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# Red- versus Blue-Shifting Hydrogen Bonds: Are There Fundamental Distinctions?

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The OH covalent bond of conventional hydrogen bonds of the OH...O type undergoes a lengthening as a result of the complex formation, and the OH stretching frequency shifts to the red; the same is true of many CH...O H-bonds. However, a subset of CH...O H-bonds behave in an opposite fashion, with the CH bond contracting, and its stretching frequency shifting to the blue. Ab initio calculations are performed to determine whether the two contrasting behaviors can be traced to different patterns of electron density shifts within the complex or they are associated with very different geometrical perturbations within the proton donor molecule. The calculations reveal that the density shifts of red- and blue-shifting H-bonds are very much alike, as are the covalent bond length changes that occur within the donor molecule. It is concluded that there are no fundamental distinctions between the two sorts of H-bonds.

## Introduction

Some very early suggestions<sup>1–5</sup> that the CH group, like OH and NH, could act as a proton donor in a hydrogen bond were largely dismissed for some time, mainly due to lack of conclusive evidence. Modernization of the capabilities of experimental and theoretical methods has resuscitated the concept and indeed brought it to the point of widespread acceptance.<sup>6–13</sup> The importance of these CH...O hydrogen bonds extends into the realm of biomolecules such as proteins and nucleic acids where there is evidence they are at least partly responsible for macromolecular structure.<sup>14–19</sup>

While there is no question that the CH proton donor and various acceptor groups approach one another in such a way as to mimic the geometrical attributes of conventional (OH...O) hydrogen bonds, there has been some discussion concerning whether these CH...O interactions may be fairly characterized as true H-bonds. Comprehensive ab initio calculations have confirmed that these interactions not only are attractive but also can be comparable in binding energy to conventional H-bonds.<sup>20–27</sup> There has also been a spate of evidence that other aspects of the interaction, e.g., sensitivity of the interaction energy to geometric distortions, topology of the electron density, changes in atomic charges, and various spectroscopic features, fit the classic fingerprint of a standard H-bond.<sup>25,28–38</sup>

There remains a particular subset of such CH...O bonds, however, where one aspect of the interaction is curiously opposite to what is observed in conventional H-bonds. In a number of cases where the proton donor is sp<sup>3</sup>-hybridized (e.g., CF<sub>3</sub>H, acetone), its interaction with a proton acceptor leads to the shortening of the bridging C–H bond, not the lengthening that is generally considered a typical feature of H-bonds.<sup>39–43</sup> Associated with this uncharacteristic bond shortening is the shift to the blue of this bond's stretching frequency, relative to its properties as an isolated molecule.<sup>38,44–46</sup> This blue shift is opposite to the normally expected red shift. Some have interpreted this unusual "improper blue-shifting" behavior as a symptom of a system that is really quite distinct from other H-bonds,<sup>23,47–49</sup> while others have argued that this one anomaly

is not sufficient for such a categorization as it does not in and of itself outweigh the many other features that the red- and blue-shifting sorts of H-bonds have in common.<sup>32,33,36–38,50</sup>

Recent discussion of this problem has centered upon the contention<sup>23,51,52</sup> that the uniqueness of the blue-shifting CH...O bonds rests first upon the idea that geometry changes occurring within the proton donor molecule as a result of the interaction are much smaller in the vicinity of the C–H bond than in more distant parts of the molecule. For example, when CF<sub>3</sub>H forms a complex, the C–F bond lengths are changed more than is the bridging C–H bond. These authors go on to attribute these large C–F bond changes to electron density that accumulates on the F atoms as a result of the interaction. They contrast this behavior to red-shifting H-bonds where the bulk of the electron density is shifted instead to the C–H bond region. In particular, it is claimed that it is this latter excess density in the σ\* antibond that leads to the stretching of the C–H (or O–H) bond in red-shifting H-bonds, a buildup that does not occur when the shift is to the blue.

The purpose of the present communication is to examine the latter discussion in some detail, so as to conclusively address the fundamental nature of blue-shifting H-bonds. For this purpose, a set of molecular systems are considered, some blue-shifting, some red-shifting, and others hardly shifted at all, that are as like one another as possible in all other respects. The calculations are carried out at a high level of theory, including electron correlation, to be sure that the small changes are meaningful. The first question addressed is whether the geometry changes occurring within the proton donor molecule in blue-shifting systems are in fact fundamentally different from those observed in the red-shifting cases. Electron density shifts are then monitored in both sorts of systems, searching in particular for any truly different behavior in the two cases.

## Methods

Ab initio calculations were carried out using the GAUSSIAN-98 set of codes, using the 6-31+G\*\* basis set.<sup>53</sup> Electron correlation was included via the second-order Møller-Plesset (MP2) treatment.<sup>54,55</sup> Electron densities and their shifts were displayed using the MOLDEN program. A number of different

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**TABLE 1: Changes in Bond Lengths (mÅ) and CH<sub>b</sub> Stretching Frequency (cm<sup>-1</sup>) of Various Proton Donors Caused by Complexation with Water<sup>a</sup>**

	$\Delta r(\text{C}_1\text{--H}_b)$	$\Delta \nu(\text{CH}_b)$	$\Delta r(\text{C}_1\text{--C}_2)$	$\Delta r(\text{C}_1\text{--X})$		$\Delta r(\text{C}_2\text{--X})$	
				X = H	X = F	X = H	X = F
HC≡CH	4.6	-40	1.1			-0.1	
FC≡CH	5.3	-75	1.2				3.5
H <sub>2</sub> C=CH <sub>2</sub>	-0.3	0	1.0	1.1		0.5, 0.4 <sup>b</sup>	
H <sub>2</sub> C=CFH	0.0	+10	1.1		4.6	0.3, 0.1 <sup>b</sup>	
FHC=CH <sub>2</sub>	0.7	-4	-0.3	0.9		0.1	4.4
F <sub>2</sub> C=CH <sub>2</sub>	1.7	-12	-0.8	0.8			4.4, 2.1 <sup>b</sup>
F <sub>2</sub> C=CFH	1.7	-17	-0.4		4.6		3.3, 2.8 <sup>b</sup>
H <sub>3</sub> C-CH <sub>3</sub>	-1.2	+10	0.4	0.9		0.6	
H <sub>3</sub> C-CFH <sub>2</sub>	-2.7	+42	0.0	0.4	6.8	0.5, 0.1 <sup>c</sup>	
H <sub>3</sub> C-CF <sub>2</sub> H	-3.0	+58	0.1		5.3	0.4, 0.0 <sup>c</sup>	
FH <sub>2</sub> C-CH <sub>3</sub>	-0.8	+10	-1.6	0.8		0.1	3.9
H <sub>3</sub> CH	-0.4	+10		0.8			
FH <sub>2</sub> CH	-1.4	+22		0.8	4.4		
F <sub>2</sub> HCH	-2.4	+26		0.4	5.0		
F <sub>3</sub> CH	-1.6	+42			4.0		

<sup>a</sup> C<sub>1</sub> refers to C atom bonded to bridging hydrogen H<sub>b</sub>; C<sub>2</sub>, to other C. <sup>b</sup> Cis to C-H<sub>b</sub>. <sup>c</sup> Syn to C-H<sub>b</sub>.

proton donor molecules, including sp, sp<sup>2</sup>, and sp<sup>3</sup>-hybridized carbons, were paired with water as proton acceptor, and the geometries were optimized. In all cases, the C-H...O atoms were restricted to collinearity.

### Geometry Changes

A principal hypothesis of those who subscribe to the fundamentally distinct properties of the blue-shifting H-bond concerns specifically the geometry changes. Their argument goes along the lines that the bond lengths of the proton donor that are not involved directly in the CH...O interaction, i.e., bonds other than CH<sub>b</sub> (where H<sub>b</sub> refers to the bridging hydrogen) are more strongly affected when the CH<sub>b</sub> bond is compressed (blue shift) than when it is stretched. The validity of this contention can be directly assessed by examination of the data in Table 1, which reports the changes in bond lengths of a number of proton donors caused by complexation with water. In terms of nomenclature, the bridging proton H<sub>b</sub> is bonded to C<sub>1</sub>, and C<sub>2</sub> represents the more remote carbon.

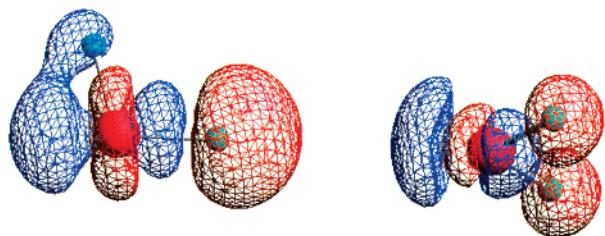
The alkynes, listed in the uppermost section of data, can be seen by the first column to undergo stretches of the CH<sub>b</sub> bond, on the order of 5 mÅ, placing them in the red-shifting class, as is affirmed by the negative values of  $\Delta \nu(\text{CH}_b)$  listed in the second column. The next column indicates that the C≡C bond is stretched by a small amount (1 mÅ). The rightmost two entries refer to the remote C-X bond. In the case of HCCH, this C-H bond is scarcely affected, but the C-F bond of FCCH is stretched by 3.5 mÅ.

The CH<sub>b</sub> bonds of the alkenes, in the next section of Table 1, undergo smaller changes in length. Ethylene is associated with a very small contraction; there is no change seen in H<sub>2</sub>C=CFH, whereas the other fluorosubstituted alkenes undergo a small bond elongation. There appears to be an inverse relationship between these CH<sub>b</sub> bonds and the C=C bonds in that the latter appear to contract when the former stretches, and vice versa. In any case, these C=C bonds change by only a small amount, 1 mÅ or less. Changes of the same order occur in the C<sub>1</sub>H bonds, but it is important to note that these bonds stretch in all cases, regardless of whether CH<sub>b</sub> stretches or shortens. This bond elongation is magnified to nearly 5 mÅ when it is a F bonded to C<sub>1</sub> and not H. Considering next the more remote bonds involving C<sub>2</sub>, all are stretched. Continuing the earlier pattern involving C<sub>1</sub>, the C<sub>2</sub>F bonds are stretched by more than C<sub>2</sub>H. There is some diminution in the effects upon moving from

C<sub>1</sub>H to C<sub>2</sub>H, but some of the C<sub>2</sub>F bonds are stretched nearly as much as are the C<sub>1</sub>F bonds.

Turning finally to the sp<sup>3</sup>-hybridized alkanes in the lowermost section of Table 1, one sees first the contractions of the CH<sub>b</sub> bonds that are typical of this class of "blue-shifting" proton donors. The magnitude of this contraction is enhanced by the presence of F atoms, particularly those bonded to C<sub>1</sub>. The effects of the H-bond upon the C-C bond length are variable, and fairly small in most cases. Just as was observed for the alkenes, C<sub>1</sub>H bonds are stretched by a small amount and C<sub>1</sub>F by quite a bit more. These same lengthening trends extend to the C<sub>2</sub>H and C<sub>2</sub>F bonds as well. The last four rows of Table 1 refer to the substituted methanes, without a C<sub>2</sub> atom. The trends are quite consistent with the ethanes in the earlier rows: shortened CH<sub>b</sub> bonds (and increased stretching frequencies) and elongated C<sub>1</sub>X. Moreover the magnitudes of these changes are similar to those of the ethanes, 0.4–0.9 mÅ for C<sub>1</sub>H and 4–7 mÅ for C<sub>1</sub>F.

We are now in a position to address the central question as to whether the peripheral bonds of the proton donor (those other than CH<sub>b</sub>) are affected more when this bond undergoes a contraction than when it elongates. The data in Table 1 would seem to provide a conclusive negative answer to this question. Considering first the C<sub>1</sub>–C<sub>2</sub> bond that is adjacent to CH<sub>b</sub>, this bond changes generally by only a small amount, about 1 mÅ or less. In any case, there does not appear to be any strong relation between the magnitude of this change and the sign of  $\Delta r(\text{CH}_b)$ . Regarding the C<sub>1</sub>H bond length changes, these are all stretches, regardless of whether the CH<sub>b</sub> bond elongates or contracts. The changes are also small, again on the order of 1 mÅ or less. Perhaps more importantly, the magnitude of the change bears no relation to the sign of  $\Delta r(\text{CH}_b)$ . The C<sub>1</sub>F bond stretches, too, are not appreciably larger when CH<sub>b</sub> contracts than when it elongates, or indeed even when it does not change at all, as in the case of H<sub>2</sub>C=CFH. These same trends continue as one moves further from the site of H-bonding, to the C<sub>2</sub> atom. The C<sub>2</sub>H bonds stretch by small amounts in nearly all cases, and the amount of this stretch is independent of the sign of  $\Delta r(\text{CH}_b)$ . This lack of correlation is repeated once again for  $r(\text{C}_2\text{F})$ ; all stretches lie in the 2–4 mÅ range, regardless of whether CH<sub>b</sub> stretches or shortens. In summary, then, the peripheral bond lengths of the proton donor molecule are affected in the same manner regardless of whether the H-bond is of blue- or red-shifting type.



**Figure 1.** Shifts of electron density occurring in water dimer as a result of formation of the complex. Blue regions denote gain, and red regions represent loss. Contour illustrated corresponds to change by 0.0005 au.

### Electron Density Shifts

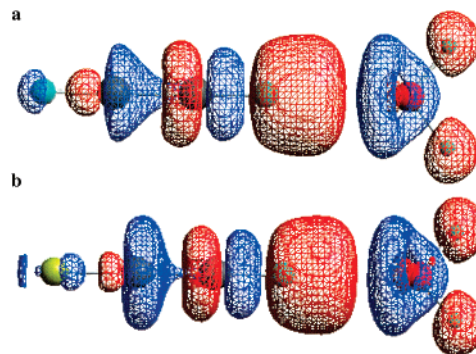
The next item to be addressed concerns the shifts in electron density that accompany formation of the putative H-bonds. Atomic charges are arbitrary by nature, and different schemes of partitioning electron density to one atom or another typically lead to discrepant charges. Consideration of single molecular orbitals, whether delocalized or localized, can be misleading since they ignore all of the rest of the electrons. Maps of total electron density in space are not subject to such arbitrariness and therefore can be trusted to reveal density shifts with some fidelity.

The shifts of electron density that result from the formation of the classic H-bond in the water dimer are illustrated in Figure 1. This map was generated by comparing the density in the dimer, point by point in space, to the same quantity in the isolated monomer. Blue regions of Figure 1 hence represent the accumulation of additional electron density as a result of the mutual approach of the two molecules; red regions indicate loss of density.

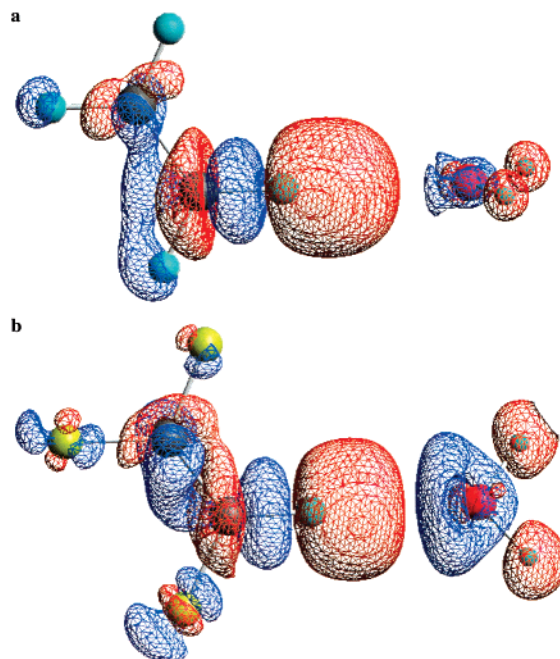
The most obvious effects of the H-bond formation include the red region that surrounds the bridging hydrogen atom, consistent with the accepted notion that this bridging hydrogen loses density. Some of this lost density is shifted to the lone pair of the proton-accepting O atom, indicated by the large blue region to its left. Other features of this conventional H-bond include density loss on the peripheral atoms of the acceptor molecule (red regions on far right) and gain on the peripheral regions of the donor molecule (blue area on far left).

Most important for our present consideration is the area along the O—H bond of the proton-donating molecule. It is apparent by the blue contours in this area that there is charge buildup along this O—H bond. This finding belies the notion that the stretching that occurs in the equilibrium length of the O—H bond in such conventional H-bonds, as well as the red shift of the OH stretching frequency, can be attributed to a loss of density in the O—H binding area. The increased density in the region between the O and H atoms would tend to strengthen (and hence shorten) the bond, were there no factors at work other than electron density shifts.<sup>56</sup>

Red shifts and OH stretches also occur in  $\equiv\text{CH}\cdots\text{O}$  interactions involving an alkynyl group. Not surprisingly, then, the density shifts that accompany the interaction between acetylene and water illustrated in Figure 2a exhibit a pattern very similar to that witnessed for the water dimer. One again sees the loss of density around the bridging proton, and the buildup in the lone pair region of the acceptor O atom. Also in common with the water dimer, there is an increase of density in the C—H bond region of the proton donor. This same pattern occurs nearly unaltered when the noninteracting H atom of acetylene is replaced by F, as is apparent in the  $\text{FC}\equiv\text{CH}\cdots\text{OH}_2$  system in



**Figure 2.** Shifts of electron density occurring in complex with water of (a) HCCH and (b) FCCH as a result of formation of the complex.



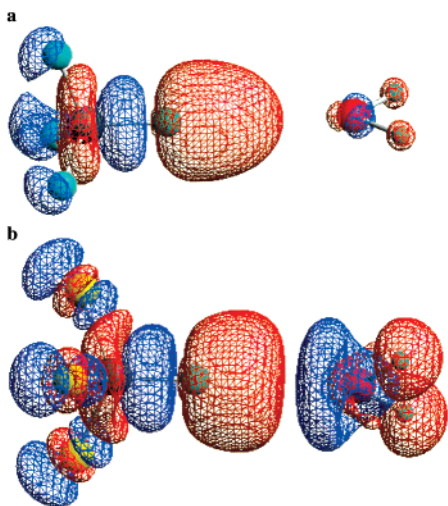
**Figure 3.** Shifts of electron density occurring in complex with water of (a)  $\text{H}_2\text{CCH}_2$  and (b)  $\text{F}_2\text{CCFH}$  as a result of formation of the complex.

Figure 2b. Whether H or F, the formation of the H-bond adds a small amount of density to this peripheral atom of the donor molecule.

The same pattern extends to the ethylene family of proton donors, wherein the C atom is  $\text{sp}^2$ -hybridized. In such cases, the C—H bond length undergoes changes (usually stretches) that are quite small, less than 0.002 Å.<sup>57</sup> Figure 3a affirms that the density difference map of ethylene...water contains the characteristic increase of density in the C—H<sub>b</sub> bond, as well as the other features common to H-bonds in general. Replacement of all three nonparticipating H atoms of ethylene by F causes little disturbance in this pattern. Focusing on the F atoms of  $\text{F}_2\text{C}=\text{CFH}\cdots\text{OH}_2$  in Figure 3b, the regions of density gain lie along the C—F bonds, with some loss occurring in an equatorial band around the F atom.

The recent proposition that the C—H bond contraction/blue-shift of  $\text{sp}^3$ -hybridized  $\text{CH}\cdots\text{O}$  bonds is caused by a different sort of polarization within the pertinent proton donor molecule than occurs in other H-bonded systems is belied by Figure 4. Figure 4a illustrates the density difference map of  $\text{H}_3\text{CH}\cdots\text{OH}_2$ ; its similarity to the previous figures is clearly evident. With specific regard to the C—H<sub>b</sub> bond in question, one again sees the blue region of charge gain, characteristic of all H-bonds, whether of  $\text{OH}\cdots\text{O}$  or  $\text{CH}\cdots\text{O}$  type. Not only is this region blue





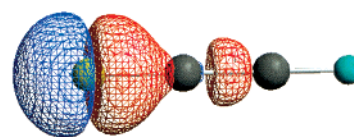
**Figure 4.** Shifts of electron density occurring in complex with water of (a) H<sub>3</sub>CH and (b) F<sub>3</sub>CH as a result of formation of the complex.

in all cases, but its nearly constant spatial extent also indicates that the magnitude of charge gain in this region is similar for red- and blue-shifting complexes. Replacement of H atoms of methane by F (Figure 4b) has little effect upon this aspect of the C—H bond.

In summary, the systems considered here comprise not only the conventional OH $\cdots$ O H-bond but also CH $\cdots$ O interactions; the hybridization of the latter C atom varies from sp to sp<sup>2</sup> to sp<sup>3</sup>. Donor molecules have also been considered in which the peripheral H atoms have been replaced by the much more electronegative F, which tends to strengthen the interaction. Regardless of which variant is considered, substituted or unsubstituted, all systems exhibit the same characteristic pattern of charge shift. There is a clear increase of density in the X—H bond of the proton donor molecule, regardless of whether this bond is lengthened, shortened, or left unchanged by its interaction with the proton acceptor molecule.

It has been suggested that the CH (or OH) bond of the proton donor is stretched in red-shifting H-bonds because of a population increase in the localized  $\sigma_{CH}^*$  NBO, which one might expect to weaken this bond.<sup>23</sup> But a single molecular orbital is not necessarily a valid indicator of total density changes, particularly if the population changes in that MO are small. As an example of the dubious value of using this single MO population in this manner, recent calculations<sup>37</sup> have shown a similar  $\sigma^*$  NBO population increase occurs also in various fluoro-substituted methanes, yet their C—H bonds are shortened and blue-shifted.

An auxiliary argument has been advanced that blue-shifting H-bonds that involve donors such as F<sub>3</sub>CH are distinct from other H-bonds in that the bulk of the electron density shifts occurring within the donor molecule are associated not with the bridging hydrogen, but rather with gains on the peripheral F atoms.<sup>23,51</sup> Perusal of the electron density maps would place this contention in serious question. Considering Figure 4b, it is first evident that there is a great deal more perturbation of the density in the vicinity of the bridging H atom of F<sub>3</sub>CH than around the F atoms. Moreover, with specific regard to these F atoms, the pattern is not so simple as pure electron gain in any case. While there is certainly gain on both sides of each F atom along the C—F axis, there is a region of loss in direct contact with the F nucleus, and surrounding it. Comparison with Figure 4a further suggests that there is a certain amount of density gain when the peripheral atoms are H, which would make F nonunique in this regard.



**Figure 5.** Shifts of electron density occurring in FCCH as a result of this molecule changing its geometry from that in the isolated monomer, to the geometry adopted within the FCCH $\cdots$ OH<sub>2</sub> complex (with  $r(\text{CH}_b)$  left unchanged). Blue regions denote gain, and red represents loss. Contour illustrated corresponds to change by 0.0005 au.

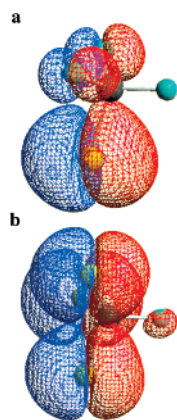
A second point must be made concerning any presumed association of shifts in peripheral atom density and the change in C—H bond length. Whereas one might interpret the complex density changes around the F atoms in F<sub>3</sub>CH $\cdots$ OH<sub>2</sub> (in which the CH bond contracts) as a gain in density, a gain is readily apparent on the F atom of FCCH $\cdots$ OH<sub>2</sub>, the CH bond of which undergoes the opposite change of a bond lengthening. Likewise, density gain occurs on the F atoms of F<sub>2</sub>C=CFH $\cdots$ OH<sub>2</sub>, wherein the C—H bond length also undergoes a stretch. Even the water dimer in Figure 1 contains clear evidence of a density gain on the peripheral H atom of the donor molecule, yet its bridging O—H bond also stretches. It would thus appear unjustified to connect any supposed density change on the peripheral atoms of the proton donor with a particular change in CH bond length.

### Connection between Geometrical and Electron Density Changes

The suggestion has been advanced<sup>51,52</sup> that the change in the CH<sub>b</sub> bond length is intimately tied to geometrical changes involving the peripheral atoms of the proton donor molecule. This would seem at first blush unlikely, since the latter geometrical adjustments are rather small (see Table 1). As an example, the CC bond of F<sub>2</sub>C=CFH is shortened by only 0.0004 Å when this molecule is complexed with water, and  $r(\text{CF})$  is stretched by 0.0028 Å. To test this hypothesis, we have examined how the geometry changes induced in the proton donor molecule by the complexation affect the electron density around the CH<sub>b</sub> bond. Specifically, the bridging C—H bond was held fixed in its optimized monomer length, while the remainder of the atoms were allowed to adjust their positions to adopt the geometry in the complex.

The FC $\equiv$ CH molecule is taken as an example in Figure 5. As a result of the complexation with water, the C $\equiv$ C bond is lengthened by 0.0012 Å, and  $r(\text{C—F})$  by 0.0035 Å. The density difference plotted in Figure 5 emphasizes these stretches, in that the motion of the F nucleus to the left drags some density along with it. More importantly, there is no discernible change in the region of the C—H bond on the far right. It would thus be unjustified to claim that the geometry changes caused in the FCCH molecule by complexation with water cause density shifts in the region of the CH<sub>b</sub> bond and thus a change in this bond's length. Indeed, if one adjusts the threshold on the contours in Figure 5 so as to make the plot 50-fold more sensitive, a small density change in the C—H bond does become visible. However, this change corresponds to an increase in density, which would lead to the expectation of a bond shortening, at odds with the actual finding that the C—H bond stretches by 0.0053 Å.

The fluorinated methanes are another case in point. Figure 6a illustrates that the distortions of the FH<sub>2</sub>CH molecule have very little influence upon the density of the bridging C—H<sub>b</sub> bond region. This finding remains correct even if the sensitivity is enhanced 50-fold. Similarly, in the case of di- and trifluoromethane, there is little evidence that the geometric changes of the remainder of the molecule result in any significant



**Figure 6.** Shifts of electron density occurring in (a)  $\text{FH}_2\text{CH}$  and (b)  $\text{F}_3\text{CH}$  as a result of this molecule changing its geometry from that in the isolated monomer, to the geometry adopted within its complex with water (with  $r(\text{CH}_b)$  left unchanged).

increases or decreases of density in the region of the bridging C–H bond. In fact, if anything, there might be a small loss of density at low enough threshold, in contrast to the shortening that is observed in this bond length. Examination of the density changes in  $\text{F}_3\text{CH}$  in Figure 6b illustrate this very slight loss in density, despite a contraction of this bond by some 0.0016 Å.

In summary, then, explicit consideration of electron density plots provides no reason to believe that the geometry changes imposed upon the proton donor molecule by its formation of a  $\text{CH}\cdots\text{O}$  H-bond produce changes in the electron density that cause, in turn, corresponding shortening or lengthening of the bridging C–H bond.

## Conclusions

The geometry changes that occur within the proton donor molecule of blue-shifting H-bonds are very similar to the analogous properties in the red-shifting analogues. Regardless of whether the  $\text{CH}_b$  bond is stretched (as with alkynes) or shortened (alkanes) by formation of the H-bond, the CX (X = H or F) bonds that are not directly involved in the H-bond are lengthened, and by similar amounts in each case. The CC bonds are affected to a smaller degree, and with no particular correlation with  $\Delta r(\text{CH}_b)$ .

Electron density shifts accompanying the formation of the H-bond also show strong similarities between red- and blue-shifting H-bonds. In all cases, there is an increased density in the region between the C and  $\text{H}_b$  atoms. The similarities extend to other regions of the proton donor molecule as well. In particular, there is no evidence that more density accumulates on the F atoms of blue-shifting fluorosubstituted alkanes, as compared to red-shifting alkynes or alkenes. Nor is there any indication that the density shifted to the donor molecule in the former (or latter) case bypasses the  $\text{CH}_b$  bond and accumulates largely on the peripheral F atoms.

Another question investigated was whether the observed changes in  $r(\text{CH}_b)$  are a direct consequence of the small geometry changes induced in the proton donor molecule by association with the acceptor. However, the density shifts that occur in the  $\text{CH}_b$  region that result from these changes in the donor molecule geometry are infinitesimal. Moreover, the very small density changes that are observed in the  $\text{CH}_b$  region do not correlate with the observed change in this bond length.<sup>58</sup>

In summary, there would not appear to be any fundamental distinctions between red- and blue-shifting H-bonds that can be associated with different patterns of geometrical perturbations or electron density shifts.

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