When a Lewis acid and base form an adduct shifts the lengths and strengths in the acid and base shift.

According to the frontier orbital description of Lewis acid-base interactions, adduct formation results in a net transfer of electron density from the base HOMO to the acid LUMO. This transfer

- increases the electron density between the acid (A) and base (D)
- alters the strength of the bonding within the base as the base LUMO becomes partially populated.

These changes result in structural and spectroscopic shifts on adduct formation that can be taken as a measure of the strength of the Lewis acid-base interaction. Since these shifts depend on the nature of the bonding in the acid and base in practice structural and spectroscopic measurements of Lewis basicity are applied to a few classes of Lewis acid-base interactions, most notably hydrogen bonding and halogen bonding. Since hydrogen bonds will be discussed in section 6.5.1, the remainder of this subsection will focus on halogen bonds.

Halogen bonds are coordinate covalent bonds formed between a Lewis bases and an organohalogen.

The halogens in compounds containing a singly-bonded halogen can engage in a special type of intermolecular interaction called halogen bonding since they are electrophilic on the opposite side of the bond. This electrophilicity is apparent from the charge distribution in $(CF_5I)$ shown in Figure 4.5.1 in which the charge is distributed on the I such that the I is Lewis basic perpendicular to the C-I bond and Lewis acidic opposite to it. This region of diminished electron density on the halogen opposite the existing sigma bond is called a $(sigma)$-hole.*

![Image](image_url)

*Figure 6.4.5.1. Electrostatic surface calculated for $(CF_5I)$ at the STO-3-21G level oriented so that the C-I bond is facing toward the viewer. The sigma hole shown is the region of positive electron density on the I atom at the front of the image.*
Schematically,

Since the halogen can act as a Lewis acid in the direction opposite the R-X bond it can form adducts with Lewis bases in that direction.

\[
\begin{align*}
R-X & \quad + \quad :B \\
\leftrightarrow \\
R-X\text{-----}B
\end{align*}
\]

The bond holding these adducts together are called halogen bonds, often abbreviated XB.

The halogen is said to act as a halogen bond donor when it forms a halogen bond with a base along that direction, with the base acting as the halogen bond acceptor. Consequently, the two previous schemes may also be given as:

The ability of singly-bonded halogen atoms to form halogen bonds forms the basis of many efforts to engineer structures in which halogen containing compounds are held together into chains, sheets, or 3D structures using halogen bonds. One easy to see example involves 1D chains formed between \( p \)-diiodotetrafluorobenzene and \( p \)-bis(dimethylamino)benzene.\(^3\)

\[\text{Figure 6.4.5.2. 1D chains of } p\text{-diiodobenzene and } p\text{-bis(dimethylamino)benzene molecules in which I shown in purple, N in blue, F in yellow, and C in grey. The chains are held together by C-I---N halogen bonds with a contact angle of 174 degrees. The figure was produced using Mercury 3.5.1 based on cambridge crystallographic database entry 172272.}\]

Trends in Halogen bond strength in a closely-related series of compounds may be assessed by examining how the vibrational stretching frequency of \( I_2 \) and the \( I_2(\pi^*\text{ to } \sigma^*) \) transition energy change on formation of the adduct.

From the description of halogen bonding above it should be apparent that the iodine charge transfer complexes
described in section 6.4.2 are held together by halogen bonds. This means that the description of the bonding in \( I_2 \) charge transfer complexes given in that section illustrate how vibrational and electronic transitions shift when a halogen bonded adduct is formed between a halogen bond donor and acceptor.

The orbital interactions involved in halogen bond formation are shown in Figure 6.4.5.3. As can be seen from that figure the formation of an adduct between \( I_2 \) and a Lewis base is expected to result in weakening of the I-I bond and a shift in the \( I_2 \rightarrow \pi^* \rightarrow \sigma^* \) transition energy to higher energy/shorter wavelengths (i.e. a blueshift). Further, both the weakening of the I-I bond and the \( I_2 \rightarrow \pi^* \rightarrow \sigma^* \) blueshift are expected to increase with the HOMO energy of the Lewis base.

![Figure 6.4.5.3.](image)

Because the I-I bond strength and \( I_2 \rightarrow \pi^* \rightarrow \sigma^* \) blueshift increase with the Lewis basicity of the donor the blueshift and the I-I vibrational stretching frequency are sometimes used as measures of donor's halogen bond affinity. However, the data obtained from such spectroscopic measurements should be interpreted with a degree of caution. As seen in Table 6.4.5.1. the extent to which the I-I bond is weakened (indicated by \( \Delta \nu_{I-I} \)) and the \( I_2 \rightarrow \pi^* \rightarrow \sigma^* \) band is blue shifted are imperfectly correlated overall. However, a careful comparison of the data in 6.4.5.1. reveals that the I-I bond weakening and \( I_2 \rightarrow \pi^* \rightarrow \sigma^* \) blue shift correlate well for Lewis bases of a given type. Consequently, shifts in the I-I stretching frequency and \( I_2 \rightarrow \pi^* \rightarrow \sigma^* \) absorption band are not useful as an absolute measure of Lewis basicity but can be used to rank the halogen bond affinity of a closely-related set of donors.

Table 6.4.5.1. Spectroscopic measures of Lewis basicity for \( I_2 \) adducts of selected bases arranged in order of extent of blue shift. The data are excerpted from the extensive compilation given in reference 4.
<table>
<thead>
<tr>
<th>Base (type)</th>
<th>(\Delta \nu_{I-I} \text{ cm}^{-1})</th>
<th>Blue shift of (l_2's: \pi \rightarrow \sigma^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-methylpyridine (pyridines)</td>
<td>29.1</td>
<td>4730</td>
</tr>
<tr>
<td>pyridine (pyridines)</td>
<td>27.4</td>
<td>4560</td>
</tr>
<tr>
<td>tetrahydrothiophene (thioethers)</td>
<td>44.5</td>
<td>3640</td>
</tr>
<tr>
<td>tetrahydrofuran, THF (ethers)</td>
<td>6.4</td>
<td>2280</td>
</tr>
<tr>
<td>diethyl ether (ethers)</td>
<td>5.5</td>
<td>1950</td>
</tr>
<tr>
<td>acetone (ketone)</td>
<td>5.0</td>
<td>1850</td>
</tr>
<tr>
<td>acetophenone (ketone)</td>
<td>4.6</td>
<td>1650</td>
</tr>
<tr>
<td>acetonitrile (nitrile)</td>
<td>4.1</td>
<td>1610</td>
</tr>
<tr>
<td>hexamethylbenzene (aromatic)</td>
<td>10.4</td>
<td>1070</td>
</tr>
<tr>
<td>benzene (aromatic)</td>
<td>4.3</td>
<td>450</td>
</tr>
</tbody>
</table>

**References and Further Reading**


**Notes**

* Other compounds also exhibit \(\sigma\)-holes (and \(\pi\)-holes) that can be used in crystal engineering. For details see reference 2.

** for more details consult reference 4, pp. 286-309.
Contributors

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