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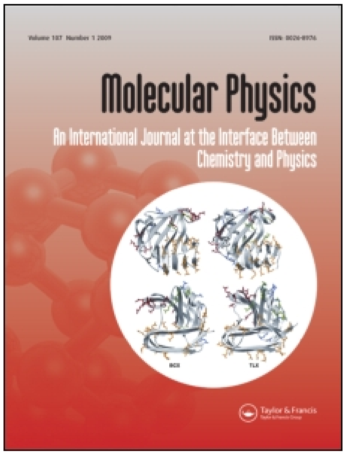

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Effects of vibrational anharmonicity on ^{19}F nuclear resonance in SF_6

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Effects of vibrational anharmonicity on ^{19}F nuclear resonance in SF_6

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The temperature dependence of the ^{19}F N.M.R. shifts in several molecules has been measured in the limit of zero pressure [1–5]. The function so obtained is $\langle\sigma\rangle^{T}-\langle\sigma\rangle^{300}$, in which the thermal average of the ^{19}F nuclear shielding, $\langle\sigma\rangle^{T}$, is observed relative to the value at an arbitrarily chosen temperature, 300 K. This can be interpreted in terms of the variation of the nuclear shielding with respect to the internal coordinates of the molecule [6].

For a molecule of the type AX_6 which is of octahedral symmetry,

$$\langle\sigma\rangle^{T}=\sigma_e+(\partial\sigma/\partial q_1)_e\langle q_1\rangle^{T}+\sum_i(\partial^2\sigma/\partial q_i^2)_e\langle q_i^2\rangle^{T}+\dots, \tag{1}$$

in which q_1 is the dimensionless normal coordinate corresponding to the symmetric stretching mode (A_{1g}). If we truncate this expansion beyond the linear term, there is only one internal coordinate which is involved, the displacement along the AX bond, Δr. We can then write

$$\langle\sigma\rangle^{T}\simeq\sigma_e+\langle\Delta r_1\rangle^{T}\left\{\sum_i^6(\partial\sigma/\partial\Delta r_i)_e\right\}. \tag{2}$$

The sum of derivatives can be considered as an empirical parameter to be determined since the experimentally determined function, $\langle\sigma\rangle^{T}-\langle\sigma\rangle^{300}$ can be least-squares fitted to the function

$$\langle\sigma\rangle^{T}-\langle\sigma\rangle^{300}=C+B\langle\Delta r_1\rangle^{T}, \tag{3}$$

yielding empirical values for $C=\sigma_e-\langle\sigma\rangle^{300}$ and $B=\sum_i^6(\partial\sigma/\partial\Delta r_i)_e$, provided the temperature dependence of the mean AX bond stretching can be determined independently. If A is the nucleus observed in AX_6, all the derivatives are identical and $B=6(\partial\sigma_A/\partial\Delta r_i)_e$. On the other hand, if X is the nucleus observed, there will be three different derivatives in the sum, $(\partial\sigma_X/\partial\Delta r_1)+(\partial\sigma_X/\partial\Delta r_{opp})_e+4(\partial\sigma_X/\partial\Delta r_{adj})_e$, but only the sum can be obtained as an empirical parameter. This would be the case when observing ^{19}F in SF_6.

The temperature dependence of ^{19}F shielding, in SF_6 has been previously reported

$$(\langle\sigma\rangle^{T}-\langle\sigma\rangle^{300})/\text{p.p.m.}=-1\cdot2073\times10^{-2}\{(T/\text{K})-300\}-2\cdot6808\times10^{-5}\{(T/\text{K})-300\}^2.$$

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The mean displacement of an AX bond length from its equilibrium value can be evaluated if the anharmonic force field of AX_n is known

$$\langle \Delta r_1 \rangle^{\mathrm{T}} = (h/4\pi^2 c\omega_1 n m_{\mathrm{x}})^{1/2}(\langle q_1 \rangle_{\mathrm{anh}}{}^{\mathrm{T}} + \langle q_1 \rangle_{\mathrm{cent}}{}^{\mathrm{T}}), \tag{4}$$

where m_{x} is the mass of atom X. Using the formulation of Toyama *et al.* [7],

$$\langle q_1 \rangle_{\mathrm{anh}}{}^{\mathrm{T}} = -[3k_{111} \coth(hc\omega_1/2kT) + \sum_{\mathrm{s}} g_{\mathrm{s}} k_{1\mathrm{ss}} \coth(hc\omega_{\mathrm{s}}/2kT)]/2\omega_1, \tag{5}$$

$$\langle q_1 \rangle_{\mathrm{cent}}{}^{\mathrm{T}} = 6(kT/4\pi c\omega_1)(hc\omega_1 n m_{\mathrm{x}} r_{\mathrm{e}}{}^2)^{-1/2}. \tag{6}$$

The difficulty with using this expression is that the net temperature dependence of Δr is dominated by the terms with low ω_{s}, the bending modes, for which the $k_{1\mathrm{ss}}$ are not as well-determined as k_{111} or other stretch–stretch cubic force constants. However, anharmonic force fields of simple molecules are beginning to be available and the agreement with observed vibrational energies continues to improve [8].

Alternatively, the mean displacement of the SF bond length from its equilibrium value can be approximated by the method of Bartell, from mean square amplitudes of vibration, using an anharmonic modified Urey–Bradley force field. Bartell's approximation for AX_n is [9]

$$\langle \Delta r \rangle = \Delta_{\mathrm{r}} + \Delta_{\mathrm{m}} + \Delta_{\mathrm{nb}} + \Delta_{\mathrm{b}} + \Delta_{\mathrm{x}}, \tag{7}$$

where the contributing terms are, respectively, the centrifugal stretching due to rotation, the Morse anharmonic stretching, the stretching due to the enhancement of non-bonded repulsions as atoms vibrate, the bending centrifugal distortion, and small terms from various cross-terms. The centrifugal stretching due to rotation is the same as in equations (4) and (6)

$$\Delta_{\mathrm{r}} = kT/8\pi^2 c^2 \omega_1{}^2 m r_{\mathrm{e}}.$$

The Morse anharmonic stretching is

$$\Delta_{\mathrm{m}} = (3a/2)(K/f_{11})\langle(\Delta r)^2\rangle, \tag{8}$$

in which a is the Morse parameter, f_{11} is the force constant for the totally symmetric stretching mode, K is the Urey–Bradley stretching force constant and $\langle(\Delta r)^2\rangle$ is the mean square amplitude of vibration parallel to the SF bond. The non-bonded contribution is given by

$$\Delta_{\mathrm{nb}} = -(n_{\mathrm{adj}} F_3/4 f_{11} r_{\mathrm{e}})\langle(\Delta R)^2\rangle, \tag{9}$$

where n_{adj} is the number of bonds in AX_n adjacent to AX_i, F_3 is the non-bonded cubic potential constant, defined by Kuchitsu and Bartell [10], and $\langle(\Delta R)^2\rangle$ is the mean square amplitude of vibration along the non-bonded distance between two adjacent X atoms. The bending term is interpreted as a centrifugal stretching of bonds which occurs as the peripheral X atoms travel over their arced trajectories in bending vibrations. Δ_{b} becomes very nearly

$$\Delta_{\mathrm{b}} \simeq (n f_{11} r_{\mathrm{e}})^{-1} \sum_{i=\mathrm{bend}} f_{ii}\langle S_i{}^2\rangle, \tag{10}$$

in which S_i are the pure bending symmetry coordinates. In the absence of strong coupling of modes, Δ_{b} becomes

$$\Delta_{\mathrm{b}} \simeq (n f_{11} r_{\mathrm{e}})^{-1} \sum_{i=\mathrm{bend}} (hc\omega_i/2) \coth(hc\omega_i/2kT). \tag{11}$$

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The remaining terms of minor importance, Δ_x can be approximated by

$$\Delta_x = n_{adj} \sin \tfrac{1}{2}\alpha_e(F'K_{XX} + F\delta_{XX})/f_{11} - (n_{adj}/2f_{11}r_e)(-\sin^2 \tfrac{1}{2}\alpha_e F' + \cos^2 \tfrac{1}{2}\alpha_e F)\langle(r_e\Delta\alpha)^2\rangle. \quad (12)$$

F' and F are the non-bonded Urey–Bradley force constants defined by Shimanouchi [11], and K_{XX} and δ_{XX} are the constants of the Bastiansen–Morino shrinkage effect [12]. The mean square amplitude $\langle(r_e\Delta\alpha)^2\rangle$ is related to the two others mentioned by [13]

$$\cos^2 \tfrac{1}{2}\alpha_e\langle(r_e\Delta\alpha)^2\rangle = \langle(\Delta R)^2\rangle - 2\sin^2 \tfrac{1}{2}\alpha_e\langle(\Delta r)^2\rangle. \quad (13)$$

Zeroth order mean square amplitudes can be used directly instead of the corrected mean square amplitudes calculated for the anharmonic force field, for it has been shown that, at least for Morse stretching, the use of the former in place of the latter compensates quite well for the other error of truncating the potential energy function beyond cubic terms [13].

The advantage of Bartell's treatment is that $\langle\Delta r\rangle^T$ is evaluated entirely from parameters (a, K, F', F, F_3) which are either readily available or more reliably estimated than the $k_{ss's''}$ constants, and from mean square amplitudes $\langle(\Delta r)^2\rangle$, $\langle(\Delta R)^2\rangle$ for which the unperturbed values are easily obtained from the standard results of normal coordinate calculations [12]. The shrinkage effect quantities K_{XX} and δ_{XX} are obtained from mean square perpendicular amplitudes from the same calculations [12].

In terms of the symmetry coordinates defined by Pistorius for SF_6 type molecules, [14], the mean square amplitudes for SF_6 are

$$\langle(\Delta r_{SF})^2\rangle = \tfrac{1}{6}\langle S_1^2\rangle + \tfrac{1}{3}\langle S_2^2\rangle + \tfrac{1}{2}\langle S_3^2\rangle, \\ = \mu_F(\langle Q_1^2\rangle + 2\langle Q_2^2\rangle)/6 + (L_{33}^2\langle Q_3^2\rangle + L_{34}^2\langle Q_4^2\rangle)/2, \quad (14)$$

$$\langle(\Delta R_{FF})^2\rangle = \tfrac{1}{3}\langle S_1^2\rangle + \tfrac{1}{6}\langle S_2^2\rangle + \tfrac{1}{2}\langle S_3^2\rangle + \tfrac{1}{8}\langle S_4^2\rangle - \tfrac{1}{2}\langle S_3S_4\rangle + \tfrac{1}{8}\langle S_5^2\rangle + \tfrac{1}{8}\langle S_6^2\rangle, \\ = \mu_F(6\langle Q_1^2\rangle + 2\langle Q_2^2\rangle + 6\langle Q_5^2\rangle + 3\langle Q_6^2\rangle)/12 + \tfrac{1}{2}(L_{33} - \tfrac{1}{2}L_{43})^2\langle Q_3^2\rangle + \tfrac{1}{2}(L_{34} - \tfrac{1}{2}L_{44})^2\langle Q_4^2\rangle. \quad (15)$$

The zeroth order averages, $\langle Q_i^2\rangle^T$ are [15]

$$\langle Q_i^2\rangle^T = (h/8\pi^2 c\omega_i) \coth (hc\omega_i/2kT). \quad (16)$$

The Bastiansen–Morino shrinkage effect is likewise derivable in terms of the same quantities [12]. For SF_6-type molecules :

$$K_{FF} = \frac{1}{4R}\{\langle S_2^2\rangle + \langle S_3^2\rangle - \langle S_3S_4\rangle + \tfrac{1}{4}\langle S_4^2\rangle + \tfrac{1}{4}\langle S_5^2\rangle + \tfrac{5}{4}\langle S_6^2\rangle\}, \quad (17)$$

$$\delta_{FF} = \frac{1}{8R\sqrt{2}}\{-\langle S_2^2\rangle - \langle S_3^2\rangle + \langle S_3S_4\rangle + \tfrac{3}{4}\langle S_4^2\rangle + \tfrac{1}{4}\langle S_5^2\rangle - \tfrac{1}{4}\langle S_6^2\rangle\}. \quad (18)$$

Just as in equations (14) and (15), these terms are expressible in terms of ω_i and the L matrix elements in the transformation between the symmetry coordinates and normal coordinates.

Bartell, Doun and Goates have applied this treatment to SF_6. They found that their results account quantitatively for the observed bond length in an

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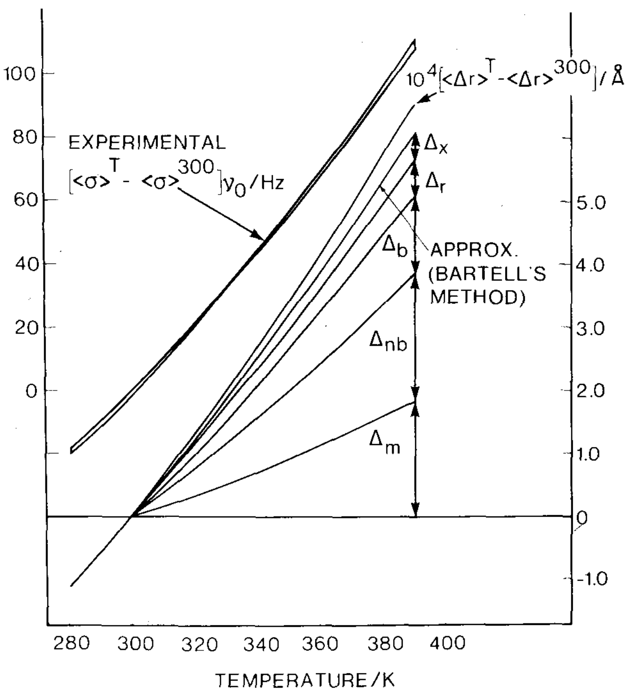

Temperature dependence of mean SF bond length in SF_6, calculated by the method of Toyama *et al.* [7] (see text, equations (4)–(6)), compared with that calculated by the approximate method of Bartell [9]. The contributions (Bartell method) from Morse anharmonicity, non-bonded repulsion, bending centrifugal stretch, rotational centrifugal stretch and minor-cross terms are also indicated. The empirical factor which relates the temperature dependence of $\langle \Delta r \rangle^T$ with the observed ^{19}F chemical shift shown above, is $(\partial\sigma/\partial\Delta r)_e$.

investigation of gaseous SF_6 at temperatures from 298 to almost 1000 K. From their given figure, it appears that the change in $\langle \Delta r \rangle^T$ from 298 to 1000 K is reproduced by 6·7 per cent centrifugal distortion due to rotation, 38·3 per cent anharmonic Morse stretching, 33·3 per cent non-bonded contribution, 16·6 per cent centrifugal stretching due to bending and 5 per cent residual cross-terms.

We use the Bartell treatment here to compare the calculated temperature dependence of σ with our experimental $\langle\sigma\rangle^T - \langle\sigma\rangle^{300}$. The force field parameters a, K, f_{11}, F', F and F_3 were taken from Bartell *et al.* [16]. The mean square amplitudes were calculated using the expressions in equations (14)–(18), with the L matrix elements and ω_i from McDowell *et al.* [17]. The results are shown in the figure. An iterative non-linear least squares fitting procedure was used to obtain the empirical parameter

$$B = \sum_i^6 (\partial\sigma_F/\partial\Delta r_i) = -2200 \text{ p.p.m. Å}^{-1}.$$

(This can be interpreted as largely $(\partial\sigma_{F_1}/\partial\Delta r_{SF_1})_e$ since the stretch of the adjacent or opposite SF bonds should have a much smaller contribution to σ_F.) This leads to an empirical value of $C = \sigma_e - \langle\sigma\rangle^{300} = 13$ p.p.m. These values compare reasonably well with values for other fluorine containing molecules (except

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F_2), for which B ranges from -2070 to -1115 p.p.m. $Å^{-1}$ and C ranges from 6 to 13 p.p.m. [6].

We can compare these results with those using $\langle \Delta r \rangle^{T}$ calculated by equations (4)–(6). The anharmonic potential constants k_{1ss} have been determined by Overend [8], using a model anharmonic force field which has been used for the calculation of anharmonic splittings and vibrational energies in SF_6 [18], and also for the interpretation of the observed intensity of a three-vibrational quantum electric dipole transition in the ν_3 manifold of SF_6 [19]. The results are shown in the figure. This leads, by the same fitting procedure, to $B = -2000$ p.p.m. $Å^{-1}$ and $\sigma_e - \langle \sigma \rangle^{300} = 12{\cdot}9$ p.p.m. The values obtained using Bartell's approximate treatment are in excellent agreement with these. However, these results are still tentative, the intramolecular potential function still needs to be improved to obtain better agreement with the most recently available vibrational anharmonicity constants X_{ij} [20], as well as the intensities of multiple quantum transitions in the I.R. spectrum of SF_6 [19].

The use of Bartell's approximate treatment appears to be very promising in the interpretation of temperature dependent chemical shifts in AX_n-type molecules. It can be very useful in cases where reliable anharmonic force constants $k_{ss's''}$ are not yet available. It requires only ω_i and L matrix elements from a standard normal coordinate analysis, and estimates of the Morse and Urey–Bradley parameters a, K and F (since F' and F_3 are related to F). There is the additional advantage that the model allows a comparison of the separate contributions, which for a polyatomic molecule are now known to be inadequately represented by the Morse anharmonicity alone.

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