The mean bond displacements in $O = CF_2$ and their effect on ^{19}F nuclear magnetic shielding

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The mass and temperature dependence of the mean bond displacements in carbonyl fluoride have been determined using a modified Urey–Bradley field, by solving the set of coupled equations relating mean bond displacements $\langle \Delta R_{\rm CF} \rangle$ and $\langle \Delta r_{\rm CO} \rangle$ to mean square-vibrational amplitudes $\langle (\Delta R_{\rm CF})^2 \rangle, \langle \Delta r \Delta R \rangle$, etc. To these vibrational terms the rotational (centrifugal distortion) contributions are added. The results are applied to the interpretation of the temperature dependence of the ^{19}F nuclear shielding in $O = CF_2$ at the zero-pressure limit. By fitting the observed $[\sigma_0(T) - \sigma_0(300)]$ for $T = 250$–350 K an empirical value of $(\partial\sigma/\partial\Delta r_{\rm CF})_e = -1146$ ppm Å^{-1} is obtained. This derivative is used to calculate the NMR isotope shifts from the mass dependent $\langle \Delta R_{\rm CF} \rangle$. The calculated value, $[\sigma_0(^{16}O^{12}CF_2) - \sigma_0(^{16}O^{13}CF_2)] = -0.096$ ppm, is in good agreement with our measured value of -0.117 ppm. From the fitting to the temperature dependence of σ_0 we also get $\sigma_e - \sigma_0$ (300 K) = 7 ppm. This and the absolute shielding σ_0 (300 K) = 221.6 ppm yields an estimate for ^{19}F shielding at the equilibrium configuration, $\sigma_e \simeq 229$ ppm. The errors which are associated with these values are discussed.

INTRODUCTION

The temperature dependence observed in the NMR chemical shifts in the gas phase in the zero-pressure limit has been interpreted in terms of the existence of a nuclear magnetic shielding surface which together with the intramolecular potential energy surface determines the rovibrationally averaged values of the shielding.[1–3] In practice the latter is measured as the residual shifts of the nuclear magnetic resonance frequencies with temperature after the intermolecular (density dependent) effects have been removed. The same interpretation is used for NMR isotopic shifts, measured as differences in resonance frequency between a nucleus in two different isotopomers, in which the isotopically substituted atom is one or more bonds away from the observed nucleus.[4,5] The derivatives of the nuclear shielding surface and the average displacement coordinates provide a standard way of expressing the temperature dependence of the shielding $[\sigma_0(T) - \sigma_0(300)]$:

$$\sigma_0(T) = \sigma_e + \sum (\partial\sigma/\partial q_i)_e \langle q_i \rangle^T + \tfrac{1}{2} \sum_{i,j} (\partial^2\sigma/\partial q_i \partial q_j) \times \langle q_i q_j \rangle^T + \cdots . \quad (1)$$

The thermal average of the dimensionless normal coordinates vanish for the linear term except for the totally symmetric normal mode. When only the leading linear term is considered, the problem is most easily solved for molecules of high symmetry. Thus, we have previously treated diatomic molecules of $D_{\infty h}$ (F_2,N_2) and $C_{\infty v}$ (CO,ClF) symmetry and polyatomic molecules of O_h (SF_6), T_d (CF_4,CH_4,SiF_4), D_{3h} (BF_3) symmetry.[2] In these cases there is only one totally symmetric q_i and it is therefore expressible entirely in terms of the bond displacements Δr. To lowest order, the bond angle deformation $\langle \Delta\alpha \rangle$ has a vanishing average since it does not appear in the totally symmetric normal coordinate. Thus, in the previous work, we have correlated the observed temperature dependence of the shielding $[\sigma_0(T) - \sigma_0(300)]$ with the temperature dependence of the mean bond displacement $\langle \Delta r \rangle^T$:

$$\sigma_0(T) = \sigma_e + [(\partial\sigma/\partial\Delta r_1)_e + (\partial\sigma/\partial\Delta r_2)_e + \cdots] \langle \Delta r_1 \rangle^T + \cdots . \quad (2)$$

Since the nuclear shielding is very much a localized property, the effects of bond stretches remote from the observed nucleus can be reasonably neglected. Furthermore, in molecules of high symmetry such as those which we have previously considered, there is only one $\langle \Delta r \rangle$ to be considered

$$\sigma_0(T) = \sigma_e + (\partial\sigma/\partial\Delta r)_e \langle \Delta r \rangle + \cdots, \quad \text{as for } ^{19}\text{F in CF}_4,$$

or (3)

$$\sigma_0(T) = \sigma_e + n(\partial\sigma/\partial\Delta r)_e \langle \Delta r \rangle + \cdots, \quad \text{as for } ^{13}\text{C in CO}_2.$$

Therefore, our previous work has been on calculations of $\langle \Delta r \rangle^T$ from the anharmonic force fields of these molecules. The fitting of the temperature dependence of $\langle \Delta r \rangle^T$ to the temperature dependence of $[\sigma_0(T) - \sigma_0(300)]$ has resulted in empirical values for $(\partial\sigma/\partial\Delta r)_e$, the derivative of nuclear magnetic shielding with respect to bond displacement.[6]

If the molecule has no more than three atoms, the anharmonic force field can still be described in terms of cubic and quartic force constants without use of simplifying models. In triatomic molecules there are just enough independent measurable spectroscopic constants to determine the nonvanishing third and fourth derivatives of the potential surface.[7] For linear triatomics such as NNO and FCN, the temperature dependence of the middle nucleus involves two bond displacements

$$\sigma_0(T) = \sigma_e + (\partial\sigma/\partial\Delta r_1)_e \langle \Delta r_1 \rangle^T + (\partial\sigma/\partial\Delta r_2)_e \langle \Delta r_2 \rangle^T + \cdots . \quad (4)$$

In bent triatomics such as H_2Se the totally symmetric vibrations involve bond angle deformations. In these cases, both $\langle \Delta r \rangle^T$ and $\langle \Delta\alpha \rangle^T$ contribute (to lowest order) to the tem-

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perature dependence of the shielding, of ^{77}Se in H_2Se, for example. These molecular types, the unsymmetrical linear and bent triatomic will be treated elsewhere.[8]

To go beyond these special cases, we need to consider molecules of lower symmetry and more than three atoms. In this paper, we consider planar tetra-atomic molecules of C_{2v} symmetry YAZ_2 type of which $O=CF_2$ is an example.

In the calculation of $\langle \Delta r\rangle^T$ we have made use of two approaches. One is to use the results from the perturbation theory (or the equivalent contact transformation theory) of rovibrational energies.[9] These give an explicit relationship between $\langle q\rangle$ and the cubic force constant and harmonic frequencies of vibration

$$\langle q_i\rangle = -\left[3k_{iii}\langle v_i+1/2\rangle + \sum_s{}' k_{iss}\langle v_s+1/2\rangle\right]\omega_i^{-1}. \tag{5}$$

The centrifugal distortion contribution to $\langle q_i\rangle$ must be added to the expression and the transformation to the internal coordinates $\langle \Delta r\rangle$ carried out. The application of this method depends on the availability of cubic force constants for the molecule. Determination of the cubic force constants usually requires that the quadratic force field be well known and additional precise spectroscopic information such as vibrational-rotational interaction constants, anharmonicity constants, etc. be available too. This method is best applied to triatomics or molecules of very high symmetry, in which only a small number of cubic force constants are required. We have used this method in our previous work almost exclusively.

The second approach that we have used is that of Bartell.[10] This has the advantage of not requiring explicit knowledge of the cubic force constants of the molecule. The anharmonicity of the force field is instead expressed in terms of specific models. For anharmonicity of the stretching modes, a Morse model is used, in which the explicit relationship between the Morse parameter a, vibrational frequency, and dissociation energy (which holds strictly only for a diatomic molecule) is applied to a polyatomic molecule. Other contributions to anharmonicity are included by introducing a parameter such as F^3 which is obtained by using a model potential function (e.g., Lennard-Jones) for nonbonded interactions. In Bartell's method, a set of coupled equations characteristic of the molecular type relate the desired mean displacements (in this case $\langle \Delta r\rangle$ and $\langle \Delta R\rangle$) and the easily calculated mean square amplitudes of vibration $[\langle(\Delta r)^2\rangle, \langle \Delta r\Delta R\rangle, \langle(\Delta R)^2\rangle$,etc.]. Thus, this is the preferred method for molecules of lower symmetry.

In the following section we present a general method for calculations of different $\langle \Delta r\rangle$ for molecular types with a central atom and negligible mean bond angle displacements. This model is based on a modified Urey–Bradley treatment of the potential energy. In a later section we apply this model to the YAZ_2 molecular type, where we have to consider two different mean bond displacements $\langle \Delta r_{AY}\rangle$ and $\langle \Delta r_{AZ}\rangle$. We also include centrifugal distortion due to molecular rotations. Numerical examples for four isotopes of carbonyl fluorides are given. In the last section we correlate the calculated $\langle \Delta r_{CF}\rangle$ to the previous measurement of $\sigma_0(T)$ for ^{19}F in $O=CF_2$. We also discuss isotope effects on σ_0 in terms of the same dynamic effects.

MEAN BOND DISPLACEMENTS DUE TO VIBRATIONAL EFFECTS

For molecules with lower symmetry especially molecules with nonequivalent bonds, the calculation of the change in bond length due to anharmonic vibrations is still an open problem. In this section we develop a general model for the calculation for molecules with one central atom A, but nonequivalent bonds, like $YAZ, YAZ_2, \cdots$. This model assumes that all changes in the mean bond angles can be neglected. When all the bonds are equivalent and all bond angles are determined by the symmetry of the point group, this treatment is valid. It is also approximately valid when the bond angle displacements sum to zero and the mean bond angle displacements nearly sum to zero. Examples are near-tetrahedral molecules such as substituted methanes and near-trigonal-planar molecules such as substituted boron halides. The possible expansion of this model to include nonvanishing mean bond angle changes will be reported later. These calculations are based on an idea first published by Bartell.[10,11]

Only for a few molecules is the general force field, including anharmonicity terms, known. In most cases we have to assume certain model potential functions. It was shown[12] that a modified Urey–Bradley (UB) potential function[13] describes vibration very well. The "classical" UB-field type of potential function is expressed as[14]

$$V = \sum_i [K_i' r_i \Delta r_i + \tfrac{1}{2}K_i(\Delta r_i)^2] + \sum_{i<j}[H_{ij}' r_{ij}^2 \Delta\alpha_{ij} + \tfrac{1}{2}H_{ij}(r_{ij}\Delta\alpha_{ij})^2] + \sum_{i<j}[F_{ij}' q_{ij}\Delta q_{ij} + \tfrac{1}{2}F_{ij}(\Delta q_{ij})^2], \tag{6}$$

where r is the bond length, α the bond angle, q the distance between atoms not bonded directly, and r_{ij} represents $(r_i r_j)^{1/2}$. K', K, H', H, F', and F are the bond-stretching, angle bending, and repulsive (between nonbonded atoms) force constants. Through the relations $q_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos\alpha_{ij}$ we can express Δq_{ij} in terms of Δr_i, Δr_j, and $\Delta\alpha_{ij}$[14]:

$$\begin{aligned}\Delta q_{ij} = {} & s_{ij}\Delta r_i + s_{ji}\Delta r_j + (t_{ij}t_{ji})^{1/2} r_{ij}\Delta\alpha_{ij} + \{t_{ij}^2(\Delta r_i)^2 + t_{ji}^2(\Delta r_j)^2 - s_{ij}s_{ji}(r_{ij}\Delta\alpha_{ij})^2 - 2t_{ij}t_{ji}\Delta r_i\Delta r_j \\ & + 2t_{ij}s_{ji}\Delta r_i(r_j\Delta\alpha_{ij}) + 2t_{ji}s_{ij}\Delta r_j(r_i\Delta\alpha_{ij})\}/2q_{ij},\end{aligned} \tag{7}$$

where

$$s_{ij} = (r_i - r_j\cos\alpha_{ij})/q_{ij}, \quad s_{ji} = (r_j - r_i\cos\alpha_{ij})/q_{ij}, \quad t_{ij} = r_j\sin\alpha_{ij}/q_{ij}, \quad t_{ji} = r_i\sin\alpha_{ij}/q_{ij}. \tag{8}$$

In these equations, r_i, r_j, α_{ij}, and q_{ij} denote equilibrium values. From Eqs. (6) and (7) the potential energy is obtained as a function of internal coordinates:

$$V = \sum_i \Big[K'_i r_i + \sum_{j\neq i} F'_{ij} s_{ij} q_{ij}\Big](\Delta r_i) + \tfrac{1}{2}\sum_i \sum_{j\neq i} [H'_{ij} r_i r_j + F'_{ij} r_i r_j \sin\alpha_{ij}](\Delta\alpha_{ij}) + \tfrac{1}{2}\sum_i \Big[K_i + \sum_{j\neq i}(t^2_{ij}F'_{ij} + s^2_{ij}F_{ij})\Big]$$
$$\times(\Delta r_i)^2 + \tfrac{1}{4}\sum_i\sum_{j\neq i}[H_{ij}r_ir_j - s_{ij}s_{ji}r_ir_jF'_{ij} + t_{ij}t_{ji}r_ir_jF_{ij}](\Delta\alpha_{ij})^2 + \tfrac{1}{2}\sum_i\sum_{j\neq i}[-t_{ij}t_{ji}F'_{ij} + s_{ij}s_{ji}F_{ij}](\Delta r_i)(\Delta r_j)$$
$$+ \sum_i\sum_{j\neq i}[t_{ij}s_{ji}r_jF'_{ij} + t_{ji}s_{ij}r_jF_{ij}](\Delta r_i)(\Delta\alpha_{ij}). \tag{9}$$

The first two sets of terms vanish as a consequence of the minimum potential energy condition for the equilibrium configuration. To also take into account the anharmonicity of vibrations we must modify the UB potential. As Bartell[15] suggested, we include the following terms:

$$V_a = \sum_i (1/6r_i)K^3_i(\Delta r_i)^3 + \tfrac{1}{2}\sum_i\sum_{j\neq i}(1/6q_{ij})F^3_{ij}(\Delta q_{ij})^3 \tag{10}$$

(neglecting bending anharmonicity).
It seems reasonable to express the stretching part of V as a potential function similar to that of a diatomic molecule. If the Morse function[16]

$$V = D_e[1 - \exp(-a\Delta r)]^2 \tag{11}$$

is used, it can shown that[15]

$$K^3 = -3aKr_e. \tag{12}$$

The quantum mechanical law of motion applied to a wave packet is given, in Cartesian coordinates, by

$$m\frac{d^2\langle x\rangle}{dt^2} = -\left\langle\frac{\partial V}{\partial x}\right\rangle. \tag{13}$$

In our molecular applications the system will be in stationary states or an equilibrium distribution among stationary states. Since the space average displacement $\langle x\rangle$ is independent of time in such a system, it follows that the space average force is zero, or

$$\langle\partial V/\partial x\rangle = 0. \tag{14}$$

Equation (13) is the molecular quantum mechanical analog to the Ehrenfest theorem.[17] It is simpler to use the Cartesian displacements from equilibrium positions, rather than internal coordinates. This would mean tht the average of the derivatives of the potential energy with respect to all Cartesian displacements should be zero—$\langle\partial V/\partial\Delta z_i\rangle = 0$, for example. We adopt the conventional Cartesian frames such that the z_i axes are taken in the direction of the A–X$_i$ bond at their equilibrium position and the x_i axes are taken on the plane X$_i$–A–X$_j$ and perpendicular to z_i. A denotes the central atom. Now we can express the internal displacment coordinates in terms of the Cartesian displacement coordinates

$$\Delta r_i = \Delta z_i + [(\Delta x_i)^2 + (\Delta y_i)^2]/2r_i + \cdots, \tag{15a}$$

$$\Delta\alpha_{ij} = \frac{\Delta x_i}{r_i} + \frac{\Delta x_j}{r_j} - \frac{\Delta x_i\Delta z_i}{r_i^2} - \frac{\Delta x_j\Delta z_j}{r_j^2} + \cdots, \tag{15b}$$

$$\Delta q_{ij} = s_{ij}\Delta z_i + s_{ji}\Delta z_j + \frac{r_ir_j\sin\alpha_{ij}}{q_{ij}}\Delta\alpha_{ij} + \cdots. \tag{15c}$$

Using Eq. (15) we can calculate the derivatives of the internal coordinates with respect to Δz_k, as

$$\partial\Delta r_i/\partial\Delta z_k = \delta_{ik} + \cdots, \tag{16a}$$

$$\frac{\partial\Delta\alpha_{ij}}{\partial\Delta z_k} = -\frac{\Delta\alpha_{kj}}{2r_k}\delta_{ik} = -\frac{\Delta\alpha_{ik}}{2r_k}\delta_{jk}, \tag{16b}$$

$$\frac{\partial\Delta q_{ij}}{\partial z_k} = s_{kj}\delta_{ik} = s_{ik}\delta_{jk}, \tag{16c}$$

where δ_{ij} is the Kronecker delta. Using the above equations we obtain

$$\langle\partial V/\partial\Delta z_k\rangle = 0 = \Big[K_k + \sum_{j\neq k}(t^2_{kj}F'_{kj} + s^2_{kj}F_{kj})\Big]\langle\Delta r_k\rangle + \sum_{j\neq k}[t_{kj}s_{jk}r_jF'_{kj} + t_{jk}s_{kj}r_jF_{kj}]\langle\Delta\alpha_{kj}\rangle$$
$$+ \sum_{j\neq k}[-t_{kj}t_{jk}F'_{kj} + s_{kj}s_{jk}F_{kj}]\langle\Delta r_j\rangle - \tfrac{1}{2}\sum_{j\neq k}[H_{kj}r_j - s_{kj}s_{jk}F'_{kj} + t_{kj}t_{jk}r_jF_k]\langle(\Delta\alpha_{kj})^2\rangle$$
$$-\tfrac{1}{2}\sum_{j\neq k}[t_{kj}s_{jk}(r_j/r_k)F'_{kj} + t_{jk}s_{kj}(r_j/r_k)F_{kj}]\langle\Delta r_k\Delta\alpha_{kj}\rangle - \tfrac{1}{2}\sum_{j\neq k}[t_{jk}s_{kj}F'_{jk} + t_{kj}s_{jk}F_{jk}]\langle\Delta r_j\Delta\alpha_{jk}\rangle$$
$$-\tfrac{3}{2}a_kK_k\langle(\Delta r_k)^2\rangle + \tfrac{1}{2}\sum_{j\neq k}(1/q_{kj})s_{kj}F^3_{kj}\langle(\Delta q_{kj})^2\rangle. \tag{17}$$

Through Eq. (7) we can express the mean square amplitude (MSA) of the displacement of nonbonded distances $\langle(\Delta q_{ij})^2\rangle$ in terms of the MSA of stretching and bonding displacements $\langle(\Delta r_i)^2\rangle$ and $\langle(\Delta\alpha_{ij})^2\rangle$ and cross products between them:

$$\langle(\Delta q_{ij})^2\rangle = s^2_{ij}\langle(\Delta r_i)^2\rangle + s^2_{ji}\langle(\Delta r_j)^2\rangle + (r_i^2r_j^2\sin^2\alpha_{ij}/q^2_{ij})\langle(\Delta\alpha_{ij})^2\rangle + 2s_{ij}s_{ji}\langle\Delta r_i\Delta r_j\rangle$$
$$+ 2s_{ij}(r_ir_j\sin\alpha_{ij}/q_{ij})\langle\Delta r_i\Delta\alpha_{ij}\rangle + 2s_{ji}(r_ir_j\sin\alpha_{ij}/q_{ij})\langle\Delta r_j\Delta\alpha_{ij}\rangle + \cdots. \tag{18}$$

In Eq. (18) we neglect all terms higher then quadratic. Substituting Eq. (18) into Eq. (17) we obtain the final equations, which connect the mean displacements with the MSA:

$$\Big[K_k + \sum_{j\neq k} (t^2_{kj}F'_{kj} + s^2_{kj}F_{kj})\Big]\langle \Delta r_k\rangle + \sum_{j\neq k}[-t_{kj}t_{jk}F'_{kj} + s_{kj}s_{jk}F_{kj}]\langle \Delta r_j\rangle + \sum_{j\neq k}[t_{kj}s_{jk}r_jF'_{kj} + t_{jk}s_{kj}r_jF_{kj}]\langle \Delta\alpha_{kj}\rangle$$
$$= \Big[\tfrac{3}{2}a_kK_k - \tfrac{1}{2}\sum_{j\neq k}(1/q_{kj})F^3_{kj}s^3_{kj}\Big]\langle(\Delta r^2_k)\rangle - \tfrac{1}{2}\sum_{j\neq k}(1/q_{kj})F^3_{kj}s_{kj}s^2_{jk}\langle(\Delta r_j)^2\rangle + \tfrac{1}{2}\sum_{j\neq k}[H_{kj}r_j - s_{kj}s_{jk}r_jF'_{kj}$$
$$+ t_{kj}t_{jk}r_jF_{kj} - (1/q^3_{jk})s_{kj}r^2_kr^2_j\sin\alpha_{kj}F^3_{kj}]\langle(\Delta\alpha_{kj})^2\rangle + \tfrac{1}{2}\sum_{j\neq k}[t_{kj}s_{jk}(r_j/r_k)F'_{kj} + t_{jk}s_{kj}(r_j/r_k)F_{kj}$$
$$- (2/q^2_{kj})s^2_{kj}r_kr_j\sin\alpha_{kj}F^3_{kj}]\langle \Delta r_k\Delta\alpha_{kj}\rangle + \tfrac{1}{2}\sum_{j\neq k}(\mathrm{t}_{jk}\mathrm{s}_{kj}F'_{jk} + t_{kj}s_{jk}F_{jk} - (2/q^2_{kj})s_{kj}s_{jk}r_kr_j\sin\alpha_{kj}]\langle \Delta r_j\Delta\alpha_{jk}\rangle$$
$$- \sum_{j\neq k}(1/q_{kj})F^3_{kj}s^2_{jk}s_{jk}\langle \Delta r_k\Delta r_j\rangle. \tag{19}$$

For a molecular type with vanishing mean bond displacements $\langle \Delta\alpha_{ij}\rangle = 0$ we obtain from Eq. (19) a set of **m** linear coupled equations for **m** nonequivalent bonds (**m** different derivatives with respect to Δz_{k_i}, $i = 1,\ldots,\mathbf{m}$). If the molecular symmetry demands also **m**′ nonzero $\langle \Delta\alpha_{ij}\rangle$, then we must calculate **m**′ derivatives with respect to Δx_{k_i} ($i = 1,\ldots,\mathbf{m}'$) as well.

APPLICATION TO A PLANAR YAZ$_2$ MOLECULE: O = CF$_2$

In this section we apply the above model to the special case of planar YAZ$_2$ molecules (C_{2v} symmetry). For this type of molecule we have to consider two different mean bond displacements, namely $\langle \Delta r_{\mathrm{AY}}\rangle$ and $\langle \Delta R_{\mathrm{AZ}}\rangle$. The sum of the in-plane bond angle displacements is zero. We will assume that the mean in-plane bond angle displacements in near-trigonal planar molecules also nearly sum to zero. The UB field would also need an out-of-plane bend which is not included here. Bartell indicates that this deficiency is partly compensated for by correctly calculated values of the mean square amplitudes.[10] Using Eq. (17) we can obtain the following set of two linear coupled equations for the effect of anharmonic vibrations:

$$(K_R + 2s^2_1F_Q + t^2_2F'_q + s^2_2F_q)\langle \Delta R\rangle + (-t_2t_3F'_q + s_2s_3F_q)\langle \Delta r\rangle$$
$$= \tfrac{3}{2}a_RK_R\langle(\Delta R)^2\rangle - (1/2Q)s_1F^3_Q\langle(\Delta Q)^2\rangle$$
$$- (1/2q)s_2F^3_q\langle(\Delta q)^2\rangle + \tfrac{1}{2}(H_\beta - s^2_1F'_Q + t^2_1F_Q)R\langle(\Delta\beta)^2\rangle + \tfrac{1}{2}(H_\alpha - s_2s_3F'_q + t_2t_3F_q)r\langle(\Delta\alpha)^2\rangle$$
$$+ (t_1s_1F'_Q + t_1s_1F_Q)\langle \Delta R\Delta\beta\rangle + \tfrac{1}{2}(t_2s_3F'_q + t_3s_2F_q)(r/R)\langle \Delta R\Delta\alpha\rangle + \tfrac{1}{2}(t_3s_2F'_q + t_2s_3F_q)\langle \Delta r\Delta\alpha\rangle \tag{20a}$$

and

$$2(-t_2t_3F'_q + s_2s_3F_q)\langle \Delta R\rangle + (K_r + 2t^2_3F'_q + 2s^2_3F_q)\langle \Delta r\rangle$$
$$= \tfrac{3}{2}a_rK_r\langle(\Delta r)^2\rangle - (1/q)s_3F^3_q\langle(\Delta q)^2\rangle + (H_\alpha - s_2s_3F'_q + t_2t_3F_q)R\langle(\Delta\alpha)^2\rangle$$
$$+ (t_2s_3F'_q + t_3s_2F_q)\langle \Delta R\Delta\alpha\rangle + (t_3s_2F'_q + t_2s_3F_q)(R/r)\langle \Delta r\Delta\alpha\rangle, \tag{20b}$$

where r denotes the A–Y bond, R the A–Z bond, α is the Y–A–Z bond angle, and β the Z–A–Z bond angle. q means the distance between the nonbonded atoms Y and Z and Q the distance between Z$_1$ and Z$_2$. The geometric parameters are the following:

$$s_1 = (R - R\cos\beta)/Q,\quad t_1 = R\cos\beta/Q,$$
$$s_2 = (R - r\cos\alpha)/q,\quad t_2 = r\cos\alpha/q, \tag{21}$$
$$s_3 = (r - R\cos\alpha)/q,\quad t_3 = R\cos\alpha/q.$$

We also could express the MSA of the nonbonded distances $\langle(\Delta q)^2\rangle$ and $\langle(\Delta Q)^2\rangle$ in terms of the MSA of the internal coordinates by Eq. (18). In this way we would obtain a set of equations for $\langle \Delta r\rangle$ and $\langle \Delta R\rangle$ analogous to Eq. (19), but with the disadvantage that these equations would not show the importance of the different UB-force constants so clearly. On the other hand, for purely numerical calculations, we would prefer to apply Eq. (19) instead of Eq. (17) because the MSA of the internal coordinates can be obtained easily.

These MSA's (which include nonvanishing crossproducts) are related to the mean square normal coordinates $\langle Q^2\rangle$ in the usual way[18]

$$\langle R_iR_j\rangle = \mathbf{U}^T\mathbf{L}\langle \mathbf{Q}^2\rangle\mathbf{L}^T\mathbf{U}, \tag{22}$$

where $\langle \mathbf{Q}^2\rangle$ is a quadratic matrix with the diagonal elements:

$$\langle \mathbf{Q}^2\rangle_{ii} = (h/4\pi^2c\omega_i)(v_i + \tfrac{1}{2}). \tag{23a}$$

The thermal average of $(v_i + \frac{1}{2})$ taken with the harmonic oscillator partition function is $(\frac{1}{2})\coth(hc\omega_i/2kT)$, giving

$$\langle Q^2\rangle_{ii} = (h/4\pi^2c\omega_i)\coth(hc\omega_i/2kT). \tag{23b}$$

The nondiagonal elements are zero. The transformation matrix **L** from normal coordinates to symmetry coordinates can be obtained by the usual GF-matrix method[19] and **U** is the transformation matrix from symmetry to internal coordinates. For the remaining UB-force constants we used the following assumptions:

(i) $F' = -0.1\,F$, as suggested by Shimanouchi;

(ii) the Morse parameter for the C=O and the C–F bond stretches can be obtained by invoking $V' = (R_e) = 4\pi^2c^2\omega_e = 2a^2D_e$. This holds strictly only for a diatomic molecule, but we can apply it to O=CF$_2$ using bond dissociation energies for the different bonds[21] and the fundamental frequencies which are primarily stretches. We obtained

$$a_r = 3.663\ \text{Å}^{-1}\quad\text{and}\quad a_R = 2.467\ \text{Å}^{-1}$$

for the CO and the CF bonds, respectively;

(iii) for the potential energy between nonbonded atoms, several empirical functions have been proposed. For fluorine–fluorine interaction, e.g., it is reasonable to assume a Lennard-Jones-type function.[22] Then it follows that

$$F_q^3 = q_e\ [(\partial^3 V(q)/\partial q^3]_e,$$

where

$$V(q) = \epsilon[(q_e/q)^{12} - 2(q_e/q)^6].$$

We applied Eq. (20) to various isotopes of carbonyl fluoride $O = CF_2$. For this molecule nearly all the necessary information (harmonic vibration frequencies for all isotopes, some UB-force constants) are published by Mallinson, McKean, Holloway, and Oxton.[20] The following values were used for the equilibrium structure: $r_{CO} = 1.1726$ Å, $R_{CF} = 1.3144$ Å, $\alpha = 126.03$, and $\beta = 107.94$ Å.[23] Using these parameters in Eqs. (20) and (21) we obtain mean bond displacements for the C=O and the C–F bonds, presented in Table I for the case of $^{16}O\ ^{12}CF_2$.

In addition to the effect of anharmonic vibrations, we also have to include the change in bond length due to rotation. This centrifugal distortion is usually one order of magnitude smaller than the effect due to anharmonic vibrations. On the other hand the centrifugal distortion is proportional to temperature. If we are interested in the temperature dependence of the mean bond displacement this effect cannot be neglected. The centrifugal distortion is calculated by assuming that the rotational level spacings are small compared to kT so that the equipartition law can be used. One form in which this term can be written is[9]

$$\langle \mathbf{R} \rangle_{\text{centr}} = kT\mathbf{U}^T\mathbf{F}_s^{-1}\mathbf{G}_S^{-1}\mathbf{UB}\Omega\mathbf{X}, \qquad (24)$$

where $\mathbf{F}_S$ and $\mathbf{G}_S$ are Wilson's F and G matrices in terms of symmetry coordinates and $\mathbf{B}$ is the usual transformation matrix between Cartesian displacement coordinates and internal coordinate $\mathbf{R}$, and $\mathbf{X}$ are the equilibrium Cartesian positions of the atoms

$$\Omega^{\alpha\alpha} = (I_{\beta\beta})^{-1} + (I_{\gamma\gamma})^{-1}, \quad \alpha = x,y,z. \qquad (25)$$

The centrifugal distortion contributions to the mean bond displacements are shown in Table I. The temperature dependence of the total mean bond displacement (sum of vibrational and rotational parts) and four different isotopes of carbonyl fluoride is illustrated in Fig. 1.

TABLE I. Mean bond displacement due to anharmonic vibration using Eq. (20) and due to rotation using Eq. (24) for $^{16}O^{12}CF_2$. (All numbers in 10^{-3} Å.)

	$\langle \Delta r_{CO} \rangle^T$			$\langle \Delta R_{CF} \rangle^T$		
T(K)	vib	rot	tot	vib	rot	tot
250	6.7909	0.2501	7.0410	5.5208	0.5061	6.0269
260	6.7942	0.2601	7.0543	5.5324	0.5264	6.0588
270	6.7978	0.2701	7.0679	5.5453	0.5466	6.0919
280	6.8016	0.2801	7.0818	5.5594	0.5668	6.1263
290	6.8058	0.2901	7.0959	5.5748	0.5871	6.1619
300	6.8101	0.3001	7.1102	5.5915	0.6073	6.1989
310	6.8148	0.3101	7.1249	5.6095	0.6276	6.2371
320	6.8197	0.3201	7.1398	5.6288	0.6478	6.2767
330	6.8249	0.3301	7.1551	5.6494	0.6681	6.3175
340	6.8305	0.3401	7.1706	5.6713	0.6883	6.3596
350	6.8363	0.3501	7.1864	5.6945	0.7086	6.4030

CORRELATION OF NMR EXPERIMENTAL DATA

The temperature dependence of the ^{19}F nuclear magnetic shielding for an isolated $^{16}O\ ^{12}CF_2$ molecule (at the zero-pressure limit) was reported earlier.[24] It was found that for $T = 230$–380 K, the observed temperature dependence can be described by

$$\begin{aligned}\sigma_0(T) - \sigma_0(300\ \text{K}) = &- 4.332\times 10^{-3}(T-300)\\ &- 1.3465\times 10^{-5}(T-300)^2\\ &+ 1.623\times 10^{-8}(T-300)^3.\end{aligned}$$

These experimental results can be fitted to the function $A + B\langle \Delta R_{CF}(T)\rangle$, where $A \simeq \sigma_e - \sigma_0(300)$ and $B = (\partial\sigma/\partial\Delta R_{CF})_e$. Since the nuclear shielding is a very localized electronic property, we can neglect the effect on σ_0 due to the change in the C=O bond length, i.e., we neglect $(\partial\sigma^F/\partial\Delta r_{CO})_e$ relative to $(\partial\sigma^{F_1}/\partial\Delta /R_{CF_1})_e + (\partial\sigma^{F_1}/\partial\Delta R_{CF_2})_e$. From this fitting we obtained

$$\sigma_e - \sigma_0(300) \cong 7.1 \pm 0.1 \text{ ppm}$$

and

$$(\partial\sigma/\partial\Delta R_{CF})_e = -1146 \pm 15 \text{ ppm/Å},$$

where the standard deviations quoted are entirely from the numerical fitting to within experimental errors and do not reflect the accuracy of these numbers. We further interpret this derivative entirely in terms of $(\partial\sigma^{F_1}/\partial\Delta R_{CF_1})_e$, i.e., we

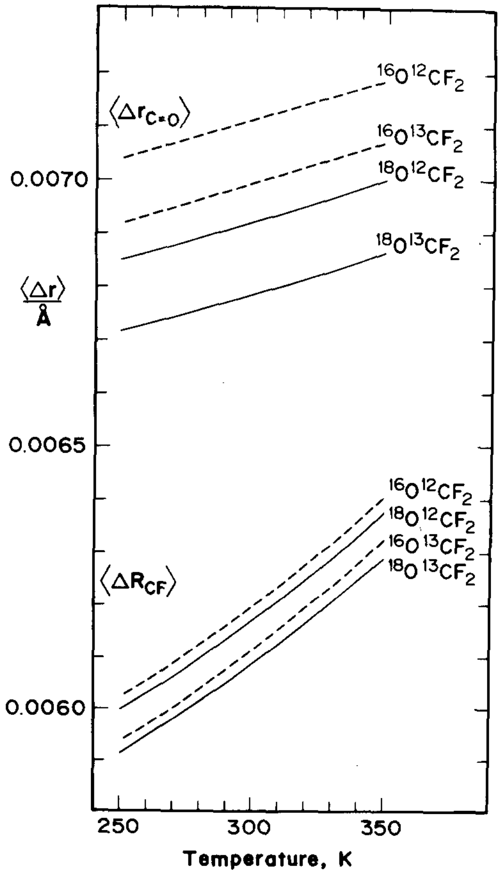

FIG. 1. Mean bond displacements in various isotopomers of $O{=}CF_2$.

neglect the effect of the other CF bond stretch.

The BF_3 molecule (D_{3h} symmetry) is isoelectronic with OCF_2. The vibrational frequencies of BF_3 are comparable to OCF_2 and the empirical derivative of ^{19}F shielding which fitted the experimental T dependence in BF_3 at the zero-pressure limit[2] was $(\partial\sigma/\partial\Delta r_{\mathrm{BF}})_e = -1115$ ppm/Å. It is somewhat surprising that the derivatives are quite similar. This again confirms the localized nature of the nuclear shielding.

Ditchfield[25] has shown that for diatomic molecules the difference between $\sigma_0(T)$ values calculated at two different temperatures shows very little change when the term in $(\partial^2\sigma/\partial\Delta r^2)_e$ was dropped since the quadratic and higher terms contribute so minimally to the T dependence of $\sigma_0(T)$. However, even when the first derivative $(\partial\sigma/\partial\Delta r_{\mathrm{CF}})_e$ may be sufficient to interpret the temperature dependence, the total dynamic effect at 300 K, the difference between $\sigma_0(300)$ and the shielding in a hypothetical rigid equilibrium configuration σ_e is due to all the terms. That is, even when the anharmonic and centrifugal distortion dominate $d\sigma_0/dT$, the harmonic terms may not be negligible in determining the absolute magnitude of σ_0 itself. This error exists in the quantity $\sigma_e - \sigma_0(300) \simeq 7$ ppm. Nevertheless, we estimate $\sigma_e \simeq 229$ ppm by using the absolute shielding value of $\sigma_0(300\ \mathrm{K}) = 221.6$ ppm,[26] which we had previously obtained with good precision relative to $\sigma_0(300\ \mathrm{K})$ for SiF_4 and the latter was measured with good precision relative to $\sigma_0(300\ \mathrm{K})$ for HF by Hindermann and Cornwell.[27] The absolute shielding of HF itself may have larger errors associated with it.

Another interesting application of our calculations is the investigation of NMR isotope shifts. We measured the ^{13}C/^{12}C-induced ^{19}F isotope shift in the gas phase: $[\sigma_0(^{16}\mathrm{O}\ ^{12}\mathrm{CF}_2) - \sigma_0(^{16}\mathrm{O}\ ^{13}\mathrm{CF}_2)] = -0.117 \pm 0.003$ ppm. This result agrees with the older published shift of -0.121 ± 0.003 ppm[28] in the liquid phase. The derivative $(\partial\sigma/\partial\Delta R_{\mathrm{CF}})_e$ is a purely electronic quantity independent of mass to the extent that the Born–Oppenheimer approximation is valid. If we include only anharmonic and centrifugal distortion terms we can calculate an isotope shift as follows:

$$\begin{aligned}\sigma_0(^{16}\mathrm{O}\ ^{12}\mathrm{CF}_2) &- \sigma_0(^{16}\mathrm{O}\ ^{13}\mathrm{CF}_2)\\ &= (\partial\sigma/\Delta R_{\mathrm{CF}})_e\\ &\quad\times[\langle\Delta R_{\mathrm{CF}}(^{16}\mathrm{O}\ ^{12}\mathrm{CF}_2)\rangle - \langle\Delta R_{\mathrm{CF}}(^{16}\mathrm{O}\ ^{13}\mathrm{CF}_2)\rangle]\\ &= -0.096\ \mathrm{ppm}.\end{aligned} \tag{26}$$

This calculated isotope shift is temperature independent since we found both isotopic species have essentially the same temperature dependence for $\langle\Delta R_{\mathrm{CF}}\rangle^T$. The above equation is only an approximation since the other terms such as $(\partial\sigma/\partial\Delta r_{\mathrm{CO}})_e \langle(\Delta r_{\mathrm{CO}})\rangle + \cdots$ have not been included. Nevertheless, the agreement with our measured isotope shift is quite good. In fact we can estimate $(\partial\sigma/\partial\Delta r_{\mathrm{CO}})_e$ from the experimental isotope shift if we assume that we can calculate the isotope shift with Eq. (26) plus the additional term

$$(\partial\sigma/\partial\Delta r_{\mathrm{CO}})_e[\langle\Delta r_{\mathrm{CO}}(^{16}\mathrm{O}\ ^{12}\mathrm{CF}_2)\rangle - \langle\Delta r_{\mathrm{CO}}(^{16}\mathrm{O}\ ^{13}\mathrm{CF}_2)\rangle].$$

This leads to $(\partial\sigma/\partial\Delta r_{\mathrm{CO}})_e \simeq -175$ ppm/Å.

Although we can use the same formula [Eq. (26)] to calculate two-bond isotope effects from the $\langle\Delta R_{\mathrm{CF}}\rangle$ for various isotopomers, the results would be very approximate. For example, using only the $(\partial\sigma^{\mathrm{F}}/\partial\Delta R_{\mathrm{CF}})_e \langle\Delta R_{\mathrm{CF}}\rangle$ term to calculate isotope shifts, we get $\sigma_0(^{16}\mathrm{O}\ ^{12}\mathrm{CF}_2) - \sigma_0(^{18}\mathrm{O}\ ^{12}\mathrm{CF}_2) = -0.033$ and $\sigma_0(^{16}\mathrm{O}\ ^{13}\mathrm{CF}_2) - \sigma_0(^{18}\mathrm{O}\ ^{13}\mathrm{CF}_2) = -0.034$. It can be seen in Fig. 1 that the $[\langle\Delta r_{\mathrm{C}^{18}\mathrm{O}}\rangle - \langle\Delta r_{\mathrm{C}^{16}\mathrm{O}}\rangle]$ difference is much larger than the differences between $\langle\Delta R_{\mathrm{CF}}\rangle$ for the $^{18/16}$O species, thus we should include the $(\partial\sigma^{\mathrm{F}}/\partial\Delta r_{\mathrm{CO}})_e \langle\Delta r_{\mathrm{CO}}\rangle$ term in calculating the two-bond isotope effects on ^{19}F. Using the additional term with the estimated $(\partial\sigma/\partial\Delta r_{\mathrm{CO}})_e \simeq -175$ ppm/Å, we obtain $\sigma_0(^{16}\mathrm{O}\ ^{12}\mathrm{CF}_2) - \sigma_0(^{18}\mathrm{O}\ ^{12}\mathrm{CF}_2) = -0.067$ ppm and $\sigma_0(^{16}\mathrm{O}\ ^{13}\mathrm{CF}_2) - \sigma_0(^{18}\mathrm{O}\ ^{13}\mathrm{CF}_2) = -0.070$ ppm. This particular two-bond isotope effect has not been measured. However, the sign of two-bond isotope shifts is usually the same as for one-bond isotope shifts and the magnitude is about right. We may be able to obtain a better estimate of $(\partial\sigma^{\mathrm{F}}/\partial\Delta r_{\mathrm{CO}})_e$ from an experimental value of the $^{18/16}$O-induced ^{19}F isotope shift.

There is another possibly important source of error in our calculations. In the theory given here, the temperature dependence appears in the form of the thermal averages of $\langle v_i + \frac{1}{2}\rangle$. Although anharmonicity is included explicitly in parameters a and F^3, the thermal average of $\langle v_i + \frac{1}{2}\rangle$ is taken with a harmonic oscillator partition function. Fowler and Raynes[29] have pointed out the magnitudes of the errors introduced by this simplifying assumption. However, it should be noted that despite such an assumption, Bartell finds that the thermal expansion observed in electron diffraction of very hot molecules (up to 1500–2000 K) is adequately described by this model.[30,31] This is reassuring since the high temperature limit provides a worst case example of the use of the harmonic oscillator partition function.

In summary, we have given a general expression [Eq. (19)] for the set of coupled equations which have to be solved to get mean bond displacements $\langle\Delta r_k\rangle$ in terms of mean square vibrational amplitudes $\langle\Delta r_i \Delta r_k\rangle$ etc., for a molecule with one central atom, several nonequivalent bonds, and a vanishing sum of mean bond angle displacements. We have applied it to the specific case of a planar YAZ_2 molecule. The temperature dependencies of the mean bond displacements are calculated for the various isotopomers of $O{=}CF_2$. The shape of $\langle\Delta R_{\mathrm{CF}}\rangle^T$ is the same as that of the observed $\sigma_0(T) - \sigma_0(300\ \mathrm{K})$ in the range 230–380 K. Fitted to $\langle\Delta R_{\mathrm{CF}}\rangle^T$, the experimental ^{19}F shielding dependence gives an empirical value of the derivative $(\partial\sigma/\partial\Delta R_{\mathrm{CF}})_e$. This derivative allows us to calculate a $^{13/12}$C-induced ^{19}F isotope shift which should probably be on the low side due to neglected terms. Nevertheless, agreement with experiment is good.

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