

Blue shifts vs red shifts in σ -hole bonding

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Abstract σ -Hole bonding is a noncovalent interaction between a region of positive electrostatic potential on the outer surface of a Group V, VI, or VII covalently-bonded atom (a σ -hole) and a region of negative potential on another molecule, e.g., a lone pair of a Lewis base. We have investigated computationally the occurrence of increased vibration frequencies (blue shifts) and bond shortening vs decreased frequencies (red shifts) and bond lengthening for the covalent bonds to the atoms having the σ -holes (the σ -hole donors). Both are possible, depending upon the properties of the donor and the acceptor. Our results are consistent with models that were developed earlier by Hermansson and by Qian and Krimm in relation to blue vs red shifting in hydrogen bond formation. These models invoke the derivatives of the permanent and the induced dipole moments of the donor molecule.

Keywords Blue shifting · Electrostatic potentials · Hydrogen bonding · Noncovalent interactions · Permanent and induced dipole moments · Red shifting · σ -hole bonding

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Red-shifting and blue-shifting hydrogen bonding

In recent years, considerable attention has focused upon the issue of red-shifting vs blue-shifting hydrogen bonds. By red-shifting is meant that the X–H bond in the complex X–H---Y is longer and has a lower vibration frequency than in isolated X–H. This had long been viewed as characteristic of hydrogen bonding [1–4], in fact a “fingerprint” by which it could be recognized. Correlations were found between the frequency shifts, bond length changes and interaction energies [2,5,6].

In blue shifting, on the other hand, the X–H bond length decreases and the X–H frequency increases. The occurrence of this is now quite well established. (See the reviews by Hobza and Havlas [7] and by Kryachko [4].) In many such cases, the hydrogen is on a carbon in the donor molecule, but examples are known in which it is on an atom of a different element [4, 8].

Why do some hydrogen-bonded complexes show blue shifts rather than red, and does this reflect a fundamental difference between them? Numerous studies have addressed these questions, and they have led to some disagreement.

Hobza et al. [7, 9] proposed that red-shifting involves largely the transfer of electronic charge from the proton acceptor Y to the σ^* X–H molecular orbital of the proton donor, which weakens the X–H bond, while blue-shifting results from electronic charge moving from the acceptor to outer portions of the donor (e.g., the fluorines in F_3C-H), followed by electronic and structural rearrangements that produce a strengthening of the X–H bond. Alabugin et al. offered a somewhat similar interpretation in that they focused upon $Y \rightarrow \sigma^*(X-H)$ hyperconjugation and X–H rehybridization [10]; they argued that both blue- and red-shifting hydrogen bonding could be explained by the

balance between these two effects. However Scheiner and Kar [11] examined computationally a series of C–H...O complexes that included blue and red shifting, and concluded that the electronic density shifts accompanying their formation to be quite similar.

Other studies have emphasized electrostatics/polarization [12], or these coupled with steric and/or Pauli repulsion [8]. The electric field due to the proton acceptor Y has also been invoked, and its consequences for the X–H bond have been examined [13–16]. Hobza and Havlas [17], Hermansson [15] and Qian and Krimm [16] have drawn attention to the key roles of the derivatives of the permanent and the induced dipole moments of X–H.

In view of the interest in blue-shifting vs red-shifting hydrogen bonding, we decided to investigate their occurrence and origins in another type of noncovalent interaction, σ -hole bonding. In an earlier study of hydrogen bonding and σ -hole bonding as competitive interactions [18], we found only red shifting in the complexes of both types that were examined. However Wang et al. [19] and Riley and Hobza [20] did observe blue-shifting in some halogen bonding, which is a subset of σ -hole bonding, and Wang et al. interpreted it in terms of the signs of the derivatives of the permanent dipole moments. In this paper, we shall look explicitly at the factors that determine whether a molecule that is capable of σ -hole bonding will blue-shift or red-shift, and whether both are possibilities. First we will give a brief description of σ -hole bonding.

σ -hole bonding

When a half-filled p orbital participates in forming a covalent bond, its electron normally tends to be somewhat localized in the internuclear region, thereby diminishing the electronic density in the outer (noninvolved) lobe of that orbital. This electron-deficient outer portion of a half-filled p bonding orbital is called a “ σ -hole” [21]. If the electronic deficiency is sufficient, a positive electrostatic potential is created; it is centered on the outer side of the atom, approximately along the extension of the covalent bond to that atom. As an example, the electrostatic potential on the molecular surface of O₂N–Cl is shown in Fig. 1. Note the positive potential on the outer side of the chlorine, where the extension of the N–Cl bond intersects the surface; on the lateral sides of the chlorine, however, the potential is negative.

Positive σ -holes have now been found computationally on the outer surfaces of Group V, VI, and VII atoms in numerous molecules [18, 21–29]. (Since Group V and Group VI atoms have three and two half-filled p bonding orbitals, respectively, they can therefore have three and two σ -holes on their surfaces.) These positive regions can

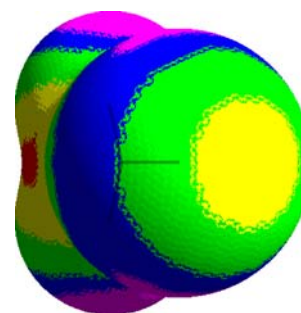


Fig. 1 Computed electrostatic potential on the molecular surface of Cl-NO₂. Color ranges, in kcal mol⁻¹, are: red, greater than 25; yellow, between 10 and 25; green, between 0 and 10; blue, between -4 and 0; purple, more negative than -4. The chlorine is facing the viewer, to the right. Note the yellow region of positive potential on the outer side of the chlorine, along the extension of the N–Cl bond. The blue region shows the sides of the chlorine to have negative potentials. The calculations were at the B3PW91/6–31G(d,p) level

interact electrostatically with negative regions on other molecules, e.g. lone pairs of Lewis acids, to produce highly-directional noncovalent “ σ -hole bonds.”

Such interactions have been observed spectroscopically [30–32], crystallographically [33–37] and computationally [18, 25–29, 38–43]. They have been shown to be competitive with hydrogen bonding [18, 31, 32, 44]. When σ -hole bonding involves Group VII atoms, it is commonly called “halogen bonding.”

The magnitudes of the positive potentials associated with σ -holes show certain overall trends, which are in general followed as well by the strengths of their interactions with negative centers [18, 25–27]. σ -Holes tend to be more positive as the atom is more polarizable and as its bonding orbitals are purer p in character; any s contribution diminishes the electron deficiency in the outer lobe. For both reasons, σ -holes usually become more positive in going from the lighter to the heavier elements in a given Group, i.e., N < P < As < Sb, O < S < Se < Te and F < Cl < Br < I. Thus the phosphorus in P(CH₃)₃ has no positive σ -hole, whereas the arsenic in As(CH₃)₃ has one on the extension of each C–As bond [27]. σ -Holes are also more positive when the remainder of the molecule is electron-withdrawing; chlorine does have a positive σ -hole in H₃CO–Cl but it does not in H₃C–Cl [18].

It is increasingly recognized that σ -hole bonding, especially involving Group VII, occurs widely in biological systems [24, 45]. There is also considerable interest and activity in applying it in crystal engineering [45, 46].

Procedure

Key components of our study are the computed electrostatic potentials on the surfaces of a series of molecules containing Group V, VI or VII atoms. For this purpose,

we followed the increasingly-common practice of taking the molecular surface to be the 0.001 au (electrons bohr⁻³) contour of the molecule's electronic density $\rho(\mathbf{r})$, as proposed by Bader et al. [47]. The electrostatic potential $V(\mathbf{r})$ that is produced at any point \mathbf{r} by the nuclei and electrons of the molecule is given by Eq. (1):

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (1)$$

Z_A is the charge on nucleus A, located at \mathbf{R}_A . $V(\mathbf{r})$ is a physical observable, which can be determined experimentally [48, 49] as well as computationally. When calculated on a molecular surface, we label it $V_S(\mathbf{r})$. For evaluating $V_S(\mathbf{r})$, we used the density functional B3PW91/6–31G(d, p)//B3PW91/6–31G(d, p) procedure. Our interest is specifically in the most positive values of $V_S(\mathbf{r})$, the local maxima $V_{S,\max}$.

For computing vibration frequencies and interaction energies ΔE , we went to a larger basis set, B3PW91/6–311G(3df,2p), first reoptimizing the geometries. ΔE is expressed by Eq. (2),

$$\Delta E = E_{\text{complex}} - E_{\text{reactants}} \quad (2)$$

where E_{complex} and $E_{\text{reactants}}$ are the energy minima at 0 K. Then we calculated ΔE at the MP2-FC/6–311++G(3df,2p) level with the same geometries. (FC means frozen core.) Since these large basis sets should minimize basis set superposition error [50], no explicit correction for it was made. Our objective in calculating the ΔE was simply to demonstrate that an attractive interaction had occurred. Energy minima were confirmed by the absence of imaginary frequencies. All computations were carried out with the Gaussian 03 code [51], except for the molecular surface electrostatic potentials, which were obtained using the HardSurf program [52].

Results

$V_{S,\max}$ of σ -hole donors

In Table 1 is a series of 12 candidates for blue-shifting σ -hole bonding. Each of these molecules contains a Group V, VI or VII atom with at least one positive σ -hole, i.e. a region of positive electrostatic potential centered approximately along the extension of one of the covalent bonds to that atom. The most positive surface potential, the $V_{S,\max}$, is given for each σ -hole and the bond to which it corresponds is indicated.

In three instances, an atom has more than one σ -hole: The sulfur is SHNO₂ and the selenium in SeHNO₂ have one on the extensions of both the N–S and H–S bonds, while the arsenic in AsH₂NO₂ has two corresponding to the

Table 1 Most positive computed electrostatic potentials, $V_{S,\max}$, on surfaces of atoms having σ -holes, located approximately on the extensions of the indicated bonds^a

Molecule	Atom	Bond	$V_{S,\max}$, kcal mol ⁻¹
ClF	Cl	F–Cl	39.9
ClCN	Cl	C–Cl	34.9
ClNO ₂	Cl	N–Cl	16.4
ClCF ₃	Cl	C–Cl	16.3
BrF	Br	F–Br	47.5
BrCN	Br	C–Br	42.1
BrNO ₂	Br	N–Br	23.1
BrCF ₃	Br	C–Br	21.4
SHNO ₂	S	N–S	39.1
	S	H–S	10.3
SeHNO ₂	Se	N–Se	36.7
	Se	H–Se	15.5
PH ₂ NO ₂	P	N–P	40.1
AsH ₂ NO ₂	As	N–As	38.4
	As	H–As	18.5
	As	H–As	18.3

^a Computational level: B3PW91/6–31G(d,p)//B3PW91/6–31G(d,p).

H–As bonds plus that for the N–As. It should also be mentioned that most of the atoms having σ -holes have some negative regions on their surfaces as well, as can be seen for ClNO₂ in Fig. 1 and for ClCF₃ and BrCF₃ in Figs. 3 and 5 of Politzer et al. [25].

In selecting the molecules in Table 1, we were guided by the fact that in many (although not all) of the hydrogen-bonded complexes exhibiting blue shifting, the donor has a strongly electron-attracting group, e.g., CF₃, linked to the hydrogen [7, 11]. Thus, the potential σ -hole donors in Table 1 have CF₃, NO₂, CN or F bonded to the Group V–VII atom.

Consistent with the usual trend that σ -holes become more positive in going to the heavier elements in a Group, the Br $V_{S,\max}$ are all more positive than the corresponding Cl. However the P, As and S, Se pairs deviate from what is expected, in that the heavier one in each instance has a slightly lower $V_{S,\max}$.

Properties of complexes

Table 2 lists 16 complexes X–D---Y formed between the molecules X–D in Table 1, acting as σ -hole donors through the atom D, and either HCN or NH₃, acting as the acceptor Y through its nitrogen lone pair. Both the B3PW91 and the MP2 interaction energies are given; they are generally within 1–2 kcal mol⁻¹ of each other, as has been our experience in the past when using the present basis sets [18, 26, 27]. The donor-acceptor separations D---Y are all less than the sums of the van der Waals radii of the respective atoms [53].

Table 2 Computed properties of σ -hole bonded complexes

Complex	$\Delta E, \text{kcal mol}^{-1}$		Changes in bond properties ^a		
	B3PW91 ^b	MP2-FC ^c	Bond	$\Delta\omega, \text{cm}^{-1}$	$\Delta R, \text{\AA}$
<i>Blue-shifting</i>					
HCN---ClNO ₂	-1.1	-2.5	Cl-N	+17	-0.027
HCN---ClCF ₃	-1.0	-2.4	Cl-C	+4	-0.008
HCN---BrNO ₂	-1.7	-3.1	Br-N	+12	-0.025
HCN---BrCF ₃	-1.3	-2.9	Br-C	+3	-0.007
HCN---SHNO ₂	-2.9	-4.9	S-N	+13	-0.013
HCN---SeHNO ₂	-3.2	-5.4	Se-N	+6	-0.011
<i>Red-shifting</i>					
HCN---ClF	-4.5	-5.7	Cl-F	-54	+0.022
HCN---ClCN	-2.5	-3.9	Cl-C	-5	+0.001
HCN---BrF	-6.7	-8.1	Br-F	-50	+0.028
HCN---BrCN	-3.3	-4.7	Br-C	-8	+0.005
HCN---PH ₂ NO ₂	-3.4	-5.5	P-N	-1	0.000
HCN---AsH ₂ NO ₂	-3.5	-5.8	As-N	-1	+0.001
H ₃ N---ClCN	-5.2	-4.8	Cl-C	-25	+0.008
H ₃ N---ClNO ₂	-5.4	-3.9	Cl-N	-13	-0.013
H ₃ N---ClCF ₃	-3.1	-3.1	Cl-C	-3	-0.006
H ₃ N---BrCN	-6.9	-6.1	Br-C	-37	+0.020

^a Changes in vibration frequency $\Delta\omega$ and bond length ΔR are defined as complex minus reactant.

^b B3PW91/6-311G(3df,2p)// B3PW91/6-311G(3df,2p)

^c MP2-FC/6-311++G(3df,2p)// B3PW91/6-311G(3df,2p)

Table 2 also shows the effect of complex formation upon the bond X–D in each case, in terms of the changes in its vibration frequency and its bond length. Six of the complexes show blue shifts; the X–D frequency increases, always accompanied by a decrease in bond length. All of the blue-shifting complexes involve HCN as the acceptor.

On the other hand, six complexes with HCN do not exhibit blue shifts; those having ClF, BrF, ClCN and BrCN as the donors have distinct red shifts, $\Delta\omega < 0$, and bond length increases, while those with PH₂NO₂ and AsH₂NO₂ as the donors show virtually no effect.

Table 3 Derivatives of permanent dipole moments of σ -hole donors

σ -Hole donor, X-D	$\partial\mu^\circ/\partial R_{X-D}, \text{D/\AA}$	Angle, deg ^a
F-Cl	2.76	0
NC-Cl	2.07	180
O ₂ N-Cl	6.70	180
F ₃ C-Cl	5.24	180
F-Br	3.13	0
NC-Br	0.97	180
O ₂ N-Br	5.78	180
F ₃ C-Br	4.49	180
O ₂ N(H)-S	3.73	156
O ₂ N(H)-Se	3.61	162
O ₂ N(H)(H)-P	0.48	164
O ₂ N(H)(H)-As	0.26	169

^a Angle between directions of dipole derivative and bond from X to D; the latter is also direction of electric field due to acceptor lone pair.

All of the NH₃ complexes display red shifts, even with donors (ClNO₂ and ClCF₃) that blue-shift with HCN. In two instances, however, the red shift is in conjunction with a decrease in the X–D bond length, rather than the expected increase.

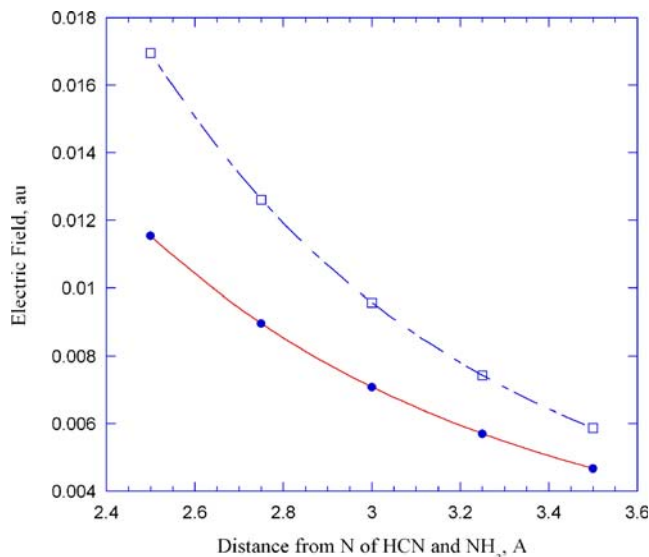


Fig. 2 Computed variation of magnitudes of electric fields produced by HCN and NH₃. The distance is measured from each nitrogen nucleus, away from the molecule, along its symmetry axis. The direction of the field is along this axis, toward the molecule. The solid circles denote the values for HCN and the open squares those for NH₃. The calculations were at the B3PW91/6-311G(3df,2p) level

Discussion and summary

In order to better understand the factors involved in blue shifting and red shifting, we turn to the work of Hermansson [15] and Qian and Krimm [16]. Applying their models to our complexes, the change in frequency of the X–D bond can be related to the magnitudes and directions of the derivatives $\partial\mu^\circ/\partial R_{X-D}$ and $\partial\mu^{\text{ind}}/\partial R_{X-D}$, where μ° is the permanent dipole moment of the molecule X–D, μ^{ind} is the dipole moment induced by the electric field due to the acceptor Y and R_{X-D} is the X–D bond length. Since the field is generated primarily by the nitrogen lone pair of Y, its direction is from X–D to Y, and that is also the direction of $\partial\mu^{\text{ind}}/\partial R_{X-D}$ (i.e., μ^{ind} increases as the X–D bond becomes longer). Assuming the electric field ϵ to be uniform and parallel to the X–D bond, Hermansson derived Eq. (3) [15], written here in terms of the system X–D---Y.

$$\Delta\omega(\epsilon) \propto -\epsilon \cdot \left[\partial\mu^\circ/\partial R_{X-D} + \frac{1}{2} \partial\mu^{\text{ind}}/\partial R_{X-D} \right] \quad (3)$$

Since $\partial\mu^{\text{ind}}/\partial R_{X-D}$ is in the direction of ϵ , it always supports a red shift. If the direction of $\partial\mu^\circ/\partial R_{X-D}$ is also the same as that of the field, then the effects of the two derivatives reinforce each other and the X–D frequency will red shift. If $\partial\mu^\circ/\partial R_{X-D}$ is opposite in direction to the field, then there may be a blue shift, but not if the contribution of the term $1/2(\partial\mu^{\text{ind}}/\partial R_{X-D})$ outweighs that of $\partial\mu^\circ/\partial R_{X-D}$. Thus, $\partial\mu^\circ/\partial R_{X-D}$ being opposite to the field is, in terms of the models, necessary but not sufficient for a blue shift.

We have calculated the dipole moment derivatives $\partial\mu^\circ/\partial R_{X-D}$ and their directions for each σ -hole donor in Table 1; the results are in Table 3. An angle of 0° means that the derivative is in exactly the same direction as the field due to the acceptor lone pair, and hence a red shift is to be expected; and angle of 180° says that the derivative is exactly opposite to the field, and thus a blue shift is possible.

Only for ClF and BrF is the derivative in the same direction as the field; accordingly these should form red-shifting complexes, as they do (Table 2). For all of the other σ -hole donors, the derivative is either opposite to the field or nearly so, the largest deviation being 24° in the case of SHNO₂. These molecules could therefore produce blue-shifting complexes, and six of them do so when HCN is the acceptor. The four that do not – ClCN, BrCN, PH₂NO₂ and AsH₂NO₂ – are the ones for which the derivative of the permanent dipole has the smallest magnitudes in Table 3, and thus can be most easily dominated by the contribution of the induced dipole derivative in Eq. (3), which favors red shifting.

Why have red shifts been obtained in all of the complexes with NH₃ that we have investigated, both in

this work and earlier [18], even when the donor showed a blue shift with HCN? We suggest that this is because NH₃ exerts a significantly stronger electric field on the σ -hole donor than does HCN, as can be seen in Fig. 2. (The distances for which the magnitudes of the fields are shown in Fig. 2 cover the range of donor-acceptor separations for the complexes in Table 2, 2.5–3.3 Å.) As was demonstrated by Hermansson [15] and by Qian and Krimm [16], a stronger field enhances the role of the induced dipole derivative in Eq. (3), and thus favors a red shift. A good example is the much greater red shifts shown by ClCN and BrCN with NH₃ than with HCN (Table 2).

In summary, the Hermansson and the Qian/Krimm models show that a necessary but not sufficient condition for blue shifting is that the derivative of the σ -hole donor's permanent dipole moment be opposite in direction to the electric field created by the acceptor. If this prerequisite is satisfied, a further requirement is that the contribution to $\Delta\omega$ of the induced dipole moment derivative, Eq. (3), not outweigh that of the permanent dipole. This requirement brings in the nature of the acceptor; if its field is sufficiently strong, this may tip the aforementioned balance in favor of the red-shift-producing induced dipole contribution, as we have observed in the NH₃ complexes that we have studied. With HCN, on the other hand, we have found the effect of the permanent dipole derivative to prevail in some instances, and that of the induced in others.

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