and fit the calculated components of the electric field gradient to a functional form given in equation (4) we can obtain the required first and second derivatives of the efg. These derivatives have to be multiplied by $(1 + \gamma)$, taking into account the electric field gradient which arises due to the polarization of the closed inner shells of the central atom due to the displaced charges, where γ is the Sternheimer antishielding parameter [23]. The values of γ and other constants used here are given in table 1.

We find that many of these derivatives vanish, and the ones that are non-zero are related to one another as follows:

$$(\partial q/\partial S_2) \equiv (\partial q_{zz}/\partial S_{2a}) = -2(\partial q_{xx}/\partial S_{2a}) = -2(\partial q_{yy}/\partial S_{2a})$$
$$= (2/\sqrt{3})(\partial q_{xx}/\partial S_{2b}) = -(2/\sqrt{3})(\partial q_{yy}/\partial S_{2b}), \tag{6}$$

$$(\partial q/\partial S_3) \equiv (\partial q_{yz}/\partial S_{3x}) = (\partial q_{zx}/\partial S_{3y}) = (\partial q_{xy}/\partial S_{3z}), \tag{7}$$

$$(\partial q/\partial S_4) \equiv (\partial q_{yz}/\partial S_{4x}) = (\partial q_{zx}/\partial S_{4y}) = (\partial q_{xy}/\partial S_{4z}). \tag{8}$$

Non-vanishing second derivatives are

$$(\partial^2 q/\partial S_2^2) \equiv (\partial^2 q_{zz}/\partial S_{2a}^2) = -2(\partial^2 q_{xx}/\partial S_{2a}^2) = -2(\partial^2 q_{yy}/\partial S_{2a}^2)$$

$$= -(\partial^2 q_{zz}/\partial S_{2b}^2) = 2(\partial^2 q_{xx}/\partial S_{2b}^2) = 2(\partial^2 q_{yy}/\partial^2 S_{2b}^2)$$

$$= -(2/\sqrt{3})(\partial^2 q_{xx}/\partial S_{2a}\,\partial S_{2b}) = (2/\sqrt{3})(\partial^2 q_{yy}/\partial S_{2a}\,\partial S_{2b}). \tag{9}$$

$$(\partial^2 q/\partial S_3^2)_E \equiv (\partial^2 q_{xx}/\partial S_{3x}^2) = (\partial^2 q_{yy}/\partial S_{3y}^2) = (\partial^2 q_{zz}/\partial S_{3z}^2)$$

$$= -2(\partial^2 q_{xx}/\partial S_{3y}^2) = -2(\partial^2 q_{yy}/\partial S_{3z}^2)$$

$$= -2(\partial^2 q_{zz}/\partial S_{3x}^2) = -2(\partial^2 q_{xx}/\partial S_{3z}^2)$$

$$= -2(\partial^2 q_{yy}/\partial S_{3x}^2) = -2(\partial^2 q_{zz}/\partial S_{3y}^2) \tag{10}$$

and similarly for S_4 (that is, replace all S_3 in equation (10) by S_4 to get the relationships involving S_4)

$$(\partial^2 q/\partial S_3^2)_F \equiv (\partial^2 q_{yz}/\partial S_{3y}\,\partial S_{3z}) = (\partial^2 q_{zx}/\partial S_{3z}\,\partial S_{3x})$$

$$= (\partial^2 q_{xy}/\partial S_{3x}\,\partial S_{3y}) \tag{11}$$

and similarly for S_4. These relationships which we found numerically are exactly as derived by Hougen and Oka [17]. Table 2 includes several first derivatives of the electric field gradient calculated in this manner.

The next step is the transformation of these derivatives into derivatives with respect to normal coordinates, making use of the relation

$$(\partial q_{\alpha\beta}/\partial Q_i) = \sum_t (\partial q_{\alpha\beta}/\partial S_t)(\partial S_t/\partial Q_i), \tag{12}$$

Table 2. Derivatives of the electric field gradient with respect to symmetry coordinates as defined in equations (6)–(8), in esu $Å^{-4}$.

Molecule	$(\partial q/\partial S_2)$	$(\partial q/\partial S_3)$	$(\partial q/\partial S_4)$
$GeCl_4$	$-6\cdot18$	$-6\cdot59$	$-3\cdot09$
$GeBr_4$	$-4\cdot16$	$-4\cdot43$	$-2\cdot08$
ClO_4^-	$-33\cdot95$	$-36\cdot18$	$-16\cdot97$
BrO_4^-	$-28\cdot40$	$-30\cdot26$	$-14\cdot20$
VO_4^{3-}	$-3\cdot57$	$-3\cdot81$	$-1\cdot78$
$CrO_4^=$	$-4\cdot09$	$-4\cdot36$	$-2\cdot04$
MnO_4^-	$-4\cdot86$	$-5\cdot18$	$-2\cdot43$
$MoO_4^=$	$-8\cdot15$	$-8\cdot69$	$-4\cdot08$
TcO_4^-	$-10\cdot11$	$-10\cdot78$	$-5\cdot06$
RuO_4	$-10\cdot33$	$-11\cdot01$	$-5\cdot16$
ReO_4^-	$-51\cdot56$	$-54\cdot95$	$-25\cdot78$
OsO_4	$-57\cdot82$	$-61\cdot64$	$-28\cdot91$

where $(\partial S_i/\partial Q_i)$ are the elements of the usual L matrix. This transformation assumes a rectilinear relation between internal and normal coordinates. The second derivatives transform in an analogous way.

In order to make use of equation (12) we have to perform a normal coordinate analysis for all molecules of interest. Fortunately Ferraro and coworkers investigated a series of tetrahedral molecules including the molecules and ions of interest here with a Urey–Bradley force field [24]. We will use their set of quadratic force constants exclusively. The cubic force constants which are required in the calculation of the vibrationally-induced nuclear quadrupole coupling constants were obtained in the following way. For the bond stretching anharmonicity we assumed a Morse potential where the parameter a was calculated using Herschbach and Laurie's exponential functions [25]. In addition we assumed an anharmonic term for the non-bonded interaction with a cubic force constant $F_3 = -10F$, where F is the quadratic force constant for non-bonded interactions in the usual Urey–Bradley potential, given by Ferraro *et al.* [24]. With these two parameters we can express the cubic force constants in internal coordinates f_{rst} by considering the appropriate geometry of the tetrahedral molecules. Using the following standard transformation we obtain the cubic force constants in normal coordinates, ϕ_{ijk} from f_{rst}

$$\phi_{ijk} = \sum_{r, s, t} L_{ir} L_{js} L_{kt} f_{rst}.$$ (13)

These cubic force constants are found to have the relationships derived by Hougen and Oka for tetrahedral molecules (their equation (36)) [17].

Using these quantities from equations (6)–(13) we obtain the nuclear quadrupole coupling constants for the $v = 1$ state, the quantities χ_s and χ_t, given by Hougen and Oka as

$$\chi_t^{(2)} = (-1/2)(\hbar^2/h\nu)eQ[(\partial^2 q/\partial Q_2^2) - (\phi_{222}/\lambda_2)(\partial q/\partial Q_2)]$$ (14)

for the $\omega_2(E)$ vibration, and

$$\chi_s^{(t)} = (2/5)(\hbar^2/h\nu)eQ$$
$$\times \{(\partial^2 q/\partial Q_t^2)_F + \tfrac{1}{2}(\partial^2 q/\partial Q_t^2)_E - (\phi_{ttt}/\lambda_t)(\partial q/\partial Q_t)$$
$$- (\phi_{ttt'}/\lambda_{t'})(\partial q/\partial Q_{t'}) - \tfrac{1}{2}(\phi_{2tt}/\lambda_2)(\partial q/\partial Q_2)\},$$ (15)

$$\chi_t^{(t)} = (2/5)(\hbar^2/h\nu)eQ$$
$$\times \{(\partial^2 q/\partial Q_t^2)_F - (3/4)(\partial^2 q/\partial Q_t^2)_E - (\phi_{ttt}/\lambda_t)(\partial q/\partial Q_t)$$
$$- (\phi_{ttt'}/\lambda_{t'})(\partial q/\partial Q_{t'}) + (3/4)(\phi_{2tt}/\lambda_2)(\partial q/\partial Q_2)\}$$ (16)

for the two F_2 vibrations $\omega_3(t = 3, t' = 4)$ and $\omega_4(t = 4, t' = 3)$, where $\lambda_i = 4\pi^2 c\omega_i^2$ and $(\partial q/\partial Q_2)$, $(\partial q/\partial Q_t)$, $(\partial^2 q/\partial Q_t^2)_F$ and $(\partial^2 q/\partial Q_t^2)_E$ are taken from equations (6)–(10).

3. Results

Using our model, we calculate numerical values for these nuclear quadrupole coupling constants in the molecules shown in table 3 for the state $v_i = 1$. For the ω_3 mode in $^{189}OsO_4$ these are, $\chi_t^{(3)} = -3\cdot8\,MHz$ and $\chi_s^{(3)} = -3\cdot0\,MHz$. These

quantities have been measured in the hyperfine pattern of the ω_3 fundamental of the OsO_4 molecule using laser saturation spectroscopy [16]. The experimental values are $\chi_t^{(3)} = -3\cdot14 \pm 0\cdot23\,\text{MHz}$ and $\chi_s^{(3)} = -4\cdot29 \pm 0\cdot17\,\text{MHz}$ [17]. The agreement is good if we consider the simplicity of several assumptions, such as the point charge model and the Urey–Bradley force field, and especially the uncertainty in the value of γ. Table 3 includes nuclear quadrupole coupling constants calculated in the same way for $GeCl_4$, $GeBr_4$, RuO_4 and for the MO_4^{n-} ions, with the same expected accuracy as in OsO_4. Having been able to reproduce the magnitudes of the $^{189}OsO_4$ coupling constants to better than a factor of 2, we expect to be able to calculate vibrationally-induced quadrupolar relaxation rates to at least the order of magnitude with this method.

Table 3. Estimated quadrupole coupling constants χ (in MHz) and relaxation time (in seconds) due to the vibrationally induced electric field gradients at 300 K.

Nucleus	Molecule	$\chi_t^{(2)}$	$\chi_t^{(3)}$	$\chi_t^{(4)}$	$\chi_s^{(3)}$	$\chi_s^{(4)}$	T_1
^{73}Ge	$GeCl_4$	−0·004	0·028	0·004	0·020	0·003	$5\cdot6 \times 10^4$
^{73}Ge	$GeBr_4$	−0·002	0·017	0·001	0·012	0·001	$9\cdot3 \times 10^4$
^{35}Cl	ClO_4^-	−0·10	−0·60	0·01	0·50	0·02	$1\cdot6 \times 10^3$
^{81}Br	BrO_4^-	0·24	−0·90	−0·21	−0·76	−0·18	$1\cdot4 \times 10^2$
^{50}V	VO_4^{3-}	0·04	−0·35	−0·08	−0·26	−0·05	$5\cdot9 \times 10^3$
^{51}V	VO_4^{3-}	−0·01	0·08	0·03	0·06	0·02	$1\cdot4 \times 10^5$
^{53}Cr	$CrO_4^{=}$	0·01	−0·04	−0·01	−0·03	−0·01	$1\cdot3 \times 10^5$
^{55}Mn	MnO_4^-	0·11	−0·68	−0·09	−0·57	−0·08	$1\cdot9 \times 10^3$
^{95}Mo	$MoO_4^{=}$	0·07	−0·31	−0·12	−0·23	−0·08	$3\cdot2 \times 10^3$
^{99}T$_c$	TcO_4^-	0·15	−0·71	−0·18	−0·58	−0·14	$4\cdot5 \times 10^3$
^{99}Ru	RuO_4	0·03	−0·16	−0·03	−0·14	−0·03	$2\cdot5 \times 10^4$
^{101}Ru	RuO_4	0·18	−0·92	−0·18	−0·79	−0·15	$7\cdot4 \times 10^2$
^{187}Re	ReO_4^-	5·48	−18·77	−7·42	−13·97	−5·42	0·58
^{189}Os	OsO_4	1·14	−3·75	−1·23	−2·99	−0·96	3·4

In our calculation of the vibrationally-induced quadrupolar relaxation we follow the model developed by Brown and Colpa [6], based on the nuclear quadrupole interaction constants of the $v_i = 1$ state. In this model the quadrupolar interaction of equation (2) is a random function of time due to excitation and de-excitation of the $v = 1$ states due to vibrationally inelastic collisions, the vibrational dephasing which occurs because of elastic collisions, and the rotational motion of the molecule in the liquid. The over-all correlation time τ_c is assumed to be dominated by the dephasing and rotational processes.

The total relaxation rate can be expressed as

$$R_1 = 1/T_1 = R_1(E) + R_1(F_2) + R_1(F_2'),\qquad(17)$$

where the individual contributions from the E and two F_2 vibrational modes are expressed as

$$R_1(E) = (9/160)(\chi_t^{(2)})^2[(2I + 3)/(2I - 1)I^2]\exp\,(-hc\omega(E)/kT)\tau_c\qquad(18)$$

and

$$R_1(F_2) = (3/800)[(2I + 3)/(2I - 1)I^2][10(\chi_s - \chi_t)^2 + 9(\chi_s + (2/3)\chi_t)^2]$$
$$\times \exp{(-hc\omega(F_2)/kT)}\tau_c. \quad (19)$$

There are several models for estimating the correlation times τ_c [26]. In this paper we do not attempt to reproduce the observed magnitudes of relaxation times since we are interested primarily in sorting out which mechanisms are important and which are not. For this purpose we assume the same correlation time for all of the systems considered here. If we assume a usual correlation time for vibrational relaxation in liquids equal to $2 \cdot 5 \times 10^{-12}$ s then we obtain from equation (17) the vibrationally-induced quadrupolar relaxation time of the ^{189}Os nucleus in OsO_4 at 300 K equal to $T_1 = 3 \cdot 4$ s. An experimental value was estimated from linewidths as $T_1 = 2 \cdot 3 \times 10^{-4}$ s [2]. Analogously we obtain vibrationally-induced Ru relaxation times in $^{99}RuO_4$ and $^{101}RuO_4$ equal to $2 \cdot 5 \times 10^4$ s and 740 s, respectively, whereas the experimental values [9] are $0 \cdot 98$ s and $0 \cdot 033$ s. Further results are shown in table 3.

In the following we present a second approach for the calculation of the vibrationally induced quadrupolar relaxation which can be more easily extended to other molecular types. We write the potential in terms of the symmetry coordinates as

$$V = \tfrac{1}{2} \sum S_i S_j F_{ij} + (1/6) \sum S_i S_j S_k F_{ijk}. \quad (20)$$

The symmetry coordinates form a complete orthonormal set if we include a redundance coordinate. Again the efg is expanded in a Taylor series (equation (4)) in terms of the symmetry coordinates. Having found that second derivatives make a minor contribution to the overall rate we truncate the expansion after the linear term:

$$q_{\alpha\beta} = (q_{\alpha\beta})_e + \sum_i (\partial q_{\alpha\beta}/\partial S_i)S_i + \ldots.$$

All first derivatives are calculated in the same way as described above using the point charge model. In order to calculate the mean values for the symmetry coordinates we make use of Ehrenfest' theorem. The average force is zero, $\langle \partial V/\partial S_i \rangle = 0$, so by calculating the derivative of V with respect to all symmetry coordinates, we obtain a set of linear equations

$$\sum_i F_{ik}\langle S_i \rangle = -(1/3) \sum_{i,j} F_{ijk}\langle S_i S_j \rangle. \quad (21)$$

The mean square amplitudes can be evaluated in the usual way

$$\langle S_i S_j \rangle = (L\langle Q^2 \rangle L^T)_{ij}, \quad (22)$$

where $\langle Q^2 \rangle_{ii} = (1/\omega_i) \coth{(hc\omega_i/2kT)}$, taking the thermal average over all vibrational states using a harmonic approximation. The q tensor obtained from equation (4) then has to be transformed into the laboratory fixed frame and averaged

over all orientations. This average is then inserted into the usual expression for quadrupolar relaxation rate

$$1/T_1 = \frac{3(2I + 3)}{40(2I - 1)I^2} (eQ/\hbar)^2 \tau_c \langle q_{zz}^2 \rangle. \tag{23}$$

Both methods yield nearly identical results for OsO_4. The error associated with leaving out the quadratic terms in equation (4) is small and partially compensated by the error connected with the assumption of a linear relation between Q and S in the first method.

If we define a reduced relaxation rate, which is $1/T_1$ divided by the nuclear properties $Q^2(2I + 3)/(2I - 1)I^2$, then the vibrationally-induced relaxation rates in these molecules can be compared directly. We find a systematic trend of decrease across each row of the transition metal series. This is consistent with the usual observations of correlations across a transition series rather than a column in the period table, and is due to the systematic changes in the intramolecular potential across a transition series, which is reflected in systematic changes in each of the Urey–Bradley force constants (e.g. increasing stretching force constants) and decreasing M–O bond length across each series.

4. Discussion

With our model we can almost reproduce $\chi_s^{(3)}$ and $\chi_t^{(3)}$ observed for $^{189}OsO_4$ in the 961 cm^{-1} fundamental level in the gas phase. This probably means that we are getting the correct order of magnitudes for efg derivatives with this calculation method, at least for OsO_4. There is no reason to believe that this is an isolated case. Using the experimental values of quadrupole coupling constants for the $\omega_3 v = 1$ state for OsO_4 Brown and Colpa concluded that the relaxation rate due to this vibration was too small to account for the observed rate, and suggested that the other two modes with lower frequencies (333 and 323 cm^{-1}) are the dominant modes in quadrupolar relaxation. We find that including all the modes still gives a relaxation rate that is orders of magnitude too small. This is true also for all the other systems studied here.

We have found that the vibrational mechanism is unimportant in these systems. What mechanisms can account for the magnitudes of relaxation rates observed and their temperature dependence? In those cases where the ratio of $Q^2(2I + 3)/(2I - 1)I^2$ is the same as the ratio of the relaxation rates, the relaxation is very likely dominated by the quadrupole mechanism, for example, for Cl and Br nuclei in ClO_4^- and BrO_4^-.

In the experimental results of Tarasov *et al.* some of the relaxation rates showed a change in temperature dependence from an Arrhenius type at low temperatures to what they considered an exp ($-hc\omega/kT$) dependence at higher temperatures. They attributed these changes to competing vibrational and some other quadrupolar mechanism. Indeed, the turning around of the curves indicates at least two mechanisms are operative, with opposite temperature behaviour. The mechanism with opposite T dependence to Arrhenius type has to be competitive in at least some cases—since turn-around is observed. The best way to determine

which are these (at least) two mechanisms is to examine the temperature dependence of the $1/T_1$ ratio for $^{101}RuO_4/^{99}RuO_4$. This ratio is found to vary monotonically from 36·8 at 260 K down to 19·9 at 340 K. The ratio of $Q^2(2I + 3)(2I - 1)I^2$ values is 33·4. Therefore, it is obvious that of the two competing mechanisms at least one is *not* quadruplar in nature. Let us make the plausible assumption that one of the two mechanisms is a quadrupolar one. For both isotopes $1/T_1$ decreases with increasing temperature, reaches a minimum and starts to increase with T at higher temperatures. Since the $1/T_1 ratio$ decreases from the purely quadrupolar one to about 2/3 of it at the high T end, it can be deduced that the *quadrupolar relaxation rate decreases with increasing T* while the other rate increases with increasing T. We have already shown that the vibrational mechanism has a T dependence given by equations (18)–(19) which have the form $1/T_1 = \sum_i a_i \exp(-hc\omega_i/kT)$. Therefore, the quadrupolar mechanism which dominates is not the vibrational one. Not only are the vibrationally-induced relaxation rates too small, they also have a temperature dependence inconsistent with the observed temperature dependence of the $1/T_1$ ratio for $^{101}RuO_4/^{99}RuO_4$. Since RuO_4 in CCl_4 does not involve any ionic charges, we suggest that the quadrupolar mechanism which may be dominant in this system is the collisional-deformation mechanism; dispersion and repulsive forces give rise to fluctuating electric field gradients produced by instantaneous cloud deformations on collision. This mechanism should be more effective at lower temperatures, as discussed below. This mechanism then has the right temperature behaviour. The competing non-quadrupolar mechanism whose rate increases with increasing temperature could be the spin-rotation mechanism, which is known to behave in just this fashion. The $1/T_1$ ratio for $^{101}RuO_4/^{99}RuO_4$ for the spin rotation mechanism is the ratio of γ^2 values which is 1·256. Thus, for RuO_4 at least, our interpretation of the experiments of Tarasov *et al.* [9] indicates that the dominant quadrupolar mechanism is not the vibrational one. Since the curves for the other systems behave similarly, there is reason to believe the two competing mechanisms for the other neutral systems are the same as for RuO_4. The collisional deformation quadrupolar mechanism dominates relaxation at low temperature and become less important with increasing temperature. On the other hand the other (non-quadrupolar) mechanism becomes more important with increasing temperature. We have suggested the spin-rotation mechanism since it has a temperature dependence which is consistent with this behaviour.

4.1. *Electric field gradients due to collisional deformation*

Now that we have ruled out the vibrational mechanism, let us consider the other possible mechanisms for quadrupolar relaxation in highly symmetric nuclear sites in neutral nonpolar molecules in gases or neat liquids. We will use a binary collision model which has been successful in the interpretation of chemical shifts of ^{129}Xe in xenon in various buffer gases, as well as other nuclei in nonpolar molecules. Collision-induced deshielding in these systems has been interpreted as arising largely from London dispersion forces. According to London, all molecules produce fluctuating instantaneous electric fields which average out to zero but which have a non-zero mean square, which leads to dispersion forces. An electric field gradient is generated at the nuclear site by the fluctuating electric fields due to the collision partner. The mean square fluctuating electric field

mutually generated by an interacting pair of atoms separated by distance r is given by

$$\overline{E^2} = \frac{3}{2} \frac{\alpha_2}{r^6} \frac{I_1 I_2}{I_1 + I_2} \tag{24}$$

at the position of atom 1. This is a slightly modified version of the equation originally proposed by Raynes, Buckingham and Bernstein to explain chemical shifts in gases with increasing density [27]. The quantities which determine the magnitudes of these electric fields in non-polar molecules are the electric dipole polarizability α of the collision partner, and ionization energies I_1 and I_2 of the pair.

We calculate the instantaneous electric field gradient generated by this electric field as follows:

$$q = -3 \left[\frac{3}{2} \alpha_2 \frac{I_1 I_2}{I_1 + I_2} \right]^{1/2} (1 + \gamma) r^{-4} \tag{25}$$

for the component along the interatomic axis. The factor $(1 + \gamma)$ includes the polarization of the core electrons of the atom in question due to the electric field gradient generated by the collision partner at long range r. What we need is the square of this instantaneous value which then is averaged over all the collision partners and all orientations, $\langle q_{zz}^2 \rangle$, which is given by

$$\langle q_{zz}^2 \rangle = (1 + \gamma)^2 \frac{27}{2} \alpha_2 \frac{I_1 I_2}{I_1 + I_2} 4\pi\rho \int_0^\infty r^{-8} \exp\left(-V(r)/kT\right) r^2 \, dr. \tag{26}$$

Values of the averages $\langle r^{-8} \rangle$ have been calculated for potentials of the form

$$V = 4\varepsilon\{(r_0/r)^{12} - (r_0/r)^6\} \tag{27}$$

$$\langle r^{-8} \rangle = \frac{H_8(y)}{12 r_0^5 y^4}, \tag{28}$$

where $H_8(y)$ are tabulated by Buckingham and Pople [28], for values of

$$y = 2(\varepsilon/kT)^{1/2}. \tag{29}$$

In the extreme marrowing limit, the quadrupole relaxation rate can be written as

$$\frac{1}{T_1} = \frac{I + 3}{20 I^2 (2I - 1)} (eQ/\hbar)^2 \int_0^\infty \langle \text{Tr } \mathbf{q}(0) \cdot \mathbf{q}(t) \rangle \, dt. \tag{30}$$

We use the usual assumption that the field gradient time correlation function decays exponentially with a time constant τ_c which implies that the relaxation rate can be written as

$$\frac{1}{T_1} = \frac{3(2I + 3)}{40 I^2 (2I - 1)} (eQ/\hbar)^2 \langle q_{zz}^2(0) \rangle \tau_c, \tag{31}$$

where $\langle q_{zz}^2(0) \rangle$ and τ_c are estimated separately. Thus, the relaxation rate due to collisional deformation by long-range interactions with molecules of type 2 is given by

$$1/T_1 = \frac{3(2I+3)(1+\gamma)^2}{40I^2(2I-1)}(eQ/\hbar)^2\tau_c\frac{9\pi}{2}\rho_2\alpha_2\frac{I_1I_2}{I_1+I_2}\frac{H_8(y)}{r_0^5y^4}. \qquad (32)$$

The temperature dependence of the collision-induced electric field gradient is that of $H_8(y)/y^4$ which decreases with increasing temperature. For example, for $\varepsilon/k = 300$ K, $H_8(y)/y^4 = 12\cdot69$ at 133 K, and $5\cdot14$ at 300 K. Thus, the quadrupolar relaxation rate by this mechanism decreases with increasing temperature. This behaviour is similar to that of the collision-induced chemical shifts which decrease with increasing temperature. It is important to note that the quadrupolar relaxation rate associated with the collisional-deformation-induced field gradient as modelled here has a temperature dependence associated with the correlation time as well as the temperature dependence explicitly given in equation (32). Thus, it would not be unusual to find that the relaxation rate of a quadrupolar nucleus in a highly symmetric site has a temperature dependence that is different from that of ^{13}C or ^{1}H in the same molecule, even under the assumption of identical correlation times for relaxation of the various nuclei.

For a mixture, the $\rho_2\alpha_2 I_1 I_2 H_8(y)/(I_1+I_2)r_0^5 y^4$ term is replaced by

$$\sum_i \rho_i\alpha_i I_1 I_i H_8(y_i)/(I_1+I_i)r_{0i}^5 y_i^4.$$

In this mechanism, a nucleus will have greater relaxation rate in a solvent which has a higher polarizability. ^{73}Ge in neat GeBr$_4$ will have a greater relaxation rate than ^{73}Ge in neat GeCl$_4$, on the basis of polarizabilities and ionization energies of these molecules. Furthermore, ^{73}Ge in GeBr$_4$ in a mixture containing GeBr$_4$ and GeCl$_4$ will have a lower relaxation rate than in neat GeBr$_4$, whereas ^{79}Ge in GeCl$_4$ in a mixture of GeCl$_4$ and GeBr$_4$ will have a greater relaxation rate. This comes about not only from the α_i and I_i terms but also the potential well depth ε_{1i} in $H_8(y)$ which is related to the product of polarizabilies of the observed molecule 1 and the collision partner i. Thus, the ordering of the ^{73}Ge relaxation rates in molecules in a mixture of GeCl$_{4-n}$Br$_n$ which was observed by Tarasov *et al.* [10] is easily explained. In the same mixture, if no intrinsic efg is present in any of these molecules, the collisional deformation by long range interactions gives relaxation rates in the same order that would be expected from the medium-induced chemical shifts: GeBr$_4$ > GeClBr$_3$ > GeCl$_2$Br$_2$ > GeCl$_3$Br > GeCl$_4$. However, the presence of an intrinsic efg in the static isolated molecules gives the mixed halogermanes the larger relaxation rates compared to the symmetrical ones. The most asymmetric one, GeCl$_2$Br$_2$, should have the largest static electric field gradient with GeClBr$_3$ and GeCl$_3$Br following in the order of their polarizabilities. Indeed the experimental relaxation rates are $1\cdot7$, $2\cdot2$, $2\cdot6$, $4\cdot0$, $4\cdot6$ s^{-1} for GeCl$_4$, GeBr$_4$, GeCl$_3$Br, GeClBr$_3$, GeCl$_2$Br$_2$ at 295 K. Furthermore the rates for GeCl$_4$ and GeBr$_4$ decrease with increasing temperature, as predicted by this model.

To determine if the magnitudes of the collisional deformation quadrupolar relaxation rate are comparable with the experimental rates, we need to calculate $1/T_1$ for at least one case. For ^{73}Ge in neat liquid GeCl$_4$ we calculate the relaxation rate at 300 K using the following data: [29] $\alpha = 16\cdot8 \times 10^{-24}$ cm^3.

$\varepsilon/k = 300\,\text{K}$, $r_0 = 5\cdot32\,\text{Å}$, $\rho = 8\cdot6\,\text{mol}\,\text{l}^{-1}$, $I = 12\,\text{eV}$, and $\tau_c = 2\,\text{ps}$. The other constants are given in table 1. With equation (32) we obtain $1/T_1 = 2\,\text{s}^{-1}$ to be compared with the observed rate which is $1\cdot2\,\text{s}^{-1}$ [10].

In our simple model we have made the usual assumption that the time correlation function of the induced electric field gradient has a simple exponential form. If the decay of the time correlation function is non-exponential then the correlation time τ_c in equation (32) is an 'effective' one, containing both structural and dynamical information. It has been shown by molecular dynamic simulation for Li^+, Na^+, and Cl^- in H_2O that the $\langle\text{Tr}\,\mathbf{q}(0)\cdot\mathbf{q}(t)\rangle$ time correlation function exhibits a rapid initial decay and a successive second decay of a more diffusive character, rather than the single exponential character which is usually assumed [30]. The character of the time correlation function for a neutral MO_4 or MX_4 in a non-polar solvent such as CCl_4 may also be non-exponential. However, we are concerned here primarily with determining which mechanisms provide quadrupolar relaxation rates of the appropriate order of magnitude rather than with the details of the true time correlation function of the efg. Therefore, we simply assumed an 'effective' correlation time τ_c which is of the order of 1–2 ps for translational or reorientation motion of the molecules in a typical solution at room temperature.

4.2. *Electric field gradients due to electrical moments of solvent molecules*

For the same highly symmetric non-polar molecule in a polar solvent, there will be additional interactions. The field along the intermolecular axis due to a linear dipolar molecule 2 is given by

$$E = 2\mu_2\,r^{-3}P_1(\cos\theta) + 3\Theta_2\,r^{-4}P_2(\cos\theta) + 4\Omega_2\,r^{-5}P_3(\cos\theta) + \ldots, \quad (33)$$

where θ is the angle the dipole makes with this axis. The instantaneous electric field gradient generated by this is

$$q = (1 + \gamma)\{-6\mu_2\,r^{-4}P_1(\cos\theta) - 12\Theta_2\,r^{-5}P_2(\cos\theta)$$
$$- 20\Omega_2\,r^{-6}P_3(\cos\theta)\} + \ldots \quad (34)$$

for the component along the intermolecular axis. The average of the square of this over all collision partners and orientation is

$$\langle q_{zz}^2\rangle = (1 + \gamma)^2\rho_2\{36\mu_2^2\langle r^{-8}(P_1(\cos\theta))^2\rangle + 144\Theta_2^2\langle r^{-10}(P_2(\cos\theta))^2\rangle$$
$$+ 400\Omega_2^2\langle r^{-12}(P_3(\cos\theta))^2\rangle + \ldots, \quad (35)$$

where the averages on the right hand side of the equation are over the anisotropic intermolcular potential. If we consider only the leading term in the electric dipole moment μ and neglect the anisotropy of the intermolecular potential, we obtain

$$\langle q_{zz}^2\rangle = \{(1 + \gamma)^2\mu_2^2\,4\pi\rho_2/r_0^5\}\,\frac{H_8(y)}{y^4}. \quad (36)$$

This leads to

$$(1/T_1)_\mu = \frac{3(2I + 3)(1 + \gamma)^2}{40I^2(2I - 1)}\,(eQ/\hbar)^2\,\frac{\tau_c\,4\pi\rho_2\,\mu_2^2}{r_0^5}\,\frac{H_8(y)}{y^4}. \quad (37)$$

This may be compared with the expression derived by Hertz (his equation (55) using his assumption of $P = \frac{1}{2}$) [3]

$$(1/T_1) = \frac{3(2I + 3)(1 + \gamma)^2}{40I^2(2I - 1)} (eQ/\hbar)^2 \tau_{H_2O} \cdot 4\pi c_{H_2O}(\mu_{H_2O}^2/r_0^5), \tag{38}$$

where our r_0 is the Lennard–Jones parameter whereas Hertz' r_0 is $r_{H_2O} + r_{ion}$. Our equation (37) has the extra factor $H_8(y)/y^4$. An equation similar to equation (38) has been used in interpreting relaxation rates for ^{131}Xe in polar solvents [31].

We can also consider the contributions of higher electrical moments to the relaxation rate in a tetrahedral non-polar solvent. The electrical field due to a tetrahedral molecule at a distance r and oriented such that the end atoms are at alternate corners of a cube and the cube is oriented such as to have angles θ_x, θ_y and θ_z between its x, y, and z axes respectively and the vector r, is given by [32]

$$E = 24\Omega r^{-5} \cos \theta_x \cos \theta_y \cos \theta_z. \tag{39}$$

Ω is the electric octopole moment of the tetrahedral molecule. This electric field generates an electric field component along $\mathbf{r}$

$$q = -120\Omega r^{-6} \cos \theta_x \cos \theta_y \cos \theta_z. \tag{40}$$

At the nuclear site this is enhanced by a factor $(1 + \gamma)$, so that if we neglect the anisotropy of the intermolecular potential and assume a Lennard–Jones form for $V(r)$,

$$\langle q_{zz}^2 \rangle = (1 + \gamma)^2 14400\Omega^2 \langle \cos^2 \theta_x \cos^2 \theta_y \cos^2 \theta_z \rangle \times 4\pi\rho H_{12}(y)/(12r_0^9 y^4). \tag{41}$$

The spherical average of $\cos^2 \theta_x \cos^2 \theta_y \cos^2 \theta_z$ is $\pi^2/64$, so that

$$(1/T_1)_\Omega = \frac{3(2I + 3)(1 + \gamma)^2}{40I^2(2I - 1)} (eQ/\hbar)^2 \tau_c \frac{75\pi^3 \rho \Omega^2}{r_0^9} \frac{H_{12}(y)}{y^4}. \tag{42}$$

We can now compare this contribution to the dispersion contribution. As before, we use $\varepsilon/k = 300$ K and $r_0 = 5.32$ Å and obtain $H_{12}(y)$ from the tables of Buckingham and Pople [28]. At 300 K $H_{12}(y) = 50.5475$. If the dispersion contribution to the relaxation rate is approximated by the expression in equation (32) and the octopolar contribution by equation (42), then these two contributions become equal if the octopole moment for GeCl$_4$ is equal to 35.7×10^{-34} esu cm^3. The octopole moment of GeCl$_4$ is not known but there are values available for other tetrahedral molecules. For CH$_4$ $\Omega = 1.81 \times 10^{-34}$ esu cm^3 [33], for SiF$_4$ $\Omega = 5.3 \times 10^{-34}$ [34]. The octopole moment of a molecule can be evaluated from

$$\Omega = (5/2) \sum_i e_i x_i y_i z_i. \tag{43}$$

If we assume point charges f for the end atoms then

$$\Omega \simeq (5/2)f 4(r_c/\sqrt{3})^3 \tag{44}$$

or else bond dipole moments μ at distance d_0 from the centre give an octopole moment equal to $\Omega = (10/\sqrt{3})\mu d_0^2$. The octopole moment of CH$_4$ in the point charge model corresponds to a charge on each H atom equal to ± 0.153 e. For GeCl$_4$ to have an octopole moment as large as 35.7×10^{-34} esu cm^3 in this point charge model, each Cl atom has a charge ± 0.43 e. The bond moments in GeCl$_4$

have been estimated to be 3·2 D [35]. If placed at the midpoint of the bonds, these give $\Omega = 20 \times 10^{-34}$ esu cm^3. We see that the relaxation rates due to electric field gradients induced by dispersion and by the octopole moment of the collision partner are comparable in magnitude and are of the same order of magnitude as the observed relaxation rates in the GeCl$_4$ solutions.

The expressions derived here are in the binary collision model. For the liquid phase a continuum model such as that based on an Onsager reaction field which has been used in the interpretation of solvent-induced shifts or quadrupolar relaxation in electrolytes may be more appropriate [36].

Finally, let us consider the similarity of temperature-dependent chemical shifts and temperature-dependent quadrupolar relaxation rates. Nuclear shielding σ in the dilute gas phase is dependent on density ρ and temperature T, in a way which is described by the leading terms in a virial expansion [28]

$$\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \ldots \tag{45}$$

The first term, $\sigma_0(T)$, is the temperature-dependent nuclear shielding for an isolated molecule due to vibrational and rotational effects. These effects are fairly large, due to centrifugal distortion, anharmonic vibration, and harmonic vibration, involving first derivatives of the nuclear shielding accompanied by cubic force constants, and second derivatives of shielding, somewhat similar to the terms in equations (14)–(16) [37]. These effects dominate ^{19}F shifts with temperatures at low densities. The second term, $\sigma_1(T)\rho$ is due to intermolecular interactions. Deformation of the electronic distribution around the nucleus during a collision arises from long range van der Waals (and also electrical interactions when polar molecules are involved) and short range overlap and exchange interactions. The second term and higher order terms in density become dominant at high densities, so that in the liquid phase only the temperature dependence of the intermolecular interaction terms are observable. Only in low density gas in the limit of zero pressure is it possible to observe only the rovibrationally-induced chemical shifts.

The analogous situation occurs in quadrupolar relaxation. The electric field gradient tensor components which are induced by vibrational excitation can only be observed in the low density gas in the limit of zero pressure. At higher densities, and certainly in the neat liquid or in solution, the electric field gradients induced by collisional deformation are more important and will dominate quadrupolar relaxation. In the gas phase at constant density, this latter mechanism is more important at lower temperatures, because the averaging takes place primarily in the attractive part of the intermolecular potential. In the liquid phase other temperature-dependent factors enter, such as the decrease in density of the liquid with increasing temperature in the usual constant pressure relaxation experiment. Although a turn-around with temperature in the function $\sigma_1(T)$ in the chemical shift experiment has not yet been observed, there is no physical argument that rules it out, if sufficiently high temperatures are reached. By analogy, the collisional deformation-induced electric field gradient could exhibit a turn-around in its temperature behaviour. However, this is extremely unlikely for the relatively narrow temperature ranges of the experiments by Tarasov *et al.* The observed turn-around with temperature is more plausibly attributed to the growing importance of a second mechanism. Certainly in the case of RuO$_4$, the systematic change with increasing temperature of the ratio of relaxation rates of

^{101}Ru and ^{99}Ru away from the ratio of quadrupole moments is unequivocal evidence for the growing importance of a non-quadrupolar mechanism.

5. Conclusions

The calculated relaxation rates due to vibrationally-induced electric field gradients are orders of magnitude too small compared to experiment. Since we are able to reproduce the vibrationally-induced nuclear quadrupole coupling constants observed for ^{189}Os in OsO_4 with the model presented here, we expect the calculated relaxation rates to be about right. Only the correlation time is unknown and this cannot differ very much from several picoseconds in these liquids. Our conclusion therefore is that the rate of the vibrational mechanism is far too small to make a significant contribution to the relaxation rate in liquids. Since the vibrational mechanism is too small to be dominant in the liquid phase for the neutral species considered here, it is less likely to be descriptive of relaxation in aquo complexes where electrostatic contributions play an important role. On the other hand our experience with intermolecular effects on shielding suggests that collisional deformation due to long-range van der Waals interactions can give rise to fluctuating electric field gradients. The binary collision model presented here has an explicit temperature dependence and depends on polarizabilities and other molecular properties in a way that is consistent with the observed experimental data for neutral species. For charged species, dipolar-solvent-induced electric field gradients are more likely to be important. A unified theory which describes both the relaxation and the chemical shifts in electrolyte solutions would be very useful.

It is clear that temperature-dependent studies are essential in sorting out mechanisms for relaxation in these highly symmetric nuclear sites.

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