Resonance Contributors and the LUMO Reveal a Consistent Picture of Carbonyl Polarity

The molecular orbital model is consistent with the above resonance picture. The LUMO ($\pi^*$) of formaldehyde is shown; the $\pi^*$ lobe on carbon is much larger than on oxygen. In other words, carbon contributes more to $\pi^*$ than does oxygen. Nucleophiles will be attracted to the largest lobe of the LUMO. Conclusion: Carbon (not oxygen) is the electrophilic site in carbonyl groups.
Structure-Reactivity and the Carbonyl Group

Aldehydes are more reactive than ketones.

Reason:
- Better electrophile
- Steric factors

Electronic factors; LUMO energy level

A

CH₃

CH₃

CH₃

CH₃

CF₃

CH₃

CH₃

CH₃

CH₃

CH₃
The Carbonyl Oxygen is Protonated Under Acidic Conditions

The carbonyl is converted into a more powerful electrophile by protonating the carbonyl oxygen.

Characteristic of a more powerful electrophile, the protonated carbonyl has a lower lying $\pi^*$ (LUMO) energy than the neutral carbonyl.
On the Basicity of Carbonyl Oxygen

Which carbonyl is the stronger base?

\[
\text{CH}_3\text{C} = \text{O} + \text{H}^+ \rightleftharpoons \text{CH}_3\text{C} = \text{O}^+ \text{H}^-
\]

\[
\text{CH}_3\text{C} = \text{O} \cdot \cdot \cdot + \text{H}^+ \rightleftharpoons \text{CH}_3\text{C} = \text{O}^+ \text{H}^-
\]

Which of these protonated forms (A or B) is more stable? Why?

_**delocalized charge**_

Circle the stronger base

\[
\text{A} \quad \text{pK}_a = -7.2 \quad \text{(stronger acid)}
\]

\[
\text{B} \quad \text{pK}_a = -6.5 \quad \text{(weaker acid)}
\]