Identification of Localized Bonds in the Hydrocarbons

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From measured Compton profiles of CH_4, C_2H_4, and C_2H_6, experimental values are found for the Compton profiles of C-H, C-C, and C=C bonds. These profiles are then used successfully to predict within experimental accuracy the measured Compton profiles of C_3H_6, C_6H_6, C_6H_{12}, C_6H_{14}, and C_8H_{10}. This success is strong evidence that the identified C-H, C-C, and C=C bonds are indeed localized and transferrable.

We report here Compton x-ray scattering experiments which provide strong evidence for the existence of localized bonds in the hydrocarbons and which for the first time provide detailed microscopic information about the nature of the localized bonds. The existence of a set of bonding orbitals which is transferrable from one molecule to another would offer the hope of theoretically being able to calculate wave functions for large complex molecules while only having to calculate small simple ones. The search for such orbitals has consequently been the focal point of numerous investigations since Pauling[1] and Slater[2] introduced the concept. The additivity of the dipole moments in the hydrocarbons has for a long time strongly suggested the existence of localized bonding orbitals. In this work we use a simple model to decompose the valence electrons of some hydrocarbons into C-H, C-C, and C=C bond electrons. We determine the Compton profiles of those bond electrons by measuring the Compton profiles of CH_4, C_2H_4, and C_2H_6. The bond profiles are then used successfully to predict within experimental accuracy the measured Compton profiles of C_3H_6, C_6H_6, C_6H_{12}, C_6H_{14}, and C_8H_{10}. An analysis of the transferrable bond profiles yields some interesting observations about π bonding and provides an indication of the cause of the surprising success of a pure C-C and C=C bond description of the resonant benzene ring.

The Compton-scattering technique is well documented in the literature.[3-8] Previous work on H_2,[7] N_2, and O_2[8,9] has demonstrated the technique's ability to measure the effects of molecular binding. As previously described, the Waller-Hartree[10] theory of inelastic x-ray scattering when applied to weakly bound electrons is referred to as the impulse approximation.[5,11] The resultant cross section for the process is given as

$$\frac{d\sigma}{d\Omega\, d\omega} = \frac{d\sigma_{\mathrm{Th}}}{d\Omega}\frac{\omega_1}{\omega_2}\int \rho(\vec{p})\, d^3p\, \delta\left(\omega - \frac{k^2}{2m} - \frac{\vec{k}\cdot\vec{p}}{m}\right), \quad (1)$$

where $d\sigma_{\mathrm{Th}}/d\Omega$ is the Thomson cross section, ω_1 and ω_2 are the initial and final energies of the photon, $\omega = \omega_1 - \omega_2$ is the energy loss, and $\vec{k} = \vec{k}_1 - \vec{k}_2$ is the momentum transfer to the system, $\vec{k}_1$ and $\vec{k}_2$ being the initial and final photon momenta, respectively. The quantity $\rho(\vec{p})$ is the three-dimensional electron density distribution in momentum space. It appears in Eq. (1) because the impulse approximation permits a substitution of the original inelastic form factor of the Waller-Hartree theory by an expectation value involving only the momentum of the ground state of the system. For isotropic or spherically averaged systems, Eq. (1) can be written to take the form

$$\frac{d\sigma}{d\Omega\, d\omega} = \frac{d\sigma_{\mathrm{Th}}}{d\Omega}\frac{\omega_1}{\omega_2}\frac{m}{|k|}J(q), \qquad J(q) = \frac{1}{2}\sum_{i=1}^{N}\int_q^{\infty}\frac{I_i(p)}{p}\, dp, \quad (2)$$

where $J(q)$ is the Compton profile, $I_i(p)$ is the radial probability distribution in momentum space for the ith electron in an N-electron system, and q is the projection of the electron's momentum on the scattering vector $\vec{k}$ in atomic units. The expression [Eq. (2)] for $J(q)$ assumes an independent-particle model for the electronic system. An experimental valence Compton profile (VCP) is found by subtracting from the measured $J(q)$ for the molecule those orbital contributions which one identifies with the $1s$ carbon core electrons.[12,13] The usual approach is to study the variation of the intensity of scattering as a function of the energy of the scattered photon at a fixed angle of scattering. The characteristic radiation from an x-ray tube is used as the input beam. By use of Eqs. (1) and (2), the Compton profile $J(q)$ is found from the scattered intensity with the energy δ function in Eq. (1) providing the relationship between ω and q.

The experimental procedure used in this study is identical to that previously discussed.[7,8] In this study both silver and molybdenum radiations were used to study gaseous CH_4, C_2H_4, and C_2H_6

and liquid C_6H_{14}. Only molybdenum radiation was used to study gaseous C_3H_6 and liquid C_6H_6, C_6H_{12}, and C_8H_{10}. When both radiations were used, the results for the Compton profile agreed within experimental error. In that case, the average results were used in the analysis. Experimental investigations on thick liquid samples revealed the presence of a 2–5% distortion in the Compton profile due to multiple scattering. To eliminate the effects of multiple scattering only thin liquid samples were studied. Previous measurements of Compton profiles of some hydrocarbons[14] appear to have been made on thick samples.

To a chemistry novice the simplest way of decomposing the valence electrons in the hydrocarbons is to assign them to bonds associated with the schematic classical pictures used in chemical designations of the hydrocarbons found in any elementary chemistry book. For the molecules studied here (no triple bonds), the building blocks required to construct the hydrocarbons are C-H, C-C, and C=C bonds. This simple approach is used here.

We regard that there are two electrons in a C-H bond, two in a C-C bond, and four in a C=C bond. On basis of the simple model, one can write down immediately the linear combinations of the bond Compton profiles which at each value of q should give the measured value of the VCP for the systems studied if the profiles are additive. The combinations are

$$J(q)_{\mathrm{CH_4}} = 8J(q)_{\mathrm{C\text{-}H}}, \tag{3}$$

$$J(q)_{\mathrm{C_2H_4}} = 8J(q)_{\mathrm{C\text{-}H}} + 4J(q)_{\mathrm{C=C}}, \tag{4}$$

$$J(q)_{\mathrm{C_2H_6}} = 12J(q)_{\mathrm{C\text{-}H}} + 2J(q)_{\mathrm{C\text{-}C}}, \tag{5}$$

$$J(q)_{\mathrm{C_3H_6}} = 12J(q)_{\mathrm{C\text{-}H}} + 4J(q)_{\mathrm{C=C}} + 2J(q)_{\mathrm{C\text{-}C}}, \tag{6}$$

$$J(q)_{\mathrm{C_6H_6}} = 12J(q)_{\mathrm{C\text{-}H}} + 12J(q)_{\mathrm{C=C}} + 6J(q)_{\mathrm{C\text{-}C}}, \tag{7}$$

$$J(q)_{\mathrm{C_6H_{12}}} = 24J(q)_{\mathrm{C\text{-}H}} + 12J(q)_{\mathrm{C\text{-}C}}, \tag{8}$$

$$J(q)_{\mathrm{C_6H_{14}}} = 28J(q)_{\mathrm{C\text{-}H}} + 10J(q)_{\mathrm{C\text{-}C}}, \tag{9}$$

$$J(q)_{\mathrm{C_8H_{10}}} = 20J(q)_{\mathrm{C\text{-}H}} + 12J(q)_{\mathrm{C=C}} + 10J(q)_{\mathrm{C\text{-}C}}, \tag{10}$$

where we have normalized the bond profiles to 1. Therefore, the numbers in Eqs. (3)–(10) correspond to the numbers of electrons in given bonds.

We initially used our experimental results for CH_4, C_2H_4, and C_2H_6 together with Eqs. (3)–(5) to determine the values of $J(q)_{\mathrm{C\text{-}H}}$, $J(q)_{\mathrm{C\text{-}C}}$, and $J(q)_{\mathrm{C=C}}$. Using those values we found we could predict our experimental results within experimental error for the other five molecules by use of Eqs. (6)–(10). Having established a strong indication of Compton profile additivity and bond transferability, we then determined the optimum values for $J(q)_{\mathrm{C\text{-}H}}$, $J(q)_{\mathrm{C\text{-}C}}$, and $J(q)_{\mathrm{C=C}}$ by making a least-squares fit to our data for all eight molecules using Eqs. (3)–(10). The results are given in Table I, columns 1–3. This latter approach should give greater accuracy. The average of the absolute magnitudes of the percentage deviation of the fit from the experiments for all eight molecules is given in the last column in Table I. Since the experimental error for each molecule at $q = 0$ was about ± 1% and at $q = 2$ was about ± 5%, the agreement is within experimental accuracy. This provides strong proof for the additivity of the Compton profiles and, consequently, for the localized nature of the bonding orbitals.

To obtain the experimental value for a Compton profile for one of the molecules measured, one need only use Eqs. (3)–(10) together with Table I which will give the VCP and then add on the contributions from the carbon 1s electrons[12, 13] present in that molecule. Thus, for example, the VCP for C_8H_{10} at $q = 0.4$ is $20(0.4838) + 12(0.4443) + 10(0.4002)$ or 19.060, while the profile for the whole molecule including the 1s core at $q = 0.4$ would be 23.882. We feel that the same procedure can be used to predict Compton profiles of as yet unmeasured molecules.

The C_6H_6 and C_8H_{10} molecules deserve special comment. It is known that because of the resonant nature of the benzene ring, the bonds are neither C-C nor C=C. This is clearly shown by x-ray data which find a 1.54-Å separation of the carbons in a C-C bond, a 1.34-Å separation in a C=C bond, but a 1.40-Å separation for all the carbons in the benzene ring. The view of the benzene ring used in our analysis is therefore certainly incorrect in that one cannot identify a particular site with a particular bond. But in a temporal and spatial average prediction of a property of the benzene ring, the view of benzene used in this work may not be incorrect.

It is known that there is a relationship between the amount of π bonding, bond order, and bond length.[15] From the definition of $J(q)$ given in Eq. (2), it is easily seen that $J(0)$ is the average value of $1/p$. Therefore, $J(0)$ should be proportional to the bond size. In Fig. 1, we have plotted the $J(0)$ for the C-C bond in ethane (bond order 0) and C=C bond in ethylene (bond order 1) against bond order and bond length. We then use our measured results for the benzene VCP, subtract the

TABLE I. The first three columns contain the C-H, C-C, and C=C Compton profiles found by fitting the experimental data for the eight molecules studied at each q by least squares using Eqs. (3)-(10). The last column contains the average error (absolute magnitude) for the eight molecules between the experimental results and the fit.

q	$J(q)_{C-H}$	$J(q)_{C=C}$	$J(q)_{C-C}$	Average Error(%)
.0	.585	.516	.412	.43
.1	.578	.510	.410	.40
.2	.558	.498	.410	.38
.3	.525	.475	.408	.34
.4	.484	.444	.400	.38
.5	.434	.408	.391	.48
.6	.380	.368	.374	.57
.7	.325	.326	.352	.64
.8	.271	.284	.324	.71
.9	.221	.243	.291	.73
1.0	.176	.205	.255	.79
1.2	.106	.134	.181	1.17
1.4	.064	.087	.112	1.97
1.6	.042	.057	.063	2.59
1.8	.031	.041	.034	2.69
2.0	.022	.030	.024	3.46

contribution of the C-H bonds, and then divide by 18. This gives us a $J(0)$ for benzene in which all the carbon-carbon bonds are considered to be identical. We include in Fig. 1 the results for benzene (bond order 0.667) and note that it lies on the straight line connecting the results for C-C and C=C bonds. Thus, the successful prediction of the Compton profile of the carbon-carbon bond of benzene on the basis of ethane and ethylene results can be attributed to the relationship which exists in the hydrocarbons between the phenomena of resonance, bond order, bond length, and the Compton profile.

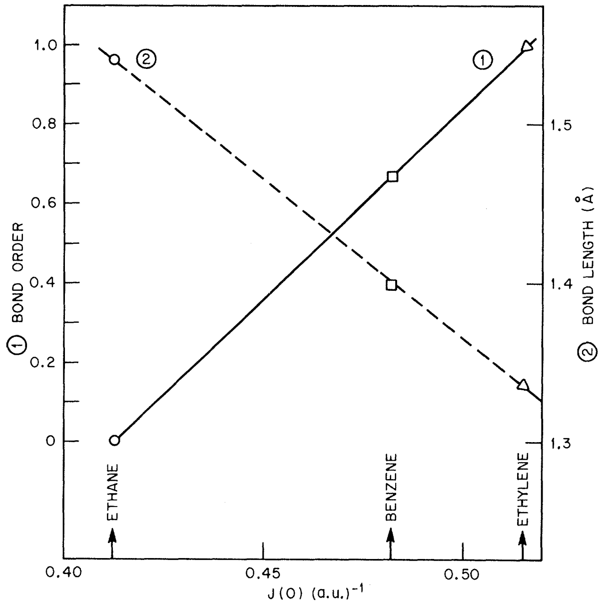

FIG. 1. The experimental values for $J(0)$ for the carbon-carbon bonds in ethane, ethlyene, and benzene are plotted against bond order (1) and bond length (2).

The effect of π bonding on delocalizing the bond is dramatically illustrated by Table I and Fig. 1. In spite of the bond length getting smaller in going from a C-C to C=C bond, $J(0)$ is getting larger. This means the delocalization in the plane perpendicular to the bond direction due to π bonding more than compensates for the increased localization occurring in the σ part of the bond due to the contraction of the bond length. If one assumed that $J(0)$ for the σ part of the bond scaled as the bond length, one would find

$$J(0)_{(C=C)_\sigma} = \frac{1.34}{1.54} J(0)_{(C=C)_\sigma}. \tag{11}$$

If in addition one assumed that one could separate the σ and π parts of the double bond,

$$2J(0)_{(C=C)} = J(0)_{(C=C)_\sigma} + J(0)_{(C=C)_\pi}, \tag{12}$$

one would find using Table I that $J(0)_{(C=C)_\sigma} = 0.358$ and $J(0)_{(C=C)_\pi} = 0.674$. These results can be contrasted with what one would obtain on the basis of an atomic model for the the double bond. The sp^2 hybrid σ orbital is usually considered to be composed of $\frac{1}{3}$ atomic carbon $2s$ and $\frac{2}{3}$ carbon $2p$ charge density while the π orbital is pure atomic carbon $2p$ in character. Using the pure atomic forms of those orbitals, one finds[13] that $J(0)_{(C=C)_\sigma} = 0.59$ and $J(0)_{(C=C)_\pi} = 0.48$. Note that not only are the atomic and deduced molecular values quantitatively different, but their relative σ-π magnitude has also changed. These contrasts dramatically illustrate the large effects of bonding and the large delocalization of the π bonds in the hydrocarbons [i.e., the large value deduced for $J(0)_{(C=C)_\pi}$]. The large effect of binding is also illustrated by the approximately 30% difference in the value for $J(0)$ found for the molecules and that predicted by atomic theory [i.e., for atomic C_2H_6, $J(0) \cong 12.2$ compared with the measured value for molecular C_2H_6 of 7.8].

There is a large body of theoretical work[16-19] which has attempted to identify localized and transferable bonds in the hydrocarbons. There has, in fact, been some strong theoretical evidence for transferrability of C-H bonds in the hydrocarbons.[20, 21] It is suggested that some attempt be made to compare the theoretical constructs with the experimentally measured VCP for C-C, C=C, and C-H bonds. For even though we have emphasized qualitatively here some interesting points based on the pattern of the values for $J(0)$, it should not be forgotten that there is an equivalent amount of quantitative information throughout the Compton profile.

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Second-Quantization Representation for Systems of Atoms, Nuclei, and Electrons*

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A many-atom representation has been derived in which bound atoms or molecules are described by elementary Bose or Fermi operators, the field operators for nuclei and electrons referring only to unbound particles. The Hamiltonian thus obtained contains not only nucleus-nucleus, electron-electron, and nucleus-electron Coulomb interactions, but also atom-atom, atom-nucleus, and atom-electron Coulomb and exchange interactions, including breakup and recombination terms.

There are many problems involving systems of composite particles in which their internal degrees of freedom cannot validly be ignored. Examples are high-temperature gases and partially ionized plasmas, molecular gases, and chemical and nuclear reactions. In these and other problems, a representation in which the existence of the composite particles is treated kinematically, through use of appropriate composite-particle dynamical variables, is desirable. One such representation, in which dynamical variables of the constituents are completely eliminated in favor of those of *both bound and continuum* states of the composite particles, has been described previously.[1] However, such a representation is difficult to apply in practice because of the nonlocality and complicated structure of the atomic continuum states. A different representation, in which the atomic annihilation and creation operators refer only to *bound* atoms and the continuum states are described by *free*-nucleus and *free*-electron field operators, has been developed recently by Stolt and Brittin,[2] and a related but apparently distinct representation has been obtained by Sakakura.[3] A similar representation can be constructed[4] by a se-