

16.20) The tetrahedral ClO_4^- ion uses sp^3 hybrid orbitals on the central Cl (which has $SN = 4$). The pyramidal ClO_3^- also uses sp^3 hybrid orbitals on the central Cl, which has $SN = 4$.

16.22) The carbon atom in $\text{N}\equiv\text{C}-\text{Cl}$ has a steric number of 2. It is sp hybridized, and the molecule should be linear.

16.24) For NO_2^+ , sp hybrid orbitals on central N atom, forming σ -bonds with p_z orbitals on outer oxygen atoms (4 electrons).

Lone pair $2s$ orbitals on outer oxygens (4 electrons).

π_x , π_y , π_x^{nb} and π_y^{nb} each with 2 electrons.

Linear and not paramagnetic.

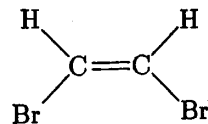
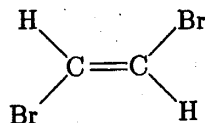
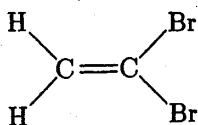
For NO_2 and NO_2^- , sp^2 hybrid orbitals on central N atom, two forming σ -bonds with outer $2p$ orbitals and one with a lone pair on N (6 electrons).

Lone pair $2s$ and $2p$ orbitals on outer atoms (8 electrons).

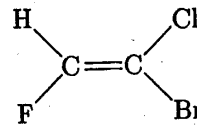
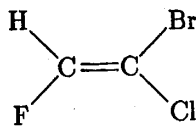
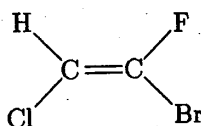
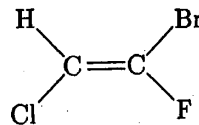
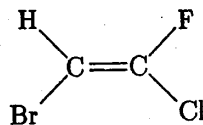
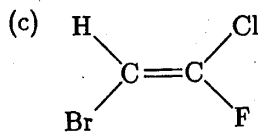
π orbital containing 1 (NO_2) or 2 (NO_2^-) electrons.

Both are non-linear, but only NO_2 is paramagnetic.

16.30) (a)



(b) Same as (a), with one Br replaced by Cl.



17.8 (a) Average interval between lines is $0.623 \times 10^{12} \text{ s}^{-1} = \frac{h}{4\pi^2 I}$

$$I = \frac{h}{4\pi^2(0.623 \times 10^{12} \text{ s}^{-1})} = \frac{6.626 \times 10^{-34} \text{ J s}}{4\pi^2(0.623 \times 10^{12} \text{ s}^{-1})} = 2.69 \times 10^{-47} \text{ kg m}^2$$

(b) $0 - J$ transition: $\nu = \frac{h}{8\pi^2 I} [J(J+1) - 0] = \frac{h}{4\pi^2 I} \frac{J(J+1)}{2}$

$0 - 1$: $\nu = 0.623 \times 10^{12} \text{ s}^{-1}$; $\Delta E = h\nu = 4.13 \times 10^{-22} \text{ J}$

$0 - 2$: $\nu = 3 \times 0.623 \times 10^{12} \text{ s}^{-1}$; $\Delta E = h\nu = 1.24 \times 10^{-21} \text{ J}$

$0 - 3$: $\nu = 6 \times 0.623 \times 10^{12} \text{ s}^{-1}$; $\Delta E = h\nu = 2.48 \times 10^{-21} \text{ J}$

(c) Using isotope masses from Table 14.1 gives the reduced mass μ .

$$\mu = \frac{(1.0078 \text{ g mol}^{-1})(34.969 \text{ g mol}^{-1})(10^{-3} \text{ kg g}^{-1})}{(1.0078 + 34.969 \text{ g mol}^{-1})(6.022 \times 10^{23} \text{ mol}^{-1})} = 1.627 \times 10^{-27} \text{ kg}$$

$$R_e = (I/\mu)^{1/2} = 1.29 \times 10^{-10} \text{ m} = 1.29 \text{ \AA}$$

(d) The absorptions are the 3-4, 4-5, 5-6, and 6-7 transitions.

17.10 The population of energy level E_i relative to the ground state E_f is

$$\frac{N_i}{N_f} = \frac{g_i}{g_f} e^{-(E_i - E_f)/k_B T}$$

The rotational energy levels are

$$E_J = J(J+1) \frac{h^2}{8\pi^2 I} \quad J = 0, 1, 2, \dots$$

and the degeneracy is $2J + 1$. The population of energy level E_J relative to the ground state is therefore

$$\frac{N_J(E_J)}{N_0(E_0)} = g_J e^{-J(J+1)h^2/8\pi^2 I k T}$$

First we evaluate the part of the exponential factor that will recur in each calculation

$$\frac{h^2}{8\pi^2 I k T} = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8\pi^2 (66.8 \times 10^{-47} \text{ kg m}^2) (1.38 \times 10^{-23} \text{ J K}^{-1}) (298.15 \text{ K})} = 2.01 \times 10^{-3}$$

Note that all the units cancel away. The exponential factor of each term is $e^{J(J+1)(0.00201)}$.

The specific relative populations are

(a) $\frac{N_5}{N_0} = (2 \cdot 5 + 1)e^{-(5)(6)(0.00201)} = 11e^{-0.060} = 10.4$

(b) $\frac{N_{25}}{N_0} = (2 \cdot 25 + 1)e^{-(25)(26)(0.00201)} = 51e^{-1.31} = 13.8$

(c) $\frac{N_{15}}{N_0} = (2 \cdot 15 + 1)e^{-(15)(16)(0.00201)} = 31e^{-0.482} = 19.1$

Thus, energy levels above the ground state are significantly populated at room temperature, and rotational spectra will include transitions for which $J_i > 0$. This rotational distribution includes much higher values of J than does the distribution in problem 17.9 because the separation between rotational levels for N_2O is smaller than for NaH , thanks to its much larger moment of inertia.

17.18) The electron lost in the ionization of C_2H_4 will be from a bonding π -orbital because the π system in C_2H_4 is less than half filled, a fact that assures that all of the π -electrons are bonding electrons (in the ground state). The bond order between the two carbons in $C_2H_4^+$ is $3/2$, less than that in C_2H_4 .

17.22) The π -electrons in naphthalene are more delocalized in both the ground state and the excited states than the π -electrons in benzene, but the energy of the orbitals are lowered more in the excited state than in the ground state. This shifts the maximum absorption of light to a wavelength longer than 255 nm.

17.26) The spectrum will have two peaks, one for the chemically equivalent group of 4 protons on the benzene ring and one for the chemically equivalent group of 6 protons on the two methyl groups. The areas of the peaks will have ratio 1 : 1.5 or 4 : 6.

17.28

$$\begin{aligned}\text{Binding energy} &= h\nu_{\text{photon}} - 1/2m_e v^2 \\ &= 1253.6 \text{ eV} - \frac{1/2(9.109 \times 10^{-31} \text{ kg})(1.57 \times 10^7 \text{ m s}^{-1})^2}{1.60218 \times 10^{-19} \text{ J eV}^{-1}} \\ &= 1253.6 \text{ eV} - 700.7 \text{ eV} = 553 \text{ eV}\end{aligned}$$

From Figure 17.33, this must have been emitted from the σ_{g1s} orbital of O_2 .