

# Volume-rendering representations of *ab initio* electron densities

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*Many molecular properties are three-dimensional scalar fields, making the representation of their values throughout the molecular volume a four-dimensional problem. Volume rendering offers a means of graphically displaying the value of a property throughout a volume. In this paper we present the result of an interface of the *ab initio* electronic structure program, GAUSSIAN 85, and the interactive volume-rendering program, VOXEL-VIEW PLUS, and its initial application: the representation of electron densities for acetylene and difluoroacetylene, and transition structures for the corresponding vinylidene isomerizations.*

**Keywords:** volume rendering, electron density, difluoroacetylene

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## INTRODUCTION

The need to portray the results of electronic structure calculations in a manner quickly and easily comprehended by chemical researchers is greater today than it has ever been. Advances in computer hardware allow more extensive calculations for more complicated molecules. New electronic structure software runs faster, allowing treatment of larger systems, and is more user friendly, allowing laboratory chemists to perform meaningful calculations. Large quantities of electronic structure data are generated by researchers who have little time to spend pouring through pages of numbers.

Many molecular properties can be defined at any point in the molecular volume. They are functions of three variables, and require four dimensions for a complete graphical representation. Examples include electron densities, the Laplacian and gradient magnitudes of electron densities, electrostatic potentials, and molecular orbitals.

Previous work has focused on reducing the dimensionality of the graphical representation from four to three. A traditional approach is to represent the value of the function in a plane or slice through the molecule via contour plots or distorted nets.<sup>1</sup> This works well for small molecules, or those of high symmetry, but for unsymmetric polyatomic mole-

cules, many slices are needed to visualize the function. Dimensionality reduction has also been accomplished by limiting the representation to surfaces defined by constant density,<sup>2</sup> potential, or atomic Van der Waals radii,<sup>3</sup> with color used to show the value of the function on that surface.<sup>4</sup> This gives visually stimulating images, but the approach fails to show diffuse or tightly bonded electrons that may be of interest in a chemical system.

Volume rendering is a graphics approach to displaying the value of a function at each point in a three-dimensional space,<sup>5,6</sup> that is, a method of conveying to the viewer a four-dimensional image. Volume rendering has become important in medical imaging,<sup>5,6</sup> but applications to chemistry have been few.<sup>5-7</sup> In this report we explore the use of one volume-rendering technique to the presentation of electron densities in molecules of chemical interest.

## METHODS

Because considerable progress has been made in the graphics display of volume data by those interested in applications to medical imaging, we have chosen to use an existing package for the graphics display and to interface it with an *ab initio* electronic structure program. We have interfaced VoxelView/PLUS from Vital Images<sup>8</sup> and GAUSSIAN 85,<sup>9</sup> with both packages running on a Silicon Graphics 40120 GTX work station.

In VoxelView/PLUS, the volume is divided into volume elements (voxels), and each is assigned a value, representing the function, from 0 to 255 that can be used for both opacity and color information, with function values increasing from violet to red. Planes of voxels are superimposed to create a representation of the data volume. An advantage of our system is that VoxelView/PLUS is a fast, interactive program with a good user interface. Color and opacity assignments are easily modified to produce the most informative image without the need to repeat the electronic structure calculation.

GAUSSIAN 85 is a version from the GAUSSIAN series of *ab initio* electronic structure programs that has been implemented on our Silicon Graphics workstation. All of our calculations were done at the closed-shell RHF level with a 6-31G\* basis set. The molecular geometries were optimized with this basis (for the reactants/products), or were taken from the literature<sup>10-11</sup> (for the transition states). The orbitals, molecular geometry, and basis set information were saved in binary files at the conclusion of each calculation.

The interface program uses the output from GAUSSIAN

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Color Plates for this article are on page 44.

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85 to calculate a density matrix, and then the electron density on a coarse grid of points ( $33 \times 33 \times 33$ ) covering the volume of the molecule. The electron density is interpolated to a finer grid ( $128 \times 128 \times 128$ ) for use in forming the image. The function values are converted to a range of 0–255 to form a series of two-dimensional byte files that represent voxel values. VoxelView/PLUS then combines these to generate the four-dimensional image. Although volume images are emphasized here, slices and contour plots are also easily generated with this system.

## RESULTS

The chemical systems that we are studying are vinylidene and its difluoro analog and their isomerizations to acetylene and difluoroacetylene, respectively (Figure 1). These systems have been the subject of numerous theoretical studies,<sup>10,11</sup> and are highly symmetrical systems that should be good for an initial evaluation of a new means of representing theoretical chemistry data. Electronic structure calculations have indicated that the potential energy barrier for rearrangement of difluorovinylidene is much greater than that for vinylidene,<sup>10,11</sup> which could account for the fact that the matrix isolation of difluoroacetylene has only been accomplished very recently,<sup>12</sup> while difluorovinylidene has been formed in the gas phase for much longer.<sup>13</sup>

Color Plates 1A and 1B are views from a direction perpendicular to the plane of the molecule (top views) of the electron density in the transition states for the isomerization of vinylidene and difluorovinylidene to acetylene and difluoroacetylene, respectively. Comparison of the two structures shows that there is a much larger overlap of electron density between the migrating species and the lone pair carbon atom (as well as with the rest of the structure) in the acetylene transition state. This is an indication of the initial stages of bond formation, and is consistent with the much smaller energy barrier in the vinylidene system and its comparatively easy rearrangement to acetylene. This conclusion is consistent with the overlap populations between the migrating species and the lone pair carbon atom (Table 1).

Color Plates 1C and 1D show oblique views of the acetylene and difluoroacetylene electron densities, respectively. The main feature obvious from a comparison of the shape and the color of the two representations is a concentration of electron density around the fluorine cores and the formation of polar bonds between them and the carbon atoms.

To examine the  $\sigma$  withdrawing effect of the fluorine

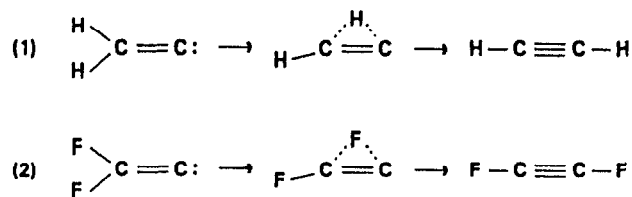


Figure 1. Interconversion of vinylidene to acetylene (1) and difluorovinylidene to difluoroacetylene (2). Transition states are shown above arrows.

substituents, we used one of the interactive features of VoxelView/PLUS to highlight the volumes corresponding to the carbon cores and the intercarbon bonding region. We removed voxels corresponding to the intermediate electron density values given in Color Plate 1. The cut-off values were determined from the upper limit that resulted in the appearance in the image of continuous density in the  $\sigma$  bonding region for each difluoro structure.

Top views of the acetylene and difluoroacetylene equilibrium structures are shown in Color Plates 1E and 1F. The carbon cores have the highest values for the electron density and appear red, while the intercarbon region is a pale-orange that appears almost grey in the reproductions (Color Plates 1E and 1F). Comparison of the pale-orange volumes shows that there is more electron density between the carbons in acetylene than in difluoroacetylene. This is consistent with acetylene having a stronger  $\text{C}\equiv\text{C}$  bond and being a more stable molecule.<sup>14</sup> The increased density is in the region normally associated with  $\sigma$  bond formation, and correlates with qualitative molecular orbital arguments that indicate F would destabilize the  $\text{C}\equiv\text{C}$  bond by  $\sigma$  electron density withdrawal.<sup>15</sup> This also agrees with the overlap populations (Table 2).

Distortions of a molecule from its equilibrium geometry lead to increases in energy that can be related to electron density changes. These changes can be seen in our graphics representations. Electron densities were calculated and displayed for acetylene and difluoroacetylene with slightly shortened ( $-0.125 \text{ \AA}$ ) or elongated ( $+0.125 \text{ \AA}$ )  $\text{C}\equiv\text{C}$  bonds. Larger deformations were avoided because we are using SCF wave functions and the importance of configuration interaction rapidly grows with larger changes in bond length.<sup>16</sup>

When the bond is compressed (Color Plates 1G and 1H), the shift to red of the  $\sigma$  bonding region in both figures

Table 1. Energies and overlap populations of migrating species with lone-pair carbon atom for vinylidene-acetylene isomerizations: X is the migrating species, and C is the carbon atom corresponding to vinylidene's lone-pair carbon

Structure	Energy (au)	Total C-X overlap (au)
Vinylidene	-76.76339512	-0.0085
Difluorovinylidene	-274.42678695	-0.0285
Transition state (TS)	-76.73717202	0.2194
Difluoro TS	-274.34849244	0.0236
Acetylene	-76.81782648	0.3491
Difluoroacetylene	-274.45906466	0.3227

**Table 2. Energies and overlap populations for acetylene and difluoroacetylene structures\***

Formula	$R_{cc}$	Energy	Total C $\equiv$ C Overlap	$\sigma$ Overlap	$\pi$ Overlap
C <sub>2</sub> H <sub>2</sub>	2.004	-76.77123183	1.2145	0.6209	0.5954
C <sub>2</sub> H <sub>2</sub>	2.240	-76.81782648	1.1193	0.5646	0.5534
C <sub>2</sub> H <sub>2</sub>	2.476	-76.78826737	1.0219	0.5084	0.5108
C <sub>2</sub> F <sub>2</sub>	1.965	-274.40830990	0.6773	0.0766	0.5750
C <sub>2</sub> F <sub>2</sub>	2.202	-274.45906466	0.7862	0.2281	0.5396
C <sub>2</sub> F <sub>2</sub>	2.438	-274.42669749	0.8068	0.2860	0.5020

\* All quantities are in atomic units.

indicates that higher amounts of density are displayed. Comparison of the two representations shows that the electron density is still greater in the acetylene structure. Comparison of the compressed and equilibrium difluoro structures (Color Plates 1F and 1H) indicates a reduction of electron density around the carbon centers with the decrease in the carbon-carbon distance. A similar comparison of the acetylene structures (Color Plates 1E and 1G) shows that electron density has been displaced from the  $\sigma$  bonding region to elongated core regions around the carbon nuclei, which is consistent with the compressed structure being a less stable nonequilibrium structure. The fuzziness of the image (see below) indicates an increased electron density in the outer portions of the electron cloud associated with  $\pi$  bonding.

The same conclusions can generally be inferred from the population analysis (Table 2), except for the comparison of the  $\sigma$  contributions between the equilibrium and compressed acetylene structures. An examination of the overlap population leads to the erroneous conclusion that the  $\sigma$  contribution to the bonding increases between the carbons as the bond is compressed.

When the bond is stretched by 0.125 Å (Color Plates 1I and 1J) a comparison of the representations shows the electron density in the  $\sigma$  bonding region decreases at each point for both structures, as indicated by the shift to a blue-green color, but the difference in their volumes becomes less. The overlap populations show a decrease in both the  $\sigma$  and total shared electron density for the acetylene, but an increase in both for the difluoro structure. The net result is that both our representations and the overlap populations predict the bonding regions become more similar, which is consistent with accepted arguments of  $\sigma$  effects being less significant with increasing distance from the withdrawing species.

## DISCUSSION

Our interface of the interactive volume rendering graphics program VoxelView/PLUS to the *ab initio* electronic structure package GAUSSIAN 85 provides a system that allows the user to quickly examine different views of the volume distribution of a calculated one-electron property, and to highlight regions of interest. By using these features to examine a highly studied chemical system, we have shown that information can be quickly and easily displayed that would be difficult and time consuming to obtain by conventional means. Information obtained visually from the graph-

ics display of electron density is consistent with other, more traditional, measures of chemical bonding. There are indications that in some cases, inferences made from the images are more reliable than those made from population analysis. Features, from the obvious polarity of the C-F bonds, to the subtle changes due to small distortions from equilibrium geometry, are clearly seen in the images. Problems with the technique include the blurring of images and mixing of colors that occurs when layers are superimposed, making comparisons particularly difficult between structures with different densities in their outer layers (Color Plates 1E and 1G). Future work will include further technique refinement to try to reduce these problems, and the initiation of additional studies on this and other chemical systems.

## ACKNOWLEDGEMENTS

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