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Quantum-Mechanical Studies of Atomic, Bond, and Molecular Polarizabilities: Dimanganese Iron Tetradecacarbonyl

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The earlier work on the vibrational and structural studies has been given for the metal-carbon-oxygen bonds and the metal-metal bonds in dimanganese iron tetradecacarbonyl, (manganese)$_2$iron(carbonyl)$_{14}$. The δ-function potential model is developed and shown to be valuable in evaluating important quantities through the use of the variational method and the δ-function electronic wave functions. It is then applied to calculations of bonding and nonbonding electron contributions to the parallel and perpendicular components of the bond polarizability, and the average molecular polarizability of both diatomic and polyatomic molecules. The δ-function strengths, the values of the parameter c, and the atomic polarizabilities of all the atoms in dimanganese iron tetradecacarbonyl were calculated. The bond polarizabilities and contributions to their parallel and perpendicular components due to nonbonding electrons were calculated, and the average molecular polarizabilities were computed for both crystallographic versions of dimanganese iron tetradecacarbonyl.

INTRODUCTION

In recent years, extensive efforts have been made in the synthesis of compounds containing metal-metal bonds, and these studies have been accompanied by numerous investigations of the vibrational, structural, and other physicochemical properties of metal-metal-bonded systems. Woodward[1] was the first to establish a vibrational assignment for metal-metal bonds in a Raman study of mercurous ion in aqueous solutions. The importance of Raman and infrared spectra in the study of metal-metal vibrations have been emphasized by a number of investigators.[2–9] The preparations and properties of various polymetallic carbonyls, both linear and nonlinear, have been studied by a number of investigators.[10–18] The bonding of metal atoms in polynuclear carbonyls can be divided into two types: one which is accompanied by bridging carbonyls, as in diiron enneacarbonyl,[10] and the other in which the metal atoms are directly linked, as in dimanganese decacarbonyl[11,12] and its rhenium and technetium analogs.[13,16,18] Compounds with bridging carbonyls show characteristic infrared absorption in the region of 1850 cm^{-1}. Evans, Wozniak, and Sheline[9] studied the infrared and Raman spectra of dimanganese tetradecacarbonyl, and they concluded that no bridging carbonyls were present in this molecule in view of the absence of infrared absorption in this region. This conclusion was well supported by the x-ray diffraction studies of Agron, Ellison, and Levy,[19] who found that the structure of dimanganese iron tetradecacarbonyl consists of a planar iron tetracarbonyl moiety inserted between two axial manganese pentacarbonyl groups. In the crystalline state, two crystallographically distinct molecules of $C_{2h}-2/mm$ symmetry are observed with a molecular geometry that ideally conforms to $D_{4h}-4/m\ 2/m\ 2/m$ symmetry. The iron atoms are situated at the nonequivalent symmetry centers, 000 and $0\frac{1}{2}\frac{1}{2}$, of the monoclinic unit cell. Both molecules have linear arrangements of the metal atoms without bridging carbonyl linkages. Each metal atom is in an essentially octahedral environment, with the equatorial carbonyls on the manganese atoms oriented 45° to those on the central iron atom. The two molecules differ in the disposition of symmetry elements: In the one, the three metal atoms, the two axial terminal carbonyls, and two of the carbonyl ligands on the iron atom all lie in the mirror plane, and the other two carbonyl ligands on the iron atom lie along the diad. In the other molecule, the three metal atoms and the axial carbonyls lie along the diad, and the four carbonyl ligands on the iron atom lie in the mirror plane. The structures and the disposition of the mirror planes are shown in Figs. 1 and 2. Evans, Wozniak, and Sheline[9] confirmed the existence of the two different crystallographic molecules of $Mn_2Fe(CO)_{14}$, from infrared and Raman spectral studies which showed two asymmetrical iron-manganese stretching vibrations, separated by 6–8 cm^{-1}, and no similar doublet for the symmetrical iron-manganese stretching vibration.

In this work, the atomic polarizabilities and the bond polarizabilities (both parallel and perpendicular components) were computed, on the basis of a δ-function potential model, along with contributions from nonbonding electrons, to obtain mean molecular polarizabilities for the two crystallographic versions of the dimanganese iron tetradecacarbonyl molecule. These results show the usefulness of polarizability as a criterion to test the utility of the chosen wave function, and to show the utility of the δ-function potential model, among the various quantum-mechanical models in existence, in the derivation of atomic, bond, and molecular polarizabilities of both diatomic and polyatomic molecules not only of main-group elements, but of transition elements as well.

ATOMIC POLARIZABILITIES

In recent years many investigators[20–35] proposed different quantum-mechanical models, and computed the polarizabilities for many ions, atoms, and simple diatomic molecules in order to test the polarizability as a useful criterion for judging the utility of the wave functions chosen. However, the potential models so far developed were partly successful in the cases of lighter atoms, ions, and diatomic molecules, but not largely extended even to simple triatomic molecules. The first use of a δ-function potential model was made by Rüdenberg and his associates[36–37] and later extended by Frost,[38] Lippincott,[39] and Lippincott and Dayhoff[40] for the calculations of energies of conjugated hydrocarbons,[38] and dissociation energies, vibrational frequences, anharmonicities, and internuclear distances for many diatomic and polyatomic systems.[39, 40] Recently, Lippincott and Stutman[41] with a semiempirical δ-function potential model calculated the bond and molecular polarizabilities for various diatomic and polyatomic molecules having their elements only from and beyond the IV A group of the Periodic Table but not from the IA, IIA, IIIA, VIII or any of the B groups of the Periodic Table.

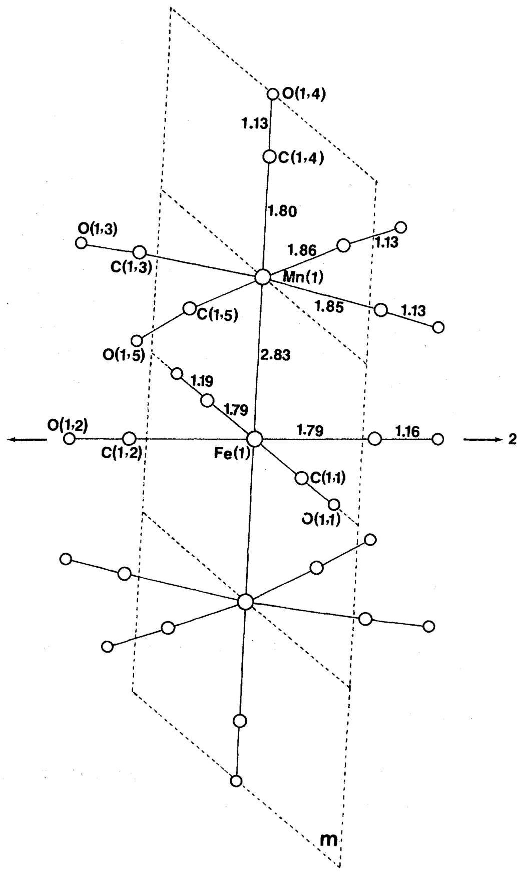


FIG. 1. Internuclear distances in Å for molecule 1 of dimanganese iron tetradecacarbonyl at the equilibrium configuration.

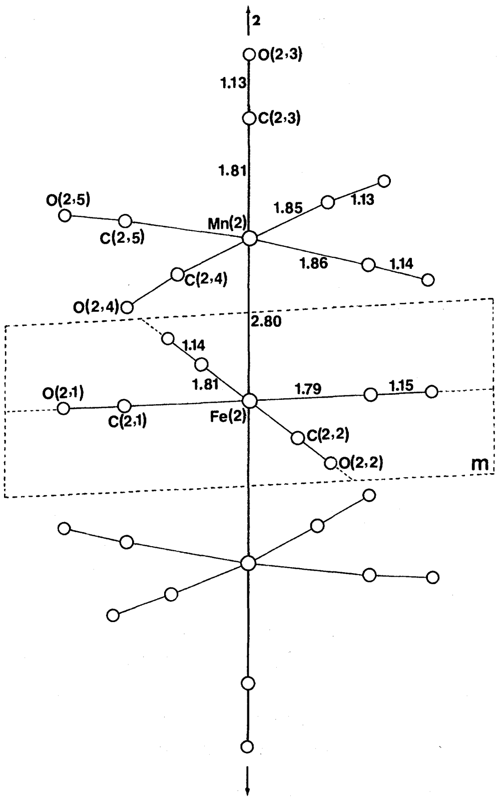


FIG. 2. Internuclear distances in Å for molecule 2 of dimanganese iron tetradecacarbonyl at the equilibrium configuration.

The potential energy for the n-electron problem is considered to be the sum of the single δ-function potentials, each having the form for a diatomic system:

$$V = -[A_1 g\delta(x - \tfrac{1}{2}a) + A_2 g\delta(x + \tfrac{1}{2}a)]\,, \qquad (1)$$

where x is the coordinate of motion along the internuclear axis; a, the δ-function spacing; A_1 and A_2, the δ-function strengths or reduced electronegativities for the nuclei 1 and 2, respectively; g, the unit δ-function strength (the value for the hydrogen atom); and $\delta(x)$, a δ function whose properties are described by the following:

$$\delta(x)=0 \quad \text{when } x\neq 0 \ ,$$
$$\delta(x)=\infty \quad \text{when } x=0 \ , \tag{2}$$
$$\int_{-\infty}^{\infty}\delta(x)\,dx=1 \ .$$

Thus, the potential is zero everywhere except at the δ-function positions where it is infinite in such a way that

$$A_1 g\int_{-\infty}^{\infty}\delta(x-\tfrac{1}{2}a)\,dx=A_1 g \ ,$$
$$A_2 g\int_{-\infty}^{\infty}\delta(x+\tfrac{1}{2}a)\,dx=A_2 g \ . \tag{3}$$

The δ-function strength obtainable from separated atom energies E_i is defined as $A=(-2E_i)^{1/2}$. This can be obtained either from the first ionization potential or from the solution of the atomic problem using the δ-function potential model.

The solution of Schrödinger equation for the molecular problem yields separate wave functions for the bonds, and correspondingly the ith bond wave function has the following form:

$$\Psi_i=N(e^{-c_i|x_i+a/2|}\pm e^{-c_i|x_i-a/2|}) \tag{4}$$

where

$$N=[(2/c_i)(1\pm e^{-c_i a})\pm a c_i e^{-c_i a}]^{-1/2},$$
$$c_i=(-2E_i)^{1/2} \ .$$

The δ-function branching conditions by Frost[38] can then be applied to obtain the following expression for the homonuclear case:

$$c_i=Ag(1\pm e^{-c_i a}) \ , \tag{5}$$

where the plus and minus signs correspond to the attractive and repulsive states, respectively. By combining the above equation with $A=(-2E_i)^{1/2}$, one may have the following relation:

$$\lim_{a\to\infty} c_i=Ag=(-2E_i)^{1/2}_{a=\infty} \ . \tag{6}$$

Following this, a resultant c written as c_R may be obtained as follows:

$$c_R=A(nN)^{1/2} \quad \text{for the homonuclear case,} \tag{7}$$
$$c_{R_{12}}=(c_{R_1}c_{R_2})^{1/2}=n_1 n_2 N_1 N_2 (A_1 A_2)^{1/2} \quad \text{for the heteronuclear case}\ , \tag{8}$$

where A, n, and N stand for the δ-function strength, principal quantum number, and the number of electrons making the contributions to the binding, respectively.

Two kinds of δ-function strengths were considered. The δ-function strength for a singly bonded atom differs from that of a multiple bonded atom due to the differences in the electron distributions. The δ-function strength for the sulfur atom in SO molecule is different from that of the same in SO_2 and SO_3 molecules, whereas the δ-function strength for the oxygen atom is considered to be the same for all these three molecules. The two kinds of δ-function strengths, in line with the earlier studies,[40] are as follows:

$$A=[x/(2.6n-1.7p-0.8D+3.0F]^{1/2} \ ,$$
$$(A^*)^2=A^2(n-3)/(n-1) \ , \tag{9}$$

where x is the electronegativity on the Pauling's scale[42]; n, the principal quantum number; p is 1 for an atom with p electrons in the valence shell; D, the total number of completed p and d shells in an atom; F, the total number of completed f shells in an atom; A, the δ-function strength for an atom in a bond of a diatomic molecule; and A^*, the δ-function strength for an atom in a bond of a polyatomic molecule.

On the basis of the variational treatment[43] first introduced by Hylleraas[22] and Hasse,[20] one may generate the polarizability component α_{xx} in the following form:

$$\alpha_{xx}=\frac{4nA}{a_0}\,[\langle(x_1-\langle x\rangle)^2\rangle - (n-1)\langle(x_1-\langle x\rangle)(x_2-\langle x\rangle)\rangle]^2 \ , \tag{10}$$

where x is the coordinate of any one of n equivalence class of electrons which falls in the first equivalence class; $\langle x\rangle$, the average coordinate of any one of these electrons; and a_0, the radius of the first Bohr orbit of the atomic hydrogen. If the δ-function potentials are symmetrically placed, all the bonding electrons are equivalent, and no electron correlation is allowed, the above equation can, then, be reduced to

$$\alpha_{xx}=\frac{4nA}{a_0}\,(\langle x_1^2\rangle)^2$$

or, equivalently,

$$\alpha_{xx}=\frac{4nA}{a_0}\,(\langle x_i^2\rangle)^2 \ . \tag{11}$$

If every atom is assumed to be perfectly isotropic, we will have the following:

$$\langle x^2\rangle=\langle y^2\rangle=\langle z^2\rangle=\tfrac{1}{3}\langle r^2\rangle \ . \tag{12}$$

If the δ-function potential model is located at the nucleus, we may have the following:

$$\Psi=Ne^{-Ar} , \tag{13}$$

where $N=A^{3/2}\Pi^{-1/2}$ on normalization. Thus we have

$$\langle r^2\rangle=\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty}\Psi r^2\Psi^* r^2\sin\theta\,d\theta\,d\phi\,dr=3/A^2 \tag{14}$$

and hence,

$$\langle x^2\rangle = 1/A^2 \ . \tag{15}$$

Solution of the Hamiltonian for the negative value of E yields to the following:

$$-\frac{1}{2}\,\frac{\delta^2\Psi}{\delta r^2} = -\tfrac{1}{2}A^2\Psi = E\Psi \ . \tag{16}$$

Hence, $A = (-2E_i)^{1/2}$ is the same δ-function strength of the atom obtainable from the first ionization potential or from the reduced electronegativities of the elements. Finally, the polarizability along the x axis of an atom is given as

$$\alpha_{xx} = 4/a_0^3A^3 \ . \tag{17}$$

This equation gives the polarizability component of an atom in any desired direction. Then, the atomic polarizability of any atom may easily be obtained from the polarizability components.

BOND POLARIZABILITIES

Considering a diatomic molecule which has an axis of symmetry, the mean molecular polarizability can be written as

$$\overline{\alpha}_M = \tfrac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}) \ , \tag{18}$$

where $\alpha_{\parallel}$ is the parallel component of the bond polarizability and $\alpha_{\perp}$, the bond perpendicular component of the polarizability. The bond parallel component is, in line with the earlier studies,[41] obtained from the contributions by the bonding and nonbonding electrons. The contribution to the parallel component of the polarizability by the bonding electrons is calculated by using a linear combination of atomic δ-function wave functions representing the two nuclei involved in the bond, i.e., the expectation value of the electronic position squared $\langle x^2\rangle$ along the bond axis is calculated, and this is used to obtain the parallel component of the bond polarizability $\alpha_{\parallel_b}$ from the following:

$$\alpha_{\parallel_b} = \frac{4nA}{a_0}\,(\langle x^2\rangle)^2 \ , \tag{19}$$

where n is the bond order and the other quantities are well known. The evaluation of the expectation value $\langle x^2\rangle$ for a one-electron homonuclear diatomic molecule using the δ-function wave functions is, in line with the earlier studies,[41] given as follows:

$$\langle x^2\rangle = \tfrac{1}{4}R^2 + 1/2c^2 \ . \tag{20}$$

If one considers a heteronuclear diatomic molecule, Eqs. (19) and (20) can be written as

$$\alpha_{\parallel_b} = (4nA_{12}/a_0)(\langle x^2\rangle)^2 \ , \tag{21}$$

$$\langle x^2\rangle = \tfrac{1}{4}R^2 + 1/2c_{R_{12}}^2 \ , \tag{22}$$

where R is the internuclear distance at the equilibrium configuration and the other quantities are well known. For a bond of heteronuclear type, the bond parallel component of the polarizability must be corrected to allow for a charge density not in the bonding region by virtue of the polarity induced by the electronegativity difference of the atoms. The degree of polarity ρ has been defined by Pauling[42] as

$$\rho = 1 - e^{-(x_1-x_2)^2/4} \ . \tag{23}$$

Hence, the charge density in the bond region should, then, be related to the percent covalent character believed to exist in the form as

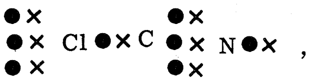
$$\sigma = e^{-(x_1-x_2)^2/4} \ , \tag{24}$$

where x_1 and x_2 are the electronegativities of the atoms 1 and 2, respectively, on the Pauling's scale.[42] When the correction factor, σ, the degree of covalency is introduced, we will have the bond parallel component of the polarizability in the form as

$$\alpha_{\parallel_p} = \sigma\alpha_{\parallel_b} \ , \tag{25}$$

where $\alpha_{\parallel_p}$ is the parallel component of the bond polarizability after making the polarity correction.

The contribution by the nonbonding electrons to the parallel component of the bond polarizability $\alpha_{\parallel_n}$ is calculated from the remaining electrons (in the valence shell of each atom) not involved in the bonding. The basis for such calculations is the Lewis-Langmuir octet rule[44, 45] modified by Linnett[46] in terms of a double quartet of electrons. As an example, the electronic configuration of chlorine cyanide in the ground state is given as



$$\begin{matrix}\bullet\times & & & & \bullet\times & & \\ \bullet\times & \mathrm{Cl} & \bullet\times & \mathrm{C} & \bullet\times & \mathrm{N} & \bullet\times \\ \bullet\times & & & & \bullet\times & & \end{matrix} \ ,$$

where the dots represent the electrons with spin quantum number $+\frac{1}{2}$ and the crosses the electrons with spin quantum number $-\frac{1}{2}$, or vice versa. Though six electrons of chlorine and two electrons of nitrogen are not involved in the bonding, there certainly must be a residual polarizability due to these electrons along the internuclear axis. Thus, the contribution by the nonbonding electrons to the parallel component of the bond polarizability $\alpha_{\parallel_n}$ can be written as

$$\alpha_{\parallel_n} = \tfrac{6}{7}\alpha_{\mathrm{Cl}} + \tfrac{2}{5}\,\alpha_N \ , \tag{26}$$

where α_{Cl} and α_N are the atomic polarizabilities of the chlorine and nitrogen atoms, respectively. This may analytically be expressed as

$$\sum \alpha_{\parallel_n} = \sum f_i\,\alpha_i \ , \tag{27}$$

where f_i is the fraction of the valence electrons in the ith atom not involved in the bonding and α_i the atomic polarizability of the ith atom obtainable from the δ-function strength A_i.

PERPENDICULAR COMPONENT OF POLARIZABILITY

The polarizability component perpendicular to the bond of a diatomic molecule is simply the sum of the two atomic polarizabilities. In a polar bond it would take on more of the character of the more electronegative element where more charge is located. If the electronic shape of an atom is assumed to be viewed from a point on a line perpendicular to the internuclear axis, and the behavior of the density on passing through the nucleus approximates that for the nonbonded atom, then this perpendicular component of the polarizability may be written as

$$\alpha_\perp = 2\alpha_A \quad \text{for a nonpolar } A_2 \text{ molecule,} \tag{28}$$

$$\alpha_\perp = \alpha_A + \alpha_B \quad \text{for a polar } AB \text{ molecule.} \tag{29}$$

If the atom A is less electronegative than the atom B, the average magnitude of the component perpendicular to the bond will be a function of the charge separation, and the atomic contributions will be considered according to the square of their respective electronegativities; accordingly, the analytical expression for the perpendicular component of the polarizability is written as

$$\alpha_\perp = 2(x_A^2 \alpha_A + x_B^2 \alpha_B)/(x_A^2 + x_B^2) \ . \tag{30}$$

For a polyatomic molecule A-B-C, the average molecular polarizability can be written as

$$\bar{\alpha}_M = \tfrac{1}{3}(\alpha_{\parallel_{AB}} + \alpha_{\parallel_{BC}} + \textstyle\sum 2\alpha_{\perp_i}) \ , \tag{31}$$

where the sum of the perpendicular components of the bond polarizability can be written as

$$\sum 2\alpha_{\perp_i} = \frac{3N - 2n_b}{N} \sum \alpha_i \ , \tag{32}$$

where N is the number of atoms in the molecule, n_b the number of bonds in the molecule, and α_i the atomic polarizability of the ith atom. Where bond electron density asymmetry is believed to exist, the perpendicular component will have a greater contribution from the atom which would tend to have the larger portion of electron density in its vicinity. On introducing the polarity correction, the analytical expression for the sum of the perpendicular components of the bond polarizability is given as

$$\sum 2\alpha_{\perp_i} = (3N - 2n_b)(\textstyle\sum x_i^2 \alpha_i / \sum x_i^2) \ , \tag{33}$$

where the factor $(3N - 2n_b)$ gives number of remaining (residual) atomic polarizability degrees of freedom n_{df}. This is directly obtained from a consideration of the symmetry or geometry of the molecular system and the assumption that every isolated atom is allowed to possess three degrees of polarizability freedom, and every bond which is formed between two atoms removes two of these degrees of freedom with the exception that if two bonds are formed from the same atom (carbon in carbon dioxide) and exist in a linear configuration, then only three atomic polarizability degrees of freedom are lost, and if three bonds are formed from the same atom (sulfur in sulfur trioxide) and exist in a planar configuration, then only five atomic polarizability degrees of freedom are lost. Thus, the analytical expression for the sum of the perpendicular components is given as follows:

$$\sum 2\alpha_{\perp_i} = n_{\text{df}}(\textstyle\sum x_i^2 \alpha_i / \sum x_i^2) \ , \tag{34}$$

where n_{df} is the number of residual atomic polarizability degrees of freedom. Schematic representations of the residual atomic polarizability degrees of freedom for a linear triatomic i-j-k molecule and a nonlinear triatomic i-j-k molecule are given in Figs. 3 and 4, respectively. The linear triatomic i-j-k molecule has six residual atomic polarizability degrees of freedom, while the nonlinear triatomic i-j-k molecule has five.

MOLECULAR POLARIZABILITY

The mean molecular polarizability can be obtained from the contributions of the parallel components and perpendicular components to the bond polarizability, and the contribution by the nonbonding electrons from the following expressions:

$$\bar{\alpha}_M = \tfrac{1}{3}[\textstyle\sum \sigma\alpha_{\parallel_{b_i}} + \sum f_i \alpha_i + n_{\text{df}}(\sum x_i^2 \alpha_i / \sum x_i^2)] \ , \tag{35}$$

$$\bar{\alpha}_M = \tfrac{1}{3}[\textstyle\sum \alpha_{\parallel_{p_i}} + \sum \alpha_{\parallel_n} + \sum 2\alpha_{\perp_i}] \ . \tag{36}$$

RESULTS

The two models of dimanganese iron tetradecacarbonyl and the values of the internuclear distances are given in Figs. 1 and 2, respectively. The δ-function strengths were calculated from Eqs. (8) and (9), and their values in atomic units for the oxygen, carbon, manganese, and iron atoms, are 1.00, 0.757, 0.367, and 0.402, respectively. The values of the parameter c were calculated by using Eq. (6), and their values in atomic units for

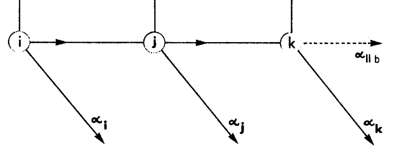


FIG. 3. Residual atomic polarizability degrees of freedom for a linear asymmetrical triatomic molecule.

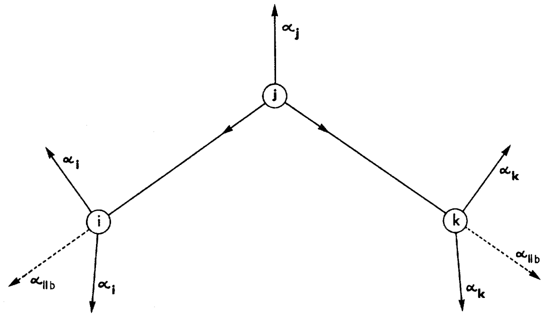


FIG. 4. Residual atomic polarizability degrees of freedom for a nonlinear asymmetrical triatomic molecule.

the oxygen, carbon, manganese, and iron atoms are 4.899, 3.028, 2.378, and 2.785, respectively. The polarizability components were calculated from Eq. (17) and they were used to obtain the atomic polarizabilities with the assumption of isotropic nature for all the atoms. Thus, the calculated values of atomic polarizabilities, in units of 10^{-25} cm^3, for the oxygen, carbon, manganese, and iron atoms are 5.92, 13.70, 120.26, and 91.50, respectively. This shows that the values of atomic polarizabilities for the nonmetals are, in contrast to their electronegativities, much smaller than those of the metals.

For the molecules 1 and 2 of dimanganese iron tetradecacarbonyl, the values of parallel and perpendicular components of the bond polarizability, contribution by the nonbonding electrons, and the average or mean molecular polarizability were obtained, and their values in units of 10^{-25} cm^3 are given in Table I. Both molecules conform to the symmetry of point group $2/m$, but with the symmetry elements differently disposed. In spite of the difference in orientation of symmetry elements, the similarity of the two molecules is striking. Though the environment of each metal atom is nearly octahedral, the equatorial carbonyl groups around each manganese atom are appreciably displaced toward the center of the molecule, resulting in an average Fe-Mn-C bond angle of 86.6°. This departure from 90° was attributed to repulsion between the apical and equatorial carbon atoms. The M-C-O angles range between 176.6° and 180°, averaging 179.1°. Hence, each oxygen atom has two residual atomic polarizability degrees of freedom, while each carbon atom has one. In other words, each oxygen atom loses one atomic polarizability degree of freedom, while each carbon atom loses two. The manganese and iron atoms lose three atomic polarizability degrees of freedom. Hence, the total number of atomic polarizability degrees of freedom lost for the entire molecule is 60. The total number of atomic polarizability degrees of freedom for the entire molecule is 93 (31×3). Thus, the number of residual (remaining) atomic polarizability degrees of freedom n_{df} is 33 for each molecule, and this value has been used to obtain the sum of the perpendicular components of the bond polarizability. Because of the striking similarity of the two molecules, the value of the sum of the perpendicular components of the bond polarizability $\sum 2\alpha_{\perp_i}$ is the same for both molecules.

Both molecules have the same electronic configuration. There is only one lone pair of electrons around the oxygen atom, while there are three lone pairs of electrons around the iron and manganese atoms. Thus, the value of the contribution by the nonbonding electrons to the parallel components of the bond polarizability $\sum \alpha_{\parallel_n}$ is the same for both molecules.

In spite of the striking similarity of the two molecular configurations and their electronic distributions, the two molecules slightly differ in their values of the sum of the parallel components of the bond polarizability, $\sum \alpha_{\parallel p_i}$; this is mainly due to the slight differences in their values of the internuclear distances. The values of the average or mean molecular polarizabilities, in units of 10^{-25} cm^3, for the molecules 1 and 2 of dimanganese iron tetradecacarbonyl are 495.0726 and 492.8782, respectively.

The parallel components as well as the perpendicular components of the bond polarizability were experimentally obtained by Denhigh,[47] and Vickery and Denhigh,[48] and their perpendicular components were qualitatively equal to the sum of the respective atomic polarizabilities calculated from the present investigation. As an example, the values of atomic polarizabilities, in units of 10^{-25} cm^3, derived from the experimental values of perpendicular components[47, 48] for the oxygen, nitrogen, and carbon atoms are 5.94, 7.24, and 10.22, respectively, while the δ-function potential model yields to 5.92, 7.43, and 9.78, respectively, for the same atoms. This shows that the values of atomic polar-

TABLE I. Polarizabilities of $Mn_2F(CO)_{14}$.

		Molecule 1			Molecule 2	
	Dist. (Å)	α (10^{-25} cm^3)		Dist. (Å)	α (10^{-25} cm^3)	
Bond		$\alpha_{\parallel b}$	$\alpha_{\parallel p}$		$\alpha_{\parallel b}$	$\alpha_{\parallel p}$
Fe-Mn	2.83	118.9038	116.5495	2.80	113.9922	111.7352
Fe-C	1.79	27.8849	24.7311	1.79	27.8849	24.7311
				1.81	29.1262	25.8320
Mn-C	1.80	27.4191	21.3539	1.81	28.0198	21.8218
	1.85	30.5191	23.7683	1.85	30.5191	23.7683
	1.86	31.1692	24.2746	1.86	31.1692	24.2746
C≡O	1.13	21.3205	16.6044	1.13	21.3205	16.6044
	1.15	22.8245	17.7757	1.14	22.0627	17.1824
	1.16	23.6062	18.3845	1.15	22.8245	17.7757
$\sum \alpha_{\parallel p_i}$		805.2672			798.6840	
$\sum \alpha_{\parallel n}$		302.4116			302.4116	
$\sum 2\alpha_{\perp i}$		377.5391			377.5391	
$\bar{\alpha}_M$		495.0726			492.8782	

izabilities obtainable from the δ-function potential model are in good agreement with those of the experimental ones. Since the molecular polarizability is composed from the bond polarizabilities, and since the bond polarizability is composed from the atomic polarizabilities which are obtainable from the δ-function potential model, the obtained values of the bond polarizabilities, perpendicular components of the polarizabilities, and mean molecular polarizabilities for both molecules of dimanganese iron tetradecacarbonyl (see Table I) are the reliable ones, and would be very useful in future for the interpretation of molecular structural data for other compounds having similar chemical bonds. Thus, the δ-function potential model is able to give the explicit expressions for the parallel and perpendicular components of the bond polarizability, contributions by the nonbonding electrons, and mean molecular polarizability. All these results are in line with the earlier investigations of Denhigh[47] in which the molar refraction of a molecule has been assumed to be the sum of the refractions of all the bonds in the molecule, and similarly, the molecular polarizability is assumed to be the sum of the bond polarizabilities. The contributions by the bond region electrons and the nonbonding electrons are clearly distinguished. The perpendicular component of the bond polarizability is a linear combination of atomic polarizabilities, and independent of the internuclear distance. The parallel components of the bond polarizabilities can easily be transferred from one molecular system to another having similar chemical bonds, irrespective of the molecular configurations of the two systems.

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