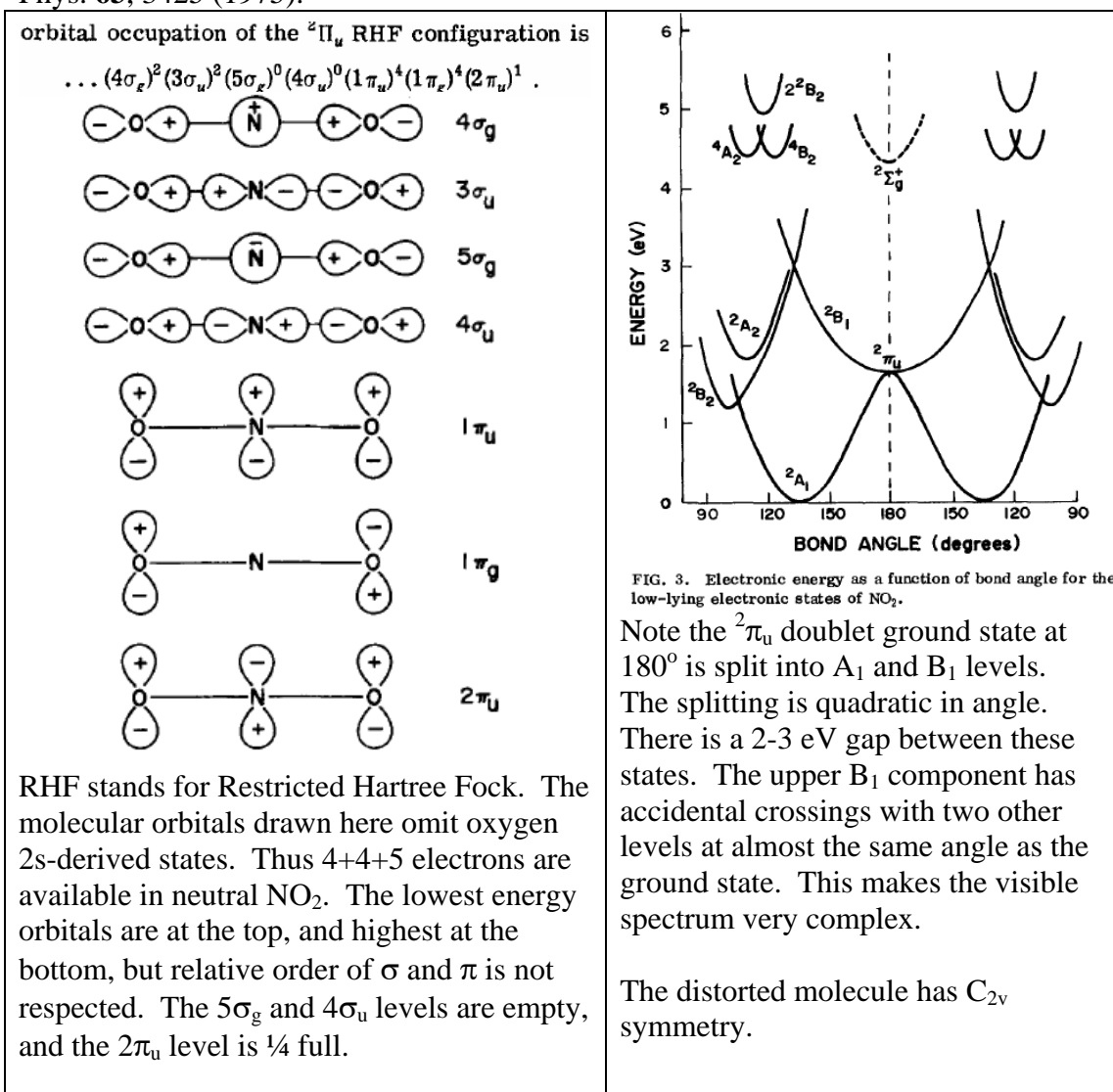


Renner-Teller effect: CO₂ vs. NO₂ and O₃ molecules.

CO₂ is linear and has a closed shell electron configuration, whereas NO₂ and O₃ 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 $\vec{u} \cdot \vec{\nabla} V$, so the effective 2×2 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.

Below are some pictures taken from G. D. Gillispie, A. U. Khan, A. C. Wahl, R. P. Hosteny, and M. Krauss, *The electronic structure of nitrogen dioxide. I. Multi-configuration self-consistent-field calculation of the low-lying electronic states*, J. Chem. Phys. **63**, 3425 (1975).



The same orbitals, but for the bent NO_2 ground state, are sketched below, taken from the paper by C. R. Brundle and D. Neumann, W. C. Price, D. Evans, A. W. Potts, and D. G. Streets, *Electronic Structure of NO_2 Studied by Photoelectron and Vacuum-uv Spectroscopy and Gaussian Orbital Calculations*, *J. Chem. Phys.* **53**, 705 (1970).

NO_2 is an open shell molecule with a valence electron configuration of the neutral ground state usually written in C_{2v} symmetry as:

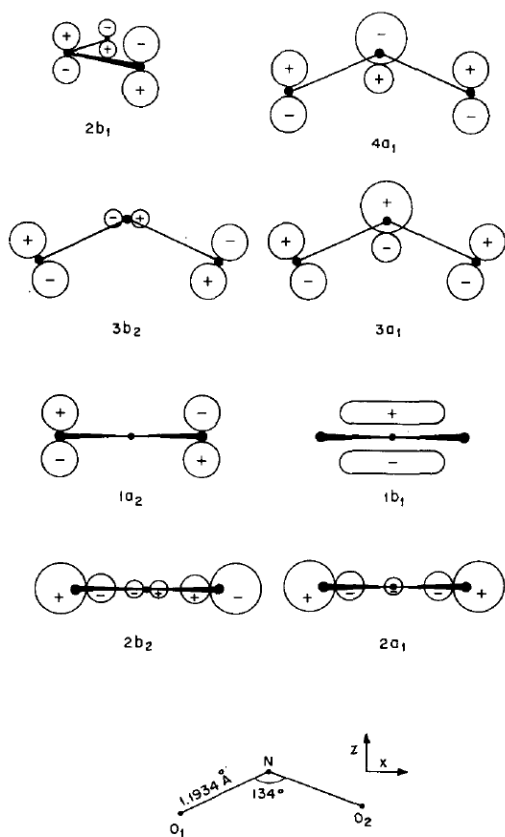
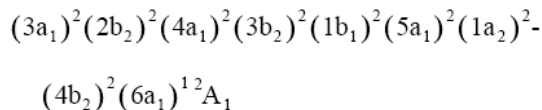


FIG. 8. Schematic orbitals for bent triatomic molecules (NO_2 , O_3 , CF_2 , NOF , NF_2 , and OF_2).

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 NO_2^+ . Recently, ab initio quantum mechanical methods have been used to determine the equilibrium bond distance, vibra-

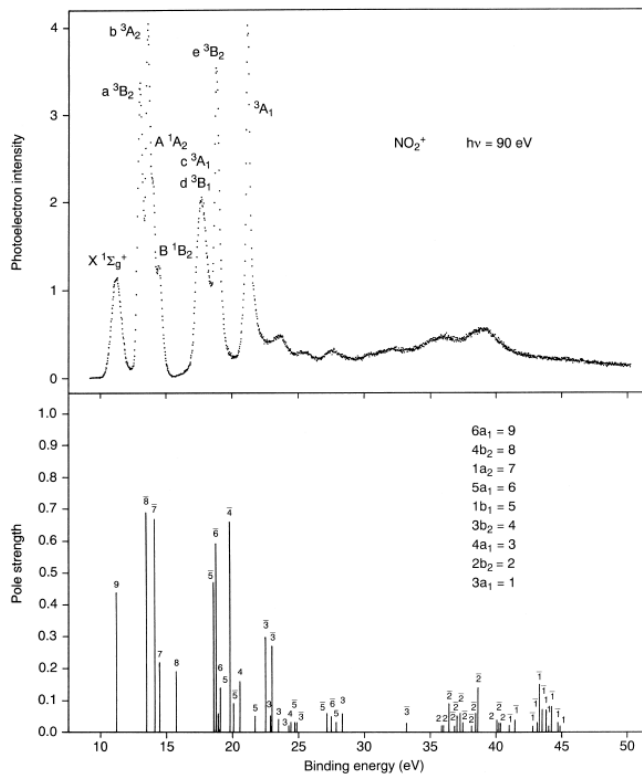


Fig. 1. Upper frame: The valence shell photoelectron spectrum of nitrogen dioxide recorded at a photon energy of 90 eV. Assignments are given for peaks that correspond to single-hole states of the ion. Lower frame: The calculated photoelectron spectrum by Schirmer et al. [10]. The relative intensities plotted are the pole strengths. Triplet states are indicated by bars above the number corresponding to the molecular orbital.

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.

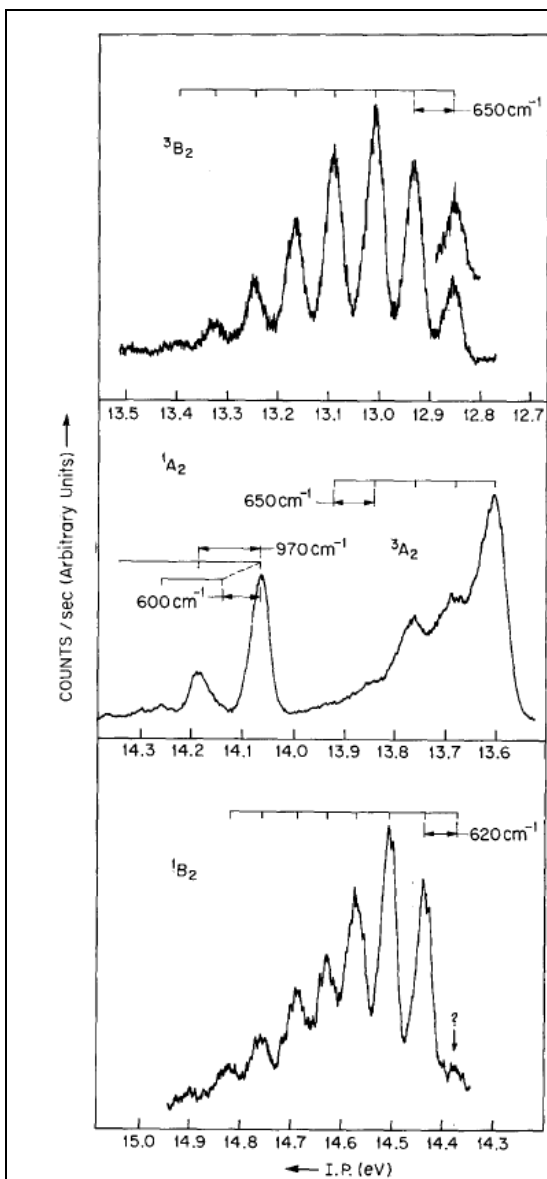


FIG. 3. The second, third, fourth, and fifth ionization potentials of NO_2 as recorded in the He I photoelectron spectrum.

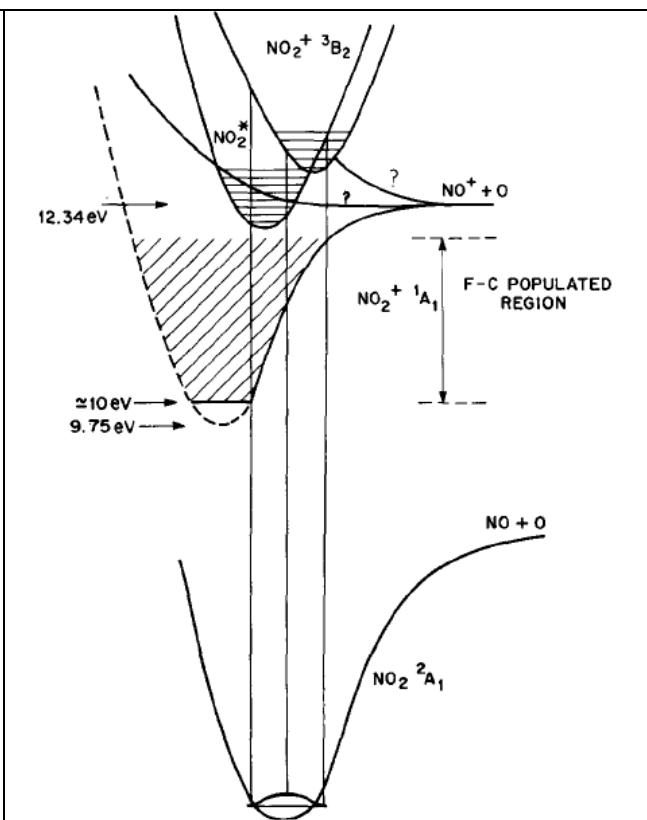


FIG. 10. Schematic representation of possible fragmentation processes for NO_2^+ .

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 (A_1) orbital of the molecule is built from π orbitals that lie in the plane of the distorted molecule, while the LUMO (B_1) 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 NO_2 gas.