Renner-Teller effect: CO$_2$ vs. NO$_2$ and O$_3$ molecules.

CO$_2$ is linear and has a closed shell electron configuration, whereas NO$_2$ and O$_3$ put their additional 1 or 2 electrons into an m=$\pm 1$ doublet (if the molecule would stay linear, which it doesn’t.) The usual Jahn-Teller argument would then say the molecule should deform to split the partially occupied HOMO orbital. However, the linear molecule is an exception. There can be no off-diagonal coupling of m=1 to m=-1 orbitals which is first order in the vector perturbation $u \cdot \nabla V$, so the effective 2 x 2 matrix for these two levels contains coupling terms of order $u^2$. The distortion may or may not be energetically preferred compared with remaining linear and saving elastic bending energy $\frac{1}{2} Ku^2$. This second-order Jahn-Teller effect is called the Renner-Teller effect.


RHF stands for Restricted Hartree Fock. The molecular orbitals drawn here omit oxygen 2s-derived states. Thus 4+4+5 electrons are available in neutral NO$_2$. The lowest energy orbitals are at the top, and highest at the bottom, but relative order of $\sigma$ and $\pi$ is not respected. The 5$\sigma_g$ and 4$\sigma_u$ levels are empty, and the 2$\pi_u$ level is $\frac{1}{4}$ full.

FIG. 3. Electronic energy as a function of bond angle for the low-lying electronic states of NO$_2$.

Note the $^2\pi_u$ doublet ground state at 180° is split into $A_1$ and $B_1$ levels. The splitting is quadratic in angle. There is a 2-3 eV gap between these states. The upper $B_1$ component has accidental crossings with two other levels at almost the same angle as the ground state. This makes the visible spectrum very complex.

The distorted molecule has $C_{2v}$ symmetry.

**NO₂** is an open shell molecule with a valence electron configuration of the neutral ground state usually written in C₂ᵥ symmetry as:

\[(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(1b_1)^2(5a_1)^2(1a_2)^2\]

\[(4b_1)^2(6a_1)^12A_1\]

In the neutral ground state the molecule is bent with a bending angle of 134°. This angle changes upon ionisation in a way that reflects the angle determining properties of the valence electrons. In the ground ionic state, reached by photoionisation from the outermost orbital, the molecule is found to have a linear equilibrium geometry. This state, which for obvious reasons is usually the best known of all states for small cations, has turned out to be very difficult to study in the case of NO₃⁺. Recently, ab initio quantum mechanical methods have been used to determine the equilibrium bond distance, vibra-

The right hand picture shows in the lower panel, a theoretical estimate using single-particle approximation, of electronic excitations, and the upper panel, a photoelectron spectrum indicating some observed levels at low resolution.
The photoelectron spectrum at higher resolution shown to the left has a Franck-Condon sequence of vibrational sidebands. A schematic representation of the Franck-Condon process is shown above.

The HOMO (A₁) orbital of the molecule is built from π orbitals that lie in the plane of the distorted molecule, while the LUMO (B₁) orbital is built from π orbitals that lie perpendicular to the plane of the distorted molecule. There is a weakly allowed electric dipole transition (light polarized perpendicular to the molecular plane) that couples these two levels. This accounts for the brown color of NO₂ gas.