Monatshefte für Chemie 104, 1607—1622 (1973)

Shrinkages of the Internuclear Distances in Some Hexafluorides of Octahedral Symmetry*

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With 4 Figures

(Received January 29, 1973)

A brief analysis of the shrinkages or shortening of the internuclear distances in many molecular systems has been made. Analytical expressions for the linear shrinkage and nonlinear shrinkage have been derived in terms of the mean-square perpendicular amplitudes. Analytical expressions for the generalized mean-square amplitudes (mean-square parallel amplitudes, mean-square perpendicular amplitudes, and mean cross products) for an octahedral XY_6 molecule have been given in terms of the mean-square amplitude matrices. The linear and nonlinear shrinkages for the hexafluorides of sulfur, selenium, tellurium, molybdenum, technetium, ruthenium, rhodium, tungsten, rhenium, osmium, iridium, platinum, uranium, neptunium, and plutonium have been computed at 298 °K and 500 °K, and the results have been briefly discussed.

Introduction

If the nuclei remain rigidly in their equilibrium positions or at least confined to a straight line for a linear molecule, it is logical to expect that the distance between the end atoms must be exactly equal to the sum of the distance between the atom pairs comprising it. Actually, this is not the case. The nuclei deviate from their equilibrium positions by the effect of thermal motion and make a zig zag chain causing the total distance to be apparently shortened.

As an example, *Karle* and *Karle*[1] experimentally determined the internuclear distances of carbon dioxide from electron diffraction studies. Their experimentally determined value for the O----O distance was not exactly double the value for the C=O distance but less. Later, *Bastiansen* and

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* This paper is based on a thesis to be submitted by *Thomas S. Adams* to the Graduate School of the Valdosta State College in partial fulfillment of the requirements for the degree of Master of Science.

his coworkers[2–4], using very high-precision electron diffraction techniques on allene and dimethyldiacetylene in the gaseous state, observed the same effect as that of *Karle* and *Karle*[1]. This shortening or the so-called "shrinkage" has also been observed experimentally in other linear skeleton molecules, e.g., carbon suboxide by *Munthe-Kass*[5] and *Breed* and his associates[6], butadiene by *Traetteberg*[7], and carbon disulfide by *Morino* and *Ijima*[8]. Though this so-called "shrinkage" effect is small, it appears to be real and is well attributed to the perpendicular modes of vibration. If this shrinkage is neglected, linear molecules may appear slightly bent. Further, this effect might confuse the electron diffraction studies of slightly bent molecules with large amplitudes of bending vibration. Bending vibrations will also complicate the structure determinations of linear molecules by spectroscopic methods based on the principal moments of inertia.

A detailed theoretical investigation has been undertaken by *Morino*[9] on the experimental observation of shrinkage for many linear molecular systems[1–8]. This shrinkage effect may be explained by allowing for intramolecular motion and accordingly the shrinkage may be evaluated on the assumption of small harmonic perpendicular vibrations. According to *Morino* and *Hirota*[10], the internuclear distances obtained by electron diffraction studies depend upon the generalized mean-square amplitudes (mean-square parallel amplitudes, mean-square perpendicular amplitudes, and mean cross products), as well as the anharmonicity terms in the potential energy function for the perpendicular modes. The influence of anharmonicity factors, which have a first-order effect on the internuclear distances, is cancelled out when the difference between the observed nonbonded distances and the sum of the bond lengths composing them is accounted for. In other words, the mean-square amplitudes obtained by electron diffraction studies may be compared with those computed by spectroscopic methods, since the anharmonicity terms of the potential energy function for the molecular force field gives only a second-order effect on the mean-square amplitudes. *Morino* and his associates[11] have compared their spectroscopic calculations with the experimental results of *Bastiansen* and his coworkers[2–4], and there is a good agreement between them. Later, many investigators[12] have introduced the name "*Bastiansen—Morino* Shrinkage Effect" in their spectroscopic calculations on this aspect. On the basis of the recent vibrational and structural data, it is aimed here to evaluate the linear and nonlinear shrinkages of the hexafluorides of sulfur, selenium, tellurium, molybdenum, technetium, ruthenium, rhodium, tungsten, rhenium, osmium, iridium, platinum, uranium, neptunium, and plutonium possessing an octahedral symmetry.

Linear Shrinkage

The equilibrium internuclear distance r^e, which has a fundamental importance in the analysis of molecular structure, is rarely obtained by the usual direct measurements except for diatomic or very simple polyatomic molecules. The measurement of microwave or infrared absorption spectra[13] yields an effective r^0 value from the rotational constant for the lowest vibrational state; in some cases, isotopic substitution[14, 15] leads to r^s values. The mean value of an arbitrary internuclear distance, or the center of gravity of the probality distribution function r^g (defined below) obtained from electron diffraction studies[16], is not the true equilibrium internuclear distance r^e but rather some distance modified by the effect of thermal motion. Let us consider the Cartesian coordinate axes for the equilibrium position of an atom pair i–j where the z axis is taken to be the internuclear axis. Then the internuclear distance at any instant can be expressed in terms of small displacements (Δx_i, Δy_i, Δz_i; Δx_j, Δy_j, Δz_j) of the atoms at both ends, and the value of an arbitrary internuclear distance r_{ij} is simply related to the equilibrium distance r^e_{ij} as follows:

$$r_{ij} = [(r^e_{ij} + \Delta z_{ij})^2 + \Delta x^2_{ij} + \Delta y^2_{ij}]^{1/2} \tag{1}$$

When we take the average of the displacements, we may have the following:

$$r^g_{ij} = \langle r_{ij} \rangle = r^e_{ij} + \langle \Delta z_{ij} \rangle + (1/2\, r^e_{ij})\, (\langle \Delta x^2_{ij} \rangle + \langle \Delta y^2_{ij} \rangle) + \ldots \tag{2}$$

where $\Delta z_{ji} = \Delta z_i - \Delta z_j$, $\Delta x_{ij} = \Delta x_i - \Delta x_j$, and $\Delta y_{ij} = \Delta y_i - \Delta y_i$. Here, the linear term $\langle \Delta z \rangle$ is the so-called anharmonicity term which depends upon the cubic potential energy constants and should vanish when the molecular vibrations are purely harmonic. The quadratic terms $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$, called the mean-square perpendicular amplitudes, primarily depend upon the quadratic potential energy constants and remain finite even if the vibrations are purely harmonic. The linear term $\langle \Delta z \rangle$ represents the real variation in the mean positions of the nuclei due to the anharmonicity of the vibration, while the terms involving the quadratic terms $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ come from the perpendicular harmonic vibrations. If the second-order term in eq. (2) is denoted by K_{ij}, then we have

$$r^g_{ij} = r^e_{ij} + \langle \Delta z_{ij} \rangle + K_{ij} \tag{3}$$

The value of r^g_{ij} for any internuclear distance may be obtained from the electron diffraction studies. The K_{ij} term may be spectroscopically computed from the usual standard normal coordinate analysis for small harmonic vibrations[10]. The quantity r^e_{ij} is not known a priori, but it may be assumed that an approximate value would be sufficient since K_{ij} is a correction term.

The shrinkage effect for a trinuclear system in a linear asymmetrical molecule i—j—k (Fig. 1) is given by taking the difference between r^g_{ik} and the sum of the individual bond lengths r^g_{ij} and r^g_{jk} composing it:

$$-\delta = r^g_{ik} - (r^g_{ij} + r^g_{jk}) \tag{4}$$

$$-\delta = K_{ik} - (K_{ij} + K_{jk}) \tag{5}$$

$$-\delta = \langle \Delta x^2_{ik} \rangle / r^e_{ik} - \langle \Delta x^2_{ij} \rangle / r^e_{ij} - \langle \Delta x^2_{jk} \rangle / r^e_{jk} \tag{6}$$

Since the linear term completely vanishes in the analytical expression for the shrinkage effect, the shrinkage begins mainly with the second-order terms which come from the perpendicular harmonic vibrations. For a linear asymmetrical triatomic molecule *i*—*j*—*k* (Fig. 1), the mean-square perpendicular amplitudes $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ are identical for the bonded as well as nonbonded atom pairs.

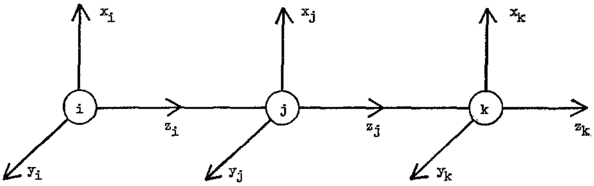

Fig. 1. Equilibrium parameters and displacement coordinates for a linear *i*—*j*—*k* molecule

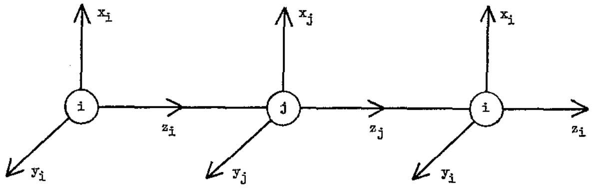

Fig. 2. Equilibrium parameters and displacement coordinates for a linear *i*—*j*—*i* molecule

The shrinkage effect for a trinuclear system in a linear symmetrical molecule *i*—*j*—*i* (Fig. 2) is given by taking the difference between r^g_{ii} and the sum of the individual bond lengths r^g_{ij} and r^g_{ji} composing it:

$$-\delta = r^g_{ij} - (r^g_{ij} + r^g_{ji}) \tag{7}$$

$$-\delta = K_{ii} - (K_{ij} + K_{ij}) \tag{8}$$

$$-\delta = K_{ii} - 2\,K_{ji} \tag{9}$$

$$-\delta = -2\,(\langle \Delta x^2_{ij} \rangle) \,/\, r^e_{ij} \tag{10}$$

Here the mean-square perpendicular amplitudes $\langle \Delta x^2_{ii} \rangle$ and $\langle \Delta y^2_{ii} \rangle$ for the nonbonded atom pair i ----- i vanish, thereby making $K_{ii} = 0$. The mean-square perpendicular amplitudes $\langle \Delta x^2_{ij} \rangle$ and $\langle \Delta y^2_{ij} \rangle$, as in the case of a linear asymmetrical triatomic molecule, are identical for the bonded atom pairs. The equilibrium parameters and displacements of the atoms for the two molecular systems are given in Figs. 1

and 2. For additional information regarding the theoretical aspect of this effect, one may refer to *Morino* and his coworkers[11, 17, 18] and *Cyvin* and his associates[12, 19–30].

Nonlinear Shrinkage

For a nonlinear asymmetrical trinuclear system *i—j—k* (Fig. 3), *Morino* and his associates[18] have defined two kinds of shrinkages, namely, "natural shrinkage", δ^n, and "practical shrinkage", δ^p. The analytical expressions for these two shrinkages are as follows:

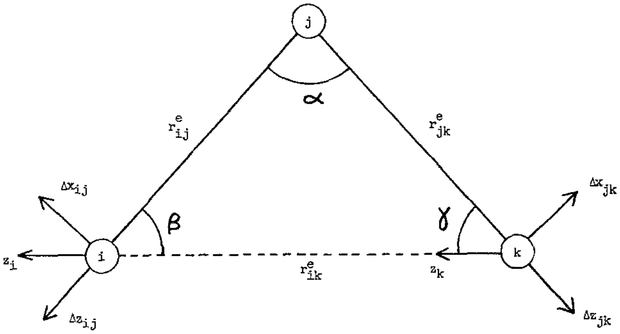

Fig. 3. Equilibrium parameters and displacement coordinates for a nonlinear *i—j—k* molecule. The dotted line is the nonbonded distance showing the explanation of nonlinear shrinkage

$$-\delta^n = r^g_{ik} - [(r^g_{ij})^2 + (r^g_{jk})^2 - 2\, r^g_{ij}\, r^g_{jk} \cos \alpha]^{1/2} \tag{11}$$

$$-\delta^p = r^g_{ik} - (r^g_{ij} \cos \beta + r^g_{jk} \cos \gamma) \tag{12}$$

For highly symmetrical molecules, the equilibrium value of an angle may be correctly determined from symmetry considerations. If such an angle is considered as α in eq. (11), the corresponding "natural shrinkage" may be calculated from the r^g values obtained from the electron diffraction studies. For a nonlinear asymmetrical trinuclear system *i—j—k* (Fig. 3), where the *y* axis is perpendicular to the plane of the paper, we have $\Delta r_{ij} = r_{ij} - r^e_{ij}$ and $\Delta r_{jk} = r^g_{jk} - r^e_{jk}$. The analytical expression for a natural shrinkage may be given as follows:

$$\begin{aligned} -\delta^n &= r^g_{ik} - (r^g_{ij} \cos \beta + r^g_{jk} \cos \gamma) \\ &- (\tfrac{1}{2} r^e_{ik})\, (\sin^2 \beta\, \Delta r^2_{ij} + \sin^2 \gamma\, \Delta r^2_{jk} - 2 \sin \beta \sin \gamma \\ &\Delta r_{ij}\, \Delta r_{jk}) + \ldots \end{aligned} \tag{13}$$

This expression is identical with that of the "practical shrinkage" to a first-order approximation [see eq. (12)]. Since the shrinkage is practically a small quantity, the difference between the natural and practical shrinkages may be ignored.

In contrast to the linear shrinkage effect, the anharmonic term $\langle \Delta z \rangle$ in the nonlinear shrinkage effect may not necessarily be cancelled out; it may be obtained as a linear combination of the symmetry coordinates $\langle S_k \rangle$ of the totally symmetrical vibrational modes (stretching and angle deformation modes), since the mean values of other symmetry coordinates vanish because of the symmetry. On the basis of simple geometric considerations, it may be shown that the contributions from the $\langle S_k \rangle$ of the totally symmetrical stretching modes to the anharmonic terms of the practical shrinkage always vanish, while those from the $\langle S_k \rangle$ of the angle deformation modes do not vanish. Many highly symmetrical molecules such as a linear XY_2 molecule, a linear symmetrical X_2Y_2 molecule, a linear symmetrical X_3Y_2 molecule, a planar symmetrical XY_3 molecule, a tetrahedral XY_4 molecule, and an octahedral XY_6 molecule have no totally symmetrical deformation modes in the ground state. There are two kinds of linear shrinkages for a linear symmetrical X_2Y_2 molecule. The planar symmetrical XY_3 and tetrahedral XY_4 molecules have only one nonlinear shrinkage, whereas an octahedral XY_6 molecule has one linear and one nonlinear shrinkage. For these highly symmetrical molecules the computation of shrinkages becomes much easier, because the anharmonic terms cancel out. The cancellation of anharmonic terms in highly symmetrical nonlinear molecules is similar to that for linear molecules[22, 23, 25, 27].

Shrinkages in Some Hexafluorides

A molecule or ion of the type XY_6 possessing an octahedral symmetry gives rise, according to the relevant symmetry considerations and selection rules[31], to fifteen vibrational degrees of freedom constituting only six fundamental frequencies which are distributed under the various irreducible representations as follows:

$$\mathrm{A_{1g}\ (R;\ p) + E_g\ (R;\ dp) + 2\ F_{1u}\ (I;\ \|) + F_{2g}\ (R;\ dp) + F_{2u}\ (inactive)}$$

where R, I, p, dp and || stand for Raman active, infrared active, polarized, depolarized, and parallel, respectively. The gerade modes are only Raman active, while the ungerade ones are only infrared active. None of the bands observed in the Raman spectrum are observed in the infrared absorption spectrum. This indicates that this system has a center of symmetry. The frequency ν_1 coming under the symmetry species $\mathrm{A_{1g}}$ represents the totally symmetrical X—Y stretching vibration whereas ν_2 under the $\mathrm{E_g}$ species and ν_3 under the $\mathrm{F_{1u}}$ species stand for the asymmetrical X—Y stretching vibrations. The frequencies ν_4

coming under the F_{1u} species, ν_5 under the F_{2g} species, and ν_6 under the F_{2u} species are essentially associated with deformation modes. Only the first five fundamental frequencies can be directly observed from spectroscopic methods. The lowest bending mode belonging to the symmetry species F_{2u} is forbidden in both Raman and infrared absorption spectra. Hence, the frequency ν_6 has to be determined either from combination tones or from specific heat data. This may also be estimated from force constants of other related molecules having similar chemical bonds by employing a suitable valence force field. Hence, this frequency will be less accurate in whichever way it is estimated. But at the same time it is strongly in favor of the octahedral symmetry; otherwise, the symmetry of this system will be strongly in favor of a planar hexagonal structure with the symmetry point group D_{6h}.

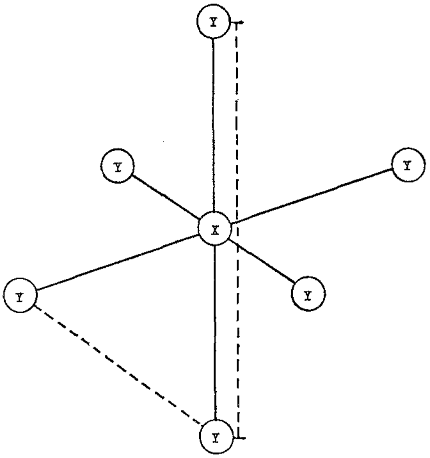

Fig. 4. An octahedral XY_6 molecule. The dotted lines are the nonbonded distances showing the explanation of linear and nonlinear shrinkages

Based on the theory of *Bloch*[32] and *James*[33], *Morino* and *Hirota*[10] extended the concept of mean-square amplitudes in the following manner: If the direction of the line connecting the atom pair i—j at the equilibrium configuration is considered to be the z axis and the directions perpendicular to it and to each other are considered to be the x and y axes, then the displacements of the two atoms in these three directions are Δx, Δy, and Δz, respectively. Then $\Delta\langle z^2\rangle$ is the mean-square parallel amplitude, $\langle\Delta x^2\rangle$ and $\langle\Delta y^2\rangle$ are the mean-square perpendicular amplitudes, and $\langle\Delta x\,\Delta y\rangle$, $\langle\Delta y\,\Delta z\rangle$, and $\langle\Delta z\,\Delta x\rangle$ are the mean cross products. *Cyvin* and many others[12, 34] referred to these as the generalized mean-square amplitudes. According to *Bye* and *Cyvin*[29], the analytical expressions for the generalized mean-square amplitudes for an octahedral XY_6 molecule are given in terms of the mean-square amplitude matrices as follows:

For the bond atom pair X—Y:

$$\langle \Delta z^2 \rangle = (1/6)\,(\Sigma_{11} + 2\,\Sigma_{22} + 3\,\Sigma_{33})$$
$$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle = (1/8)\,\Sigma_{44} + (1/16)\,\Sigma_{55} + (1/8)\,\Sigma_{66}$$
$$\langle \Delta x\, \Delta y \rangle = \langle \Delta y\, \Delta z \rangle = \langle \Delta z\, \Delta x \rangle = 0.$$

For the nonbonded atom pair Y ---- Y(linear):

$$\langle \Delta z^2 \rangle = (2/3)\,\Sigma_{11} + (4/3)\,\Sigma_{22}$$
$$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle = (1/4)\,\Sigma_{55}$$
$$\langle \Delta x\, \Delta y \rangle = \langle \Delta y\, \Delta z \rangle = \langle \Delta z\, \Delta x \rangle = 0.$$

For the nonbonded atom pair Y ---- Y(nonlinear):

$$\langle \Delta z^2 \rangle = (1/3)\,\Sigma_{11} + (1/6)\,\Sigma_{22} + (1/2)\,\Sigma_{33} + (1/8)\,\Sigma_{44} + (1/8)\,\Sigma_{55} + + (1/8)\,\Sigma_{66} - (1/2)\,\Sigma_{34}$$
$$\langle \Delta x^2 \rangle = (1/2)\,\Sigma_{22} + (1/2)\,\Sigma_{33} + (1/8)\,\Sigma_{44} + (1/8)\,\Sigma_{66} - (1/2)\,\Sigma_{34}$$
$$\langle \Delta y^2 \rangle = (1/8)\,\Sigma_{55} + (1/2)\,\Sigma_{66}$$
$$\langle \Delta x\, \Delta y \rangle = \langle \Delta y\, \Delta z \rangle = \langle \Delta z\, \Delta x \rangle = 0.$$

On the basis of the recent vibrational and structural data, root-mean-square amplitudes for both bonded and nonbonded atom pairs were computed by *Nagarajan* and *Adams*[35] for the hexafluorides of sulfur, selenium, tellurium, molybdenum, technetium, ruthenium, rhodium, tungsten, rhenium, osmium, iridium, platinum, uranium, neptunium, and plutonium. The recent values of vibrational frequencies in cm^{-1} and the internuclear distances in Å for these hexafluorides[35] are given in Table 1. On the basis of the principles postulated by *Cyvin*[12], the secular equations were constructed with help of the vibrational frequencies and structural data given in Table 1 for these fifteen hexafluorides at temperatures 298 °K and 500 °K and solved to obtain the values of symmetrized mean-square amplitude matrices (Σ). From the evaluated values of the symmetrized mean-square amplitude matrices[35], the generalized mean-square amplitudes (mean-square parallel amplitudes, mean-square perpendicular amplitudes, and mean cross products) were computed for both bonded and nonbonded atom pairs, and their values in Å^2 are given in Table 2 at the temperatures 298 °K and 500 °K for all the fifteen hexafluorides. Here the nonbonded atom pair F ---- F(linear) represents the distance between two peripheral atoms opposite to each other with the central atom at the middle, while the nonbonded atom pair F ---- F(nonlinear) represents the

Table 1. *Fundamental Frequencies in* cm^{-1} *and Internuclear Distances in* Å *for Some Hexafluorides of Octahedral Symmetry*

Molecule	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	X—Y
Sulfur Hexafluoride	773.5	641.7	939	614	525	347	1.58
Selenium Hexafluoride	706.9	658.7	780	437	405	264	1.70
Tellurium Hexafluoride	697.1	670.3	752	325	314	197	1.84
Molybdenum Hexafluoride	741.5	651.6	741.1	264	318	116	1.83
Technetium Hexafluoride	712.9	639	748	265	297	145	1.8512
Ruthenium Hexafluoride	675	624	735	275	283	186	1.8775
Rhodium Hexafluoride	634	595	724	283	269	192	1.8738
Tungsten Hexafluoride	771	677.2	711	258	320	127	1.83
Rhenium Hexafluoride	753.7	671	715	257	295	147	1.92
Osmium Hexafluoride	730.7	668	720	268	276	205	1.831
Iridium Hexafluoride	701.7	645	719	276	267	206	1.833
Platinum Hexafluoride	656.4	601	705	273	242	211	1.829
Uranium Hexafluoride	667.1	532.5	624	186.2	202	142	1.994
Neptunium Hexafluoride	654	535	624	198.6	208	164	1.98
Plutonium Hexafluoride	628	523	616	206	211	173	1.972

Table 2. *Generalized Mean-Square Amplitudes in* Å^2 *in Some Hexafluorides of Octahedral Symmetry* *

Molecule	Distance	Symbol	Mean-square amplitude	
			T = 298 °K	T = 500 °K
SF_6	S—F	$\langle \Delta z^2 \rangle$	0.0017660	0.0020629
		$\langle \Delta x^2 \rangle$	0.0026539	0.0033893
		$\langle \Delta y^2 \rangle$	0.0026539	0.0033893
	F ---- F(linear)	$\langle \Delta z^2 \rangle$	0.0028202	0.0034919
		$\langle \Delta x^2 \rangle$	0.0019800	0.0026371
		$\langle \Delta y^2 \rangle$	0.0019800	0.0026371
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0034127	0.0043782
		$\langle \Delta x^2 \rangle$	0.0025261	0.0032191
		$\langle \Delta y^2 \rangle$	0.0047192	0.0068532
SeF_6	Se—F	$\langle \Delta z^2 \rangle$	0.0016012	0.0019414
		$\langle \Delta x^2 \rangle$	0.0034331	0.0050557
		$\langle \Delta y^2 \rangle$	0.0034331	0.0050557
	F ---- F(linear)	$\langle \Delta z^2 \rangle$	0.0028427	0.0035260
		$\langle \Delta x^2 \rangle$	0.0029138	0.0041770
		$\langle \Delta y^2 \rangle$	0.0029138	0.0041770
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0050011	0.0070606
		$\langle \Delta x^2 \rangle$	0.0035857	0.0050356
		$\langle \Delta y^2 \rangle$	0.0074271	0.0113602
TeF_6	Te—F	$\langle \Delta z^2 \rangle$	0.0015901	0.0019666
		$\langle \Delta x^2 \rangle$	0.0052816	0.0081980
		$\langle \Delta y^2 \rangle$	0.0052816	0.0081980
	F ---- F(linear)	$\langle \Delta z^2 \rangle$	0.0028156	0.0034783
		$\langle \Delta x^2 \rangle$	0.0044171	0.0066763
		$\langle \Delta y^2 \rangle$	0.0044171	0.0066763
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0069040	0.0102823
		$\langle \Delta x^2 \rangle$	0.0047184	0.0069793
		$\langle \Delta y^2 \rangle$	0.0123847	0.0196551
MoF_6	Mo—F	$\langle \Delta z^2 \rangle$	0.0019984	0.0026112
		$\langle \Delta x^2 \rangle$	0.0107641	0.0173512
		$\langle \Delta y^2 \rangle$	0.0107641	0.0173512
	F ---- F(linear)	$\langle \Delta z^2 \rangle$	0.0028189	0.0034863
		$\langle \Delta x^2 \rangle$	0.0043232	0.0065198
		$\langle \Delta y^2 \rangle$	0.0043232	0.0065198
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0114342	0.0178544
		$\langle \Delta x^2 \rangle$	0.0093463	0.0147069
		$\langle \Delta y^2 \rangle$	0.0301923	0.0495241

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* $\langle \Delta x \, \Delta y \rangle = \langle \Delta y \, \Delta z \rangle = \langle \Delta z \, \Delta x \rangle = 0.$

Table 2 (continued)

Molecule	Distance	Symbol	Mean-square amplitude	
			T = 298 °K	T = 500 °K
TcF_6	Tc—F	$\langle\Delta z^2\rangle$	0.0016616	0.0020588
		$\langle\Delta x^2\rangle$	0.0079076	0.0125779
		$\langle\Delta y^2\rangle$	0.0079076	0.0125779
	F ---- F(linear)	$\langle\Delta z^2\rangle$	0.0029103	0.0036263
		$\langle\Delta x^2\rangle$	0.0048587	0.0074136
		$\langle\Delta y^2\rangle$	0.0048587	0.0074136
	F ---- F(nonlinear)	$\langle\Delta z^2\rangle$	0.0109423	0.0169671
		$\langle\Delta x^2\rangle$	0.0085784	0.0133609
		$\langle\Delta y^2\rangle$	0.0206227	0.0334684
RuF_6	Ru—F	$\langle\Delta z^2\rangle$	0.0016691	0.0020672
		$\langle\Delta x^2\rangle$	0.0063775	0.0097460
		$\langle\Delta y^2\rangle$	0.0063775	0.0097460
	F ---- F(linear)	$\langle\Delta z^2\rangle$	0.0030366	0.0038208
		$\langle\Delta x^2\rangle$	0.0052834	0.0081231
		$\langle\Delta y^2\rangle$	0.0052834	0.0081231
	F ---- F(nonlinear)	$\langle\Delta z^2\rangle$	0.0092988	0.0139461
		$\langle\Delta x^2\rangle$	0.0067072	0.0099625
		$\langle\Delta y^2\rangle$	0.0146067	0.0223142
RhF_6	Rh—F	$\langle\Delta z^2\rangle$	0.0017238	0.0021526
		$\langle\Delta x^2\rangle$	0.0060958	0.0095406
		$\langle\Delta y^2\rangle$	0.0060958	0.0095406
	F ---- F(linear)	$\langle\Delta z^2\rangle$	0.0032500	0.0041571
		$\langle\Delta x^2\rangle$	0.0057756	0.0089461
		$\langle\Delta y^2\rangle$	0.0057756	0.0089461
	F ---- F(nonlinear)	$\langle\Delta z^2\rangle$	0.0091039	0.0138793
		$\langle\Delta x^2\rangle$	0.0062606	0.0094763
		$\langle y\Delta^2\rangle$	0.0135642	0.0216286
WF_6	W—F	$\langle\Delta z^2\rangle$	0.0016128	0.0020279
		$\langle\Delta x^2\rangle$	0.0091410	0.0146986
		$\langle\Delta y^2\rangle$	0.0091410	0.0146986
	F ---- F(linear)	$\langle\Delta z^2\rangle$	0.0026853	0.0032820
		$\langle\Delta x^2\rangle$	0.0042776	0.0064437
		$\langle\Delta y^2\rangle$	0.0042776	0.0064437
	F ---- F(nonlinear)	$\langle\Delta z^2\rangle$	0.0105041	0.0162962
		$\langle\Delta x^2\rangle$	0.0084350	0.0131790
		$\langle\Delta y^2\rangle$	0.0256411	0.0418891

Table 2 (continued)

Molecule	Distance	Symbol	Mean-square amplitude	
			T = 298 °K	T = 500 °K
ReF_6	Re—F	$\langle \Delta z^2 \rangle$	0.0015327	0.0018952
		$\langle \Delta x^2 \rangle$	0.0078628	0.0125540
		$\langle y \Delta^2 \rangle$	0.0078628	0.0125540
	F ---- F(linear)	$\langle \Delta z^2 \rangle$	0.0027293	0.0033490
		$\langle \Delta x^2 \rangle$	0.0049157	0.0075088
		$\langle \Delta y^2 \rangle$	0.0049157	0.0075088
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0097803	0.0150223
		$\langle \Delta x^2 \rangle$	0.0073864	0.0113645
		$\langle \Delta y^2 \rangle$	0.0201785	0.0327231
OsF_6	Os—F	$\langle \Delta z^2 \rangle$	0.0014923	0.0018294
		$\langle \Delta x^2 \rangle$	0.0057404	0.0089973
		$\langle \Delta y^2 \rangle$	0.0057404	0.0089973
	F ---- F(linear)	$\langle \Delta z^2 \rangle$	0.0027722	0.0034130
		$\langle \Delta x^2 \rangle$	0.0055202	0.0085189
		$\langle \Delta y^2 \rangle$	0.0055202	0.0085189
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0080232	0.0121046
		$\langle \Delta x^2 \rangle$	0.0053138	0.0079223
		$\langle \Delta y^2 \rangle$	0.0122105	0.0193600
IrF_6	Ir—F	$\langle \Delta z^2 \rangle$	0.0015123	0.0018591
		$\langle \Delta x^2 \rangle$	0.0056756	0.0088902
		$\langle \Delta y^2 \rangle$	0.0056756	0.0088902
	F ---- F(linear)	$\langle \Delta z^2 \rangle$	0.0029037	0.0036152
		$\langle \Delta x^2 \rangle$	0.0058522	0.0090743
		$\langle \Delta y^2 \rangle$	0.0058522	0.0090743
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0082804	0.0125220
		$\langle \Delta x^2 \rangle$	0.0054049	0.0080628
		$\langle \Delta y^2 \rangle$	0.0122917	0.0194955
PtF_6	Pt—F	$\langle \Delta z^2 \rangle$	0.0016204	0.0020294
		$\langle \Delta x^2 \rangle$	0.0059237	0.0093050
		$\langle \Delta y^2 \rangle$	0.0059237	0.0093050
	F ---- F(linear)	$\langle z^2 \Delta \rangle$	0.0031765	0.0040401
		$\langle \Delta x^2 \rangle$	0.0069761	0.0109552
		$\langle \Delta y^2 \rangle$	0.0069761	0.0109552
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0086419	0.0131136
		$\langle \Delta x^2 \rangle$	0.0052133	0.0077293
		$\langle \Delta y^2 \rangle$	0.0124474	0.0197550

Table 2 (continued)

Molecule	Distance	Symbol	Mean-square amplitude	
			T = 298 °K	T = 500 °K
UF_6	U—F	$\langle \Delta z^2 \rangle$	0.0018082	0.0023318
		$\langle \Delta x^2 \rangle$	0.0108284	0.0175387
		$\langle \Delta y^2 \rangle$	0.0108284	0.0175387
	F ---- F(linear)	$\langle \Delta z^2 \rangle$	0.0035494	0.0046388
		$\langle \Delta x^2 \rangle$	0.0097131	0.0155406
		$\langle \Delta y^2 \rangle$	0.0097131	0.0155406
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0143479	0.0226695
		$\langle \Delta x^2 \rangle$	0.0096590	0.0151650
		$\langle \Delta y^2 \rangle$	0.0237967	0.0387846
NpF_6	Np—F	$\langle \Delta z^2 \rangle$	0.0018446	0.0023917
		$\langle \Delta x^2 \rangle$	0.0089810	0.0144425
		$\langle \Delta y^2 \rangle$	0.0089810	0.0144425
	F ---- F(linear)	$\langle \Delta z^2 \rangle$	0.0035571	0.0046494
		$\langle \Delta x^2 \rangle$	0.0092001	0.0146809
		$\langle \Delta y^2 \rangle$	0.0092001	0.0146809
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0134748	0.0211939
		$\langle \Delta x^2 \rangle$	0.0090259	0.0140935
		$\langle \Delta y^2 \rangle$	0.0189751	0.0306978
PuF_6	Pu—F	$\langle \Delta z^2 \rangle$	0.0018737	0.0024374
		$\langle \Delta x^2 \rangle$	0.0083352	0.0133611
		$\langle \Delta y^2 \rangle$	0.0083352	0.0133611
	F ---- F(linear)	$\langle \Delta z^2 \rangle$	0.0036930	0.0048661
		$\langle \Delta x^2 \rangle$	0.0089599	0.0142783
		$\langle \Delta y^2 \rangle$	0.0089599	0.0142783
	F ---- F(nonlinear)	$\langle \Delta z^2 \rangle$	0.0125715	0.0196990
		$\langle \Delta x^2 \rangle$	0.0082371	0.0127923
		$\langle \Delta y^2 \rangle$	0.0174690	0.0281723

distance between two peripheral atoms adjacent to each other. The mean cross products for both bonded and nonbonded atom vanish by symmetry of the molecular system, and hence they are not listed in Table 2. While the mean-square perpendicular amplitudes are identical for the bonded atom pair and nonbonded atom pair F ---- F(linear), they are different for the nonbonded atom pair F ---- F(nonlinear) by symmetry of the molecular system (Table 2). In the case of the nonbonded atom pair F ---- F(nonlinear), the mean-square perpendicular amplitude $\langle \Delta y^2 \rangle$ is always greater than the mean-square perpendicular amplitude $\langle \Delta x^2 \rangle$. Further, the mean-square parallel amplitudes $\langle \Delta z^2 \rangle$ are always less than the mean-square perpendicular amplitudes $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ for both the bonded and nonbonded atom pairs.

In the case of an octahedral XY_6 molecule, the analytical expressions for the linear and nonlinear shrinkages are, according to earlier studies[20, 29], given as follows:

$$\delta_{Y----Y}(\text{linear}) = (1/4\,\mathrm{R})\,(\Sigma_{44} + \Sigma_{66})$$

$$\delta_{Y----Y}(\text{nonlinear}) = (\sqrt{2}/8\,\mathrm{R})\,(-\Sigma_{22} - \Sigma_{33} + 3/4\,\Sigma_{44} + \Sigma_{34} + \\ + 1/4\,\Sigma_{55} - \Sigma_{34})$$

Table 3. *Shrinkages of the Internuclear Distances in Å for Some Hexafluorides of Octahedral Symmetry*

Molecule	δ_{F----F}(linear)		δ_{F----F}(nonlinear)	
	T = 298 °K	T = 500 °K	T = 298 °K	T = 500 °K
SF_6	0.00273	0.00346	0.00075	0.00078
SeF_6	0.00318	0.00472	0.00057	0.00080
TeF_6	0.00454	0.00710	0.00077	0.00118
MoF_6	0.01058	0.01718	0.00094	0.00100
TcF_6	0.00723	0.01159	0.00046	0.00067
RuF_6	0.00539	0.00822	0.00079	0.00126
RhF_6	0.00497	0.00780	0.00086	0.00133
WF_6	0.00882	0.01430	0.00048	0.00072
ReF_6	0.00691	0.01112	0.00072	0.00113
OsF_6	0.00476	0.00750	0.00105	0.00168
IrF_6	0.00460	0.00722	0.00097	0.00154
PtF_6	0.00457	0.00718	0.00117	0.00188
UF_6	0.00843	0.01369	0.00175	0.00287
NpF_6	0.00675	0.01240	0.00141	0.00232
PuF_6	0.00618	0.00993	0.00137	0.00224

where R stands for the x—y distance at the equilibrium configuration. The calculation of shrinkages need only the values of mean-square perpendicular amplitudes and internuclear distances at the equilibrium configuration. Very accurate values of the internuclear distances at the equilibrium configuration are, however, not required. Approximate values from microwave studies or X-ray diffraction studies or any other theoretical or experimental methods, if the results of electron diffraction studies are not available, will be quite sufficient as the second-order term involving the calculation of the shrinkage is only a minor correction term. The linear and nonlinear shrinkages were calculated at 298 °K and 500 °K and their values in Å are given in Table 3 for all the fifteen hexafluorides. Although the shrinkages due to the perpendicular displacements of the atom pairs for all the molecules studied here appear small, they are real. They are to be added to the observed nonbonded distances from electron diffraction studies at the appropriate temperatures in order to get the real nonbonded distances of the molecule. Although the electron diffraction studies have been undertaken for a few of these molecules, the values of linear and nonlinear shrinkages have not yet been reported for any of these molecules. However, the results of the present study would be useful in the future for the interpretation of the results of electron diffraction studies in determining the shrinkages of chemical bonds for these hexafluorides.

Acknowledgement

One of the authors (*T. S. A.*) is highly grateful to Prof. *James E. Martin*, Acting Head of the Department of Physics and Astronomy, for his interest and encouragement during the course of this investigation.

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