The effect of anharmonic vibration and centrifugal distortion on nuclear shielding in linear triatomic molecules: NNO and CO_2

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The temperature dependence of the mean bond displacement in linear triatomic molecules NNO and CO_2 have been determined using the well-established anharmonic force fields for these molecules. The results are applied to explain the temperature dependence of the nuclear shielding observed in the zero-pressure limit for the ^{15}N and ^{13}C nuclei in $^{15}N^{15}NO$ and $^{13}CO_2$. By fitting the observed $\sigma_0(T) - \sigma_0(300\ K)$ for $T = 250$–350 K, empirical values of $(\partial\sigma/\partial\Delta r)_e = -220$ ppm/Å (CO_2), -1030 ppm/Å (NN*O), and -5190 ppm/Å (N*NO) are obtained. These derivatives are discussed in comparison to similar molecular types. The average shielding for the vibrational states (000) and (01^10) are calculated for both ^{15}N nuclei in NNO and compared with values obtained from experimental spin-rotational constants. The empirical derivatives are also used to calculate NMR isotope shifts from the mass-dependent $\langle\Delta r\rangle$.

In our gas phase NMR studies, we have obtained the temperature variation of nuclear shielding in the zero-pressure limit, in terms of the functions $\sigma_0(T) - \sigma_0(300)$, and measured some isotope effects on NMR shielding as well. The nuclear magnetic shielding observed in a molecule at the zero-pressure limit is a thermal average isotropic shielding which depends on the thermal average of all the internuclear distances in a molecule, $r_g = r_e + \langle\Delta r\rangle^T$. Being a very localized property, the nuclear shielding is most sensitive to the internuclear distances involving the observed nucleus. To a first approximation, the temperature variation of the nuclear shielding in a molecule free of intermolecular interactions $\sigma_0(T)$, is dependent on the temperature variation of $\langle\Delta r_i\rangle^T$ for the bonds involving the observed nucleus, and on the change in the nuclear shielding with Δr, that is, the derivatives of the shielding surface with respect to displacements from the equilibrium configuration. The mass dependence of the nuclear shielding in the molecule, the so-called NMR isotope shift, is dependent on differences in the thermal average internuclear distances for isotopically related species.

The interpretation of the observed temperature dependence of nuclear magnetic shielding in the zero-pressure limit and the NMR isotope shifts involves two surfaces, the potential energy surface and the nuclear shielding surface, with simultaneous averaging on both surfaces. For the semirigid molecules that we observe in NMR (excluding molecules which are fluxional or which undergo low frequency torsions), the motions involved in the averaging take place in a small pocket of the potential energy surface close to the equilibrium configuration. The best description of the pocket for polyatomic molecules is for linear triatomics, especially one in which many isotopic species provide an abundance of spectroscopic observables from which a least squares refinement technique gives an anharmonic force field which is best fit to the data. On the other hand, it is for the triatomic molecules with the smallest number of electrons that it is feasible to do a calculation of that small part of the shielding surface corresponding to the pocket in the potential energy surface. The simplest polyatomics which provide these ideal conditions are CO_2 and NNO. Of the polyatomic molecules, these probably have the most studied potential energy surface from the point of view of vibrational spectroscopy. The anharmonic force fields up to quintic and sextic terms have been obtained from the very large set of vibrational-rotational data belonging to 10 isotopic species in the case of CO_2[1–4] and 11 in the case of NNO.[5–7] For these two molecules the vibrational-rotational energies have been calculated from these force fields by three different approaches: the application of second order perturbation theory,[3,7] by using a numerical contact transformation scheme[1,6] and by the variational method.[4,5,8,9] Thus, the force fields for these two molecules have undergone more scrutiny than others.

For CO_2 the temperature-dependent vibrational effects on the gas-phase electron diffraction cross sections between 300 and 1000 K[10] provide additional information which is of the same origin as the temperature-dependent nuclear shielding. CO_2 and NNO have magnetically active nuclei for which the temperature dependent nuclear magnetic shielding in the zero-pressure limit has been reported.[11] Furthermore, molecular beam electric resonance experiments on NNO provide components of the spin-rotation tensor (which is related to the paramagnetic shielding) for both N nuclei for the ground vibrational as well as the (01^10) state.[12] In addition we report here a $^{15/14}N$-induced isotope shift in the end ^{15}N of NNO.

For a polyatomic molecule, the nuclear magnetic shielding, as any molecular electronic property, can be expanded in terms of the normal coordinates:[13]

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

In molecules of high symmetry, only one of the normal co-

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ordinates belongs to the totally symmetric representation, in which case calculation of the linear terms in the above equation involves only[14]

$$\langle q_1 \rangle^T = (-1/2\omega_1)\Big[3k_{111}\coth(hc\omega_1/2kT) + \sum_s k_{1ss}\coth(hc\omega_s/2kT)\Big], \tag{2}$$

to which must be added the rotational contribution. The rotational contribution (the centrifugal distortion effects) is related to $a_1^{(\alpha\alpha)} = (\partial I_{\alpha\alpha}/\partial q_1)$ which can be calculated in a straightforward manner and is easily written in closed form for molecules of high symmetry.[15] Using a linear transformation (an approximation) to internal coordinates, we can express $(\partial\sigma/\partial q_1)_e$ in terms of $(\partial\sigma/\partial\Delta r_i)_e$. The latter are mass independent if the Born–Oppenheimer approximation is valid, and are more appropriate for use in calculations of isotope shifts.

The calculations using Eq. (2) and a linear transformation to internal coordinates is equivalent to using $r_e + \langle\Delta z\rangle^T + \delta r_{\text{centr}}$ for the thermal average of the internuclear distances in a molecule, where δr_{centr} is the bond extension due to centrifugal stretching and Δz denotes an instantaneous displacement of r_{AB} projected on the equilibrium A–B axis (taken temporarily as the z axis). This gives not the thermal average of the A–B internuclear distance, but, the distance between the thermal average nuclear positions of A and B. Because nuclear vibrations perpendicular to this z axis exist in a polyatomic molecule, we need to add $(\langle\Delta x^2\rangle^T + \langle\Delta y^2\rangle^T)/2r_e + \cdots$ to this, in order to obtain the thermal average internuclear distance,[16] particularly important in linear triatomic molecules in which the vibrations along the line of centers have much higher frequencies than the bending mode. These terms arise from the nonlinear nature of the transformation from interatomic distances to normal coordinates. By using a linear transformation between internal coordinates Δr and normal coordinates q, we had interpreted $\sigma_0(T)$ (in our previous work)[17] in terms of derivatives with respect to rectilinear internal coordinates rather than with respect to the true instantaneous bond stretches and bond angle bends. To get the latter, we need to use

$$\langle\Delta r\rangle^T = \langle\Delta z\rangle^T + \delta r_{\text{centr}} + (\langle\Delta x^2\rangle^T + \langle\Delta y^2\rangle^T)/2r_e + \cdots \tag{3}$$

in

$$\sigma_0(T) = \sigma_e + \sum_i(\partial\sigma/\partial\Delta r_i)_e\langle\Delta r_i\rangle^T + \cdots. \tag{4}$$

Alternatively, we can use a force field which is expressed directly in curvilinear coordinates and thus obtain empirical values of derivatives of shielding with respect to the natural bond displacements.

Only very simple molecules have been described by up to cubic and quartic terms in the potential energy. The procedure involves using a vibrational-rotational Hamiltonian formulated in rectilinear normal coordinates, truncated at quartic terms in the potential. Even for triatomic molecules there are difficulties in establishing the uniqueness of the higher order constants due to the zeroth order basis functions being based on harmonic vibrations in rectilinear normal coordinates. Recently however, variational methods of handling the vibration-rotation Hamiltonian have been developed which allow the use of a potential energy expansion directly in curvilinear coordinates. By making use of a force field expressed in curvilinear internal coordinates directly, we overcome the problems associated with the use of a nonlinear transformation between $(\partial\sigma/\partial\Delta r)$ and $(\partial\sigma/\partial q)$.

In this paper, we make use of the results of variational methods for CO_2 and NNO to calculate thermal average internuclear distances in these molecules and use these to interpret the temperature dependence of the ^{13}C and ^{15}N nuclear shielding in these molecules.

CALCULATION OF MEAN BOND DISPLACEMENTS IN THE LINEAR TRIATOMIC MOLECULE

The general force field in terms of the true curvilinear coordinates R, is

$$\begin{aligned}V = {} & K_{11}R_1^2 + K_{22}R_2^2 + K_{33}R_3^2 + K_{13}R_1R_3 \\ & + K_{111}R_1^3 + K_{113}R_1^2R_3 + K_{133}R_1R_3^2 + K_{333}R_3^3 \\ & + K_{122}R_1R_2^2 + K_{223}R_2R_3^2 \\ & + \text{higher order terms.}\end{aligned} \tag{5}$$

Here R_1 denotes the displacement coordinate of the Y–X bond R_3 the displacement of the X–Z bond and R_2 stands for the bond angle displacement $\Delta\phi$. In the following we will use a method based on an idea first introduced by Bartell.[18] The molecular system will be in stationary states or equilibrium distribution among the stationary states. According to the quantum mechanical law of motion

$$m\frac{d^2\langle\xi_i\rangle}{dt^2} = -\left\langle\frac{\partial V}{\partial\xi_i}\right\rangle \tag{6}$$

follows that the space average force is zero, or

$$\left\langle\frac{\partial V}{\partial\xi_i}\right\rangle = 0, \tag{7}$$

where ξ_i stands for any Cartesian displacement coordinates. Let us assume a molecular Cartesian frame such that the Δz_1 and Δz_3 axes are taken in the direction of the Y–X and X–Z bond. Knowing the relation between the curvilinear internal coordinates R_i and the Cartesian displacement coordinates ξ_i[19] we can calculate the first derivatives of all R_i with respect to Δz_1 and Δz_3:

$$\begin{aligned}&\frac{\partial R_1}{\partial\Delta z_1} = 1 + \cdots \quad \frac{\partial R_2}{\partial\Delta z_1} = -\frac{R_2}{2r_{YX}} + \cdots \quad \frac{\partial R_3}{\partial\Delta z_1} = 0, \\ &\frac{\partial R_1}{\partial\Delta z_3} = 0 \quad \frac{\partial R_2}{\partial\Delta z_3} = -\frac{R_2}{2r_{XZ}} + \cdots \quad \frac{\partial R_3}{\partial\Delta z_3} = 1 + \cdots.\end{aligned} \tag{8}$$

The higher order terms are in general two orders of magnitude smaller and can be neglected. From condition (7) we obtain from the expression for the general force field (5):

$$\begin{aligned}\left\langle\frac{\partial V}{\partial\Delta z_1}\right\rangle = 0 = {} & 2K_{11}\langle R_1\rangle + K_{13}\langle R_3\rangle + 3K_{111}\langle R_1^2\rangle \\ & + K_{133}\langle R_3^2\rangle + 2K_{113}\langle R_1R_3\rangle \\ & + \left(K_{122} - \frac{1}{r_{YX}}K_{22}\right)\langle R_2^2\rangle \\ & + \text{higher order terms,}\end{aligned} \tag{9}$$

$$\left\langle\frac{\partial V}{\partial \Delta z_3}\right\rangle = 0 = K_{13}\langle R_1\rangle + 2K_{33}\langle R_3\rangle + K_{113}\langle R_1^2\rangle + 3K_{333}\langle R_3^2\rangle + 2K_{133}\langle R_1R_3\rangle + \left(K_{223} - \frac{1}{r_{XZ}}K_{22}\right)\langle R_2^2\rangle. \tag{10}$$

These two equations couple the mean bond displacements $\langle R_1\rangle$ and $\langle R_3\rangle$ to the mean square amplitudes (MSA) of internal coordinates. Knowing the MSA we are able to obtain both mean bond displacements by solving the linear equation systems (9) and (10).

We will use the harmonic approximation for evaluating the mean amplitudes:

$$\langle R_iR_j\rangle \simeq \langle \mathrm{R}_i\mathrm{R}_j\rangle = \mathbf{L}\langle Q^2\rangle\mathbf{L}^T, \tag{11}$$

where

$$\langle Q^2\rangle_{ii} = (h/4\pi^2c\omega_i^2)^{1/2}\coth(hc\omega_i/2kT) \tag{12}$$

and **L** is the usual transformation matrix from normal to symmetry coordinates (the same as the internal coordinates in linear triatomic molecules) obtained by Wilson's GF matrix method. Bartell has shown that using the harmonic approximation for the mean square amplitudes does not lead to significant errors for the purpose of calculating the temperature dependence.[20]

In addition to the bond length change due to anharmonic vibration we also have to consider the effect of centrifugal stretching caused by rotation of the molecule. This may be treated classically and independently of the thermal averaging over vibrations. For linear triatomics[17]:

$$\langle \Delta r_1\rangle_{\mathrm{rot}}^T = \frac{kT}{8\pi^2c^2}\left[\frac{L_{11}}{\omega_1^2}\sum\frac{a_1^{\alpha\alpha}}{I_{\alpha\alpha}} + \frac{L_{13}}{\omega_3^2}\sum\frac{a_3^{\alpha\alpha}}{I_{\alpha\alpha}}\right]$$

and (13)

$$\langle \Delta r_3\rangle_{\mathrm{rot}}^T = \frac{kT}{8\pi^2c^2}\left[\frac{L_{31}}{\omega_1^2}\sum\frac{a_1^{\alpha\alpha}}{I_{\alpha\alpha}} + \frac{L_{33}}{\omega_3^2}\sum\frac{a_3^{\alpha\alpha}}{I_{\alpha\alpha}}\right],$$

where $a_s^{\alpha\alpha}$ are the coefficients of the normal coordinates in the moments of inertia. For linear triatomics these are known in closed form;[15]

$$\begin{aligned} a_1^{xx} &= a_1^{yy} = 2(2B_e/\omega_1)^{1/2}\zeta_{23}^x, \quad a_1^{zz} = 0,\\ a_2^{xx} &= a_2^{yy} = a_2^{zz} = 0,\\ a_3^{xx} &= a_3^{yy} = 2(B_e/\omega_3)^{1/2}\zeta_{21}^x, \quad a_3^{zz} = 0. \end{aligned} \tag{14}$$

The centrifugal distortion is usually one order of magnitude smaller than the effect due to anharmonic vibrations. If we are interested in the temperature dependence of $\langle \Delta r\rangle$ we have to include $\langle \Delta r\rangle_{\mathrm{rot}}$ because of its linear temperature dependence. The Coriolis constants for the symmetrical case are $\zeta_{23}^x = 1$ and $\zeta_{21}^x = 0$.

Symmetric case: CO$_2$

In the case of a symmetric linear triatomic molecule YXY we have to consider only one mean bond displacement. Eqs. (9) and (10) reduce to the same equation under the condition that $\langle R_1\rangle = \langle R_3\rangle$ and has the following form:

$$\langle \Delta r\rangle_{\mathrm{anh}} = -\frac{1}{(2K_{11}+K_{13})}\left\{(3K_{111}+K_{113})\langle(\Delta r)^2\rangle + 2K_{113}\langle \Delta r_1\Delta r_3\rangle + \left(K_{122} - \frac{1}{r}K_{22}\right)\langle(\Delta\phi)^2\rangle\right\}. \tag{15}$$

After a substitution of the appropriate **L** matrix elements, which can be expressed analytically for this symmetric molecule type, we obtain $\langle \Delta r\rangle$ as a function of $\langle Q^2\rangle$:

$$\langle \Delta r\rangle_{\mathrm{anh}} = -\frac{1}{(2K_{11}+K_{13})}\left\{\frac{3}{2m_y}(K_{111}+K_{113})\langle Q_1^2\rangle + (3K_{111}-K_{113})\left(\frac{1}{m_x}+\frac{1}{2m_y}\right)\langle Q_3^2\rangle + \left(K_{112} - \frac{1}{r}K_{22}\right)\left[\frac{2}{r^2}\left(\frac{2}{m_x}+\frac{1}{m_y}\right)\right]\langle Q_2^2\rangle\right\}. \tag{16}$$

The numerical results for ^{13}CO$_2$ using the force constants published by Lacy,[4] are given in Table I. Table I also includes the centrifugal distortion for this molecule, calculated from Eq. (13). The temperature dependence of $\langle \Delta r\rangle^T$ is illustrated in Fig. 1. These results are in excellent agreement with recent electron diffraction data,[10] as compared in Fig. 2.

The proper calculation of $\langle \Delta r\rangle^T$ for molecules with some low vibrational frequencies requires a theory which includes a thermal averaging over populated vibrational states. One way of doing this is by the variational method, as has been done for $\langle \Delta r_{\mathrm{CO}}\rangle^T$ in CO$_2$ by Kohl and Hilderbrandt.[21] We find that using a harmonic oscillator partition function [Eq. (12)] gives essentially the same results. For ex-

TABLE I. Mean bond displacements due to anharmonic vibration and rotation (centrifugal stretching) in ^{13}C ^{16}O$_2$ and ^{15}N ^{15}N ^{16}O, all in 10^{-3} Å.

	$\langle \Delta r_{\mathrm{CO}}\rangle^T$			$\langle \Delta r_{\mathrm{NN}}\rangle^T$			$\langle \Delta r_{\mathrm{NO}}\rangle^T$		
T, K	Anh	Rot	Tot	Anh	Rot	Tot	Anh	Rot	Tot
250	4.4802	0.1718	4.6520	4.9389	0.1425	5.0814	5.3217	0.2436	5.5652
260	4.4841	0.1787	4.6627	4.9474	0.1482	5.0956	5.3273	0.2533	5.5806
270	4.4883	0.1855	4.6738	4.9565	0.1539	5.1104	5.3336	0.2630	5.5966
280	4.4929	0.1924	4.6853	4.9661	0.1596	5.1257	5.3403	0.2728	5.6131
290	4.4978	0.1993	4.6971	4.9762	0.1653	5.1415	5.3477	0.2825	5.6302
300	4.5031	0.2062	4.7093	4.9868	0.1710	5.1578	5.3556	0.2923	5.6479
310	4.5087	0.2130	4.7218	4.9978	0.1767	5.1745	4.3641	0.3020	5.6661
320	4.5148	0.2199	4.7347	5.0093	0.1824	5.1917	5.3732	0.3118	5.6850
330	4.5211	0.2268	4.7479	5.0218	0.1881	5.2094	5.3830	0.3215	5.7045
340	4.5279	0.2336	4.7615	5.0336	0.1938	5.2274	5.3933	0.3312	5.7246
350	4.5350	0.2405	4.7755	5.0464	0.1995	5.2459	5.4044	0.3410	5.7453

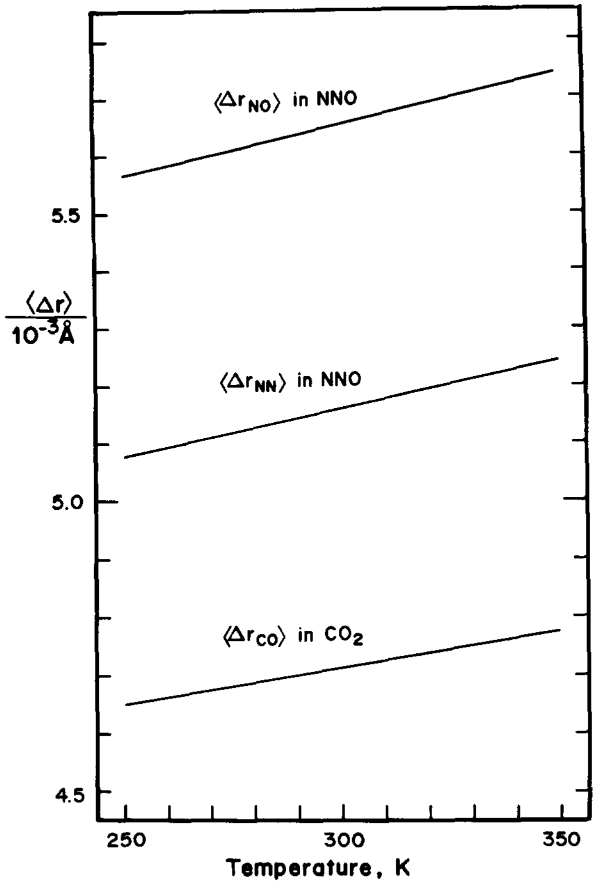

FIG. 1. Mean bond displacements in $^{13}CO_2$ and $^{15}N_2O$ as a function of temperature.

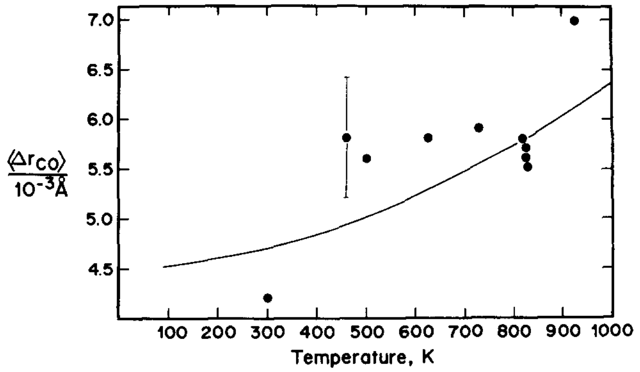

FIG. 2. Comparison between calculated mean bond displacements for $^{12}CO_2$ and electron diffraction data from Ref. 10.

ample, at 300 K we find the vibrational contribution to $\langle \Delta r_{CO} \rangle^T = 0.0045$ and $\langle \Delta r_{CO}^2 \rangle^T = 0.0012$, whereas Kohl and Hilderbrandt obtain 0.0040 and 0.0012, respectively.

Nonsymmetric case: $^{15}N^{15}NO$

In this case we have to solve the coupled Eqs. (9) and (10) for $\langle \Delta r_{NN} \rangle$ and $\langle \Delta r_{NO} \rangle$. Using the force constants from Lacy and Whiffen[5] we obtain the numerical results given in Table I and illustrated in Fig. 1. As expected the results for mean bond displacements in NNO and CO$_2$ are comparable because of the similar geometry, masses and harmonic frequencies.

CORRELATION TO NMR MEASUREMENTS

Temperature dependence of the nuclear shielding

In an earlier paper we reported the experimental temperature dependence of the nuclear magnetic shielding for ^{13}C and ^{15}N.[11] The nuclear shielding in the zero-pressure limit was described by the following functions:

for ^{13}C in CO$_2$:

$$\sigma_0(T) - \sigma_0(300\ K) = -5.369 \times 10^{-4}(T - 300), \tag{17a}$$

for the central ^{15}N in NNO:

$$\begin{aligned} &\sigma_0(T) - \sigma_0(300\ K) \\ &\quad = -3.588 \times 10^{-3}(T - 300) + 0.4102 \times 10^{-5} \\ &\qquad \times (T - 300)^2 + 0.2009 \times 10^{-7}(T - 300)^3, \end{aligned} \tag{17b}$$

for the end ^{15}N in NNO:

$$\begin{aligned} &\sigma_0(T) - \sigma_0(300\ K) \\ &\quad = -8.8816 \times 10^{-3}(T - 300) - 1.4682 \times 10^{-5} \\ &\qquad \times (T - 300)^2 + 1.9513 \times 10^{-7}(T - 300)^3. \end{aligned} \tag{17c}$$

We interpret these experimental functions of thermal average shielding in terms of Eq. (4):

$$\sigma_0(T) = \sigma_e + \sum_i (\partial\sigma/\partial\Delta r_i)_e \langle \Delta r_i \rangle^T. \tag{4}$$

For ^{13}C shielding we use

$$\sigma_0^C(T) \simeq \sigma_e + 2(\partial\sigma/\partial\Delta r_{CO})_e \langle \Delta r_{CO} \rangle^T \tag{18}$$

and for ^{15}N shielding

$$\sigma_0^{\underline{N}NO}(T) \simeq \sigma_e + (\partial\sigma/\partial\Delta r_{NN})_e \langle \Delta r_{NN} \rangle^T, \tag{19}$$

$$\sigma_0^{N\underline{N}O}(T) \simeq \sigma_e + (\partial\sigma/\partial\Delta r_{av})_e [\langle \Delta r_{NN} \rangle^T + \langle \Delta r_{NO} \rangle^T]. \tag{20}$$

That is, we neglect terms in $(\partial^2\sigma/\partial\Delta r^2)_e$ and $(\partial^2\sigma/\partial\Delta\phi^2)_e$. For diatomic molecules it has been shown by Ditchfield[22] that for fitting to the temperature dependence of $\sigma_0(T)$, leaving out the $(\partial^2\sigma/\partial\Delta r^2)_e$ term does not make a significant difference. Presently we have no information on how important the $(\partial^2\sigma/\partial\Delta\phi^2)_e$ term is to the temperature dependence. In addition, we leave out the $(\partial\sigma/\partial\Delta r_{NO})_e$ from Eq. (19). The nuclear shielding is a very localized property so that for the end N we assume that the effect of change in the bond not directly attached to the resonating nucleus is negligible. Furthermore, for the middle N shielding we assume an average $(\partial\sigma/\partial\Delta r)_e$ for $(\partial\sigma/\partial\Delta r_{NO})_e$ and $(\partial\sigma/\partial\Delta r_{NN})_e$. Under these assumptions, the experimentally determined functions $\sigma_0(T) - \sigma_0(300\ \mathrm{K})$ can be least-squares fitted to the function

$$\begin{aligned} &\sigma_0(T) - \sigma_0(300\ K) \\ &\quad = A + B\langle \Delta r \rangle^T \text{ or } A + B(\langle \Delta r_1 \rangle^T + \langle \Delta r_3 \rangle^T) \end{aligned} \tag{21}$$

yielding empirical values for $A \simeq \sigma_e - \sigma_0(300)$ and $B = (\partial\sigma/\partial\Delta r)_e$. In this way we obtain:

$$\begin{aligned} &{}^{13}\mathrm{CO_2}{:}\sigma_e-\sigma_0(300)\simeq 2\ \text{ppm}, && (\partial\sigma/\partial\Delta r_{\mathrm{CO}})_e=-220\ \text{ppm/Å},\\ &\mathrm{\underline{N}NO}{:}\sigma_e-\sigma_0(300)\simeq 27\ \text{ppm}, && (\partial\sigma/\partial\Delta r_{\mathrm{NN}})_e=-5190\ \text{ppm/Å},\\ &\mathrm{N\underline{N}O}{:}\sigma_e-\sigma_0(300)\simeq 11\ \text{ppm}, && (\partial\sigma/\partial\Delta r)_e=-1030\ \text{ppm/Å}.\end{aligned}$$

Care should be taken in extracting σ_e values from A since we have left out terms in the second derivatives of shielding which contribute to σ_0(0 K) even though they may not significantly affect the temperature dependence in the range 200–400 K.

The derivatives of the central nuclei appear to be reasonable in comparison to the diatomic molecules: For N_2 and CO, $(\partial\sigma/\partial\Delta r)_e = -777 \pm 90$ and -226 ± 40 ppm/Å, respectively,[23] for N and C in CN^- they are, respectively, -872 ± 160 and -473 ± 90 ppm/Å.[24] For $\mathrm{N\underline{N}O}$ and $\mathrm{O\underline{C}O}$, they are -1030 and -220 ppm/Å, respectively. That the derivatives of ^{15}N shielding are larger than ^{13}C is not surprising in view of the greater range of chemical shifts of N compared to C.

The empirical value -5000 ppm/Å for the end N appears unusually large. This may have something to do with the existence of a lone pair on the end N in NNO. It is well known that low-lying $n\rightarrow\pi^*$ excited states contribute significantly to the paramagnetic shielding of N nuclei with a lone pair.[25] There is indeed a fairly sizeable intermolecular effect on the end N shielding[11] which might be an indication of some lone pair involvement. Nevertheless, this derivative appears to be atypical and we reserve judgement on it at this stage. It would be very useful to have a good *ab initio* calculation of the shielding in NNO as a function of internuclear separation. The best available calculation of σ for this molecule[26] is still inadequate. For the end and middle N, Schindler and Kutzelnigg obtain $\sigma_e = 80.25$ and -43.77 ppm, respectively. These values are both too low, indicating an overestimation of the paramagnetic term. Their internal chemical shift of 124 ppm is considerably greater than the observed 88.2 ppm.[27] Since the experimental temperature dependence indicates a deshielding with increase in temperature, σ_e should be greater than the σ_0 values, which are 99.5 and 11.3 ppm, respectively, on the N absolute shielding scale[27] (based on NH_3). On the other hand, from the $\sigma_0(300)$ and $A = 27$ ppm we estimate $\sigma_e(\text{end}) = 126.3$ ppm, and from $A = 11$ ppm we estimate $\sigma_e(\text{middle}) = 22.4$ ppm. These estimates of σ_e are probably too low since the other derivatives such as $(\partial^2\sigma/\partial\Delta\phi^2)_e$ were not included in our fitting to the experimental $\sigma_0(T)$. Nevertheless, they are too large enough, compared to Schindler and Kutzelnigg's calculated σ_e values.

For NNO the spin-rotation constants have been measured for both nitrogen nuclei for the (000) and (01^{1}0) vibrational states.[12] By means of the well-known relationship between the paramagnetic shielding and spin-rotation tensors[28] the vibrationally averaged shielding for these states are[27]

$$\begin{aligned} &\mathrm{\underline{N}NO}\ \ \sigma_0(000)=105\pm 12\ \text{ppm}, && \sigma_0(01^10)=96\pm 2,\\ &\mathrm{N\underline{N}O}\ \ \sigma_0(000)=-44\pm 15\ \text{ppm}, && \sigma_0(01^10)=12\pm 2.5.\end{aligned}$$

Using the derivatives $(\partial\sigma/\partial\Delta r)_e = -5190$ and -1030 ppm/Å for the end and middle N, respectively, and the σ_e from the above discussion, using the proper averages $\langle\Delta r\rangle_{000}$ and $\langle\Delta r\rangle_{01^10}$, we find:

$$\begin{aligned} &\mathrm{\underline{N}NO}\ \ \sigma_0(000)=100\ \text{ppm}, && \sigma_0(01^10)=92\ \text{ppm},\\ &\mathrm{N\underline{N}O}\ \ \sigma_0(000)=12\ \text{ppm}, && \sigma_0(01^10)=9\ \text{ppm}.\end{aligned}$$

As discussed above, our σ_e values have some errors associated with neglect of terms in the secone derivatives. Nevertheless, the agreement is favorable for all but the $\mathrm{N\underline{N}O}$ in the (000) state. It has previously been noted that the spin-rotation constant C reported for this state may be in error.[27] We have measured T_1 values for both N in one sample of NNO gas at 260 K. If we assume that the spin-rotation mechanism dominates the relaxation, the ratio $T_1(\mathrm{\underline{N}NO}/T_1(\mathrm{N\underline{N}O})$ equals $C^2(\mathrm{N\underline{N}O})/C^2(\mathrm{\underline{N}NO})$. With this we find $C(\mathrm{N\underline{N}O})/C(\mathrm{\underline{N}NO}) = 1.44 \pm 0.03$. Reinartz *et al.*[12] reported $C_\perp$ values for the (000) state which have a ratio of 1.673. If we take their $C_\perp(\mathrm{\underline{N}NO}) = 1.829$ kHz, we estimate from our T_1 measurements $C_\perp(\mathrm{N\underline{N}O}) = 2.63 \pm 0.07$ kHz, which leads to $\sigma^{\mathrm{N\underline{N}O}} = 8 \pm 8$ ppm for the (000) state, rather than their -44 ± 15 ppm.

Isotope effects

Treating the isotopomers of CO_2 as nonsymmetric linear cases, the Eqs. (9) and (10) can be solved using the same (mass independent) force constants. In this way the mean bond displacements at 300 K can be calculated for all the isotopic species of NNO and CO_2. For this particular paper, only the species for which the shielding have been observed will be discussed. The general effect of isotopic substitution on $\langle\Delta r\rangle$ is in a separate paper. For comparison with the NMR experiment, we examine the differences:

$$\langle\Delta r(^{13}\mathrm{C}\,^{16}\mathrm{O}_2)\rangle-\langle\Delta r(^{13}\mathrm{C}\,^{18}\mathrm{O}\,^{16}\mathrm{O})\rangle=1.268\times 10^{-4}\ \text{Å},$$

$$\langle\Delta r(^{15}\mathrm{N}\,^{14}\mathrm{N}\,^{16}\mathrm{O})\rangle-\langle\Delta r(^{15}\mathrm{N}\,^{15}\mathrm{N}\,^{16}\mathrm{O})\rangle=0.793\times 10^{-4}\ \text{Å}.$$

If we assume that we can interpret the NMR isotope shifts entirely in terms of the derivatives $(\partial\sigma/\partial\Delta r)$ and ignore the change in shielding of a nucleus due to the bond displacement in the neighboring bond, then

$$\begin{aligned}&\sigma_0(^{13}\mathrm{C}\,^{16}\mathrm{O}_2)-\sigma_0(^{13}\mathrm{C}\,^{18}\mathrm{O}_2)\\ &\quad=(\partial\sigma/\partial\Delta r)_e[\langle\Delta r(^{13}\mathrm{C}\,^{16}\mathrm{O}_2)-\Delta r(^{13}\mathrm{C}\,^{18}\mathrm{O}_2)\rangle].\end{aligned}$$

Using the derivatives obtained from the temperature dependence of the shielding, we obtain

$$\sigma_0(^{13}\mathrm{C}\,^{16}\mathrm{O}_2)-\sigma_0(^{13}\mathrm{C}\,^{18}\mathrm{O}\,^{16}\mathrm{O})=-0.028\ \text{ppm}.$$

We may compare the $^{18/16}$O-induced isotope shift for ^{13}C in CO_2 with those in a variety of C = O compounds. The latter range in value from -0.033 to -0.039 ppm in esters, -0.028 to -0.036 in amides, -0.045 to -0.052 in ketones and aldehydes.[29] The esters are probably closest in electronic environment to CO_2. The agreement is quite good.

Similarly the nitrogen isotope shifts are interpreted as

$$\begin{aligned}\sigma_0(^{15}\mathrm{N}\,^{14}\mathrm{NO}) - \sigma_0(^{15}\mathrm{N}\,^{15}\mathrm{NO}) &= (\partial\sigma/\partial\Delta r_{\mathrm{NN}})[\Delta r_{\mathrm{NN}}(^{15}\mathrm{N}\,^{14}\mathrm{NO})\Delta r_{\mathrm{NN}}(^{15}\mathrm{N}\,^{15}\mathrm{NO})] \\ &= -0.412\ \mathrm{ppm}.\end{aligned}$$

This is to be compared to our present measurement of this isotope shift which gives -0.113 ppm. We see that in this case the agreement is not particularly good. This seems to indicate that our derivative for the end N may be too large. This remains an open question which poses a challenge for theoretical calculations.

In summary, we have shown a simple general expression for calculating mean bond displacements in linear triatomic molecules, symmetric or otherwise, provided the cubic force constants are known. The application of this to CO_2 molecules give results which are in good agreement with results of the variation method.

Interpretation of the temperature dependence of ^{13}C in CO_2 and ^{15}N in $^{15}N\,^{15}NO$ in the zero-pressure limit gives empirical values of derivatives of the nuclear shielding surface at the equilibrium configuration. We have assumed that the most important contributor to the temperature dependence of the shielding is the extension of the bond directly involving the observed nucleus. We have also assumed that neglecting the second derivative with respect to bending, $(\partial^2\sigma/\partial\Delta\phi^2)_e$ does not appreciably alter our conclusions. The isotope shift appears to be reasonable in the case of CO_2, less so in NNO. The vibrationally averaged shielding for the (000) and (01^10) vibrational states of NNO have been calculated using the above interpretation and the absolute shielding scale. The agreement with the molecular beam measurements is quite good except in one case, and in this case good agreement is obtained with spin-rotation data from T_1 measurements. An improved theoretical calculation of σ for NNO may answer the open question of the magnitude of $(\partial\sigma/\partial\Delta r_{\mathrm{NN}})_e$ for the end nitrogen.

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