CHEM 363
Physical Chemistry

Test: 18 May 2005 **Time allowed:** 60 minutes

Answer all questions.

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1. The molecule glyoxal ($C_2H_2O_2$) has a planar, *trans* structure.

   (a) Identify the symmetry operations of glyoxal and hence deduce its point group (see flow diagram on the next page).

   (b) Determine the symmetries of the 12 vibrational normal modes of glyoxal.

   (c) What is the symmetry of the torsional vibration?

   (d) What are the symmetry requirements for a particular vibrational mode to appear in

   (i) the infrared and
   (ii) the Raman spectrum?

   Give reasons for your answers.

   (e) State, with reasons, which of the vibrations of glyoxal are infrared active, Raman active or neither.

   (f) The mutual exclusion principle states that molecules with a centre of inversion can have no vibrations that are both infrared and Raman active. Explain this.

2. The geometry of the ion H_3^+ in its ground electronic state is that of an equilateral triangle. Its molecular orbitals can be reliably expressed as linear combinations of 1s atomic orbitals on each H atom.

   (a) Identify the symmetry operations of H_3^+ and hence deduce its point group.

   (b) Determine the symmetries of the three molecular orbitals derived from 1s orbitals centred on each of the three atoms.

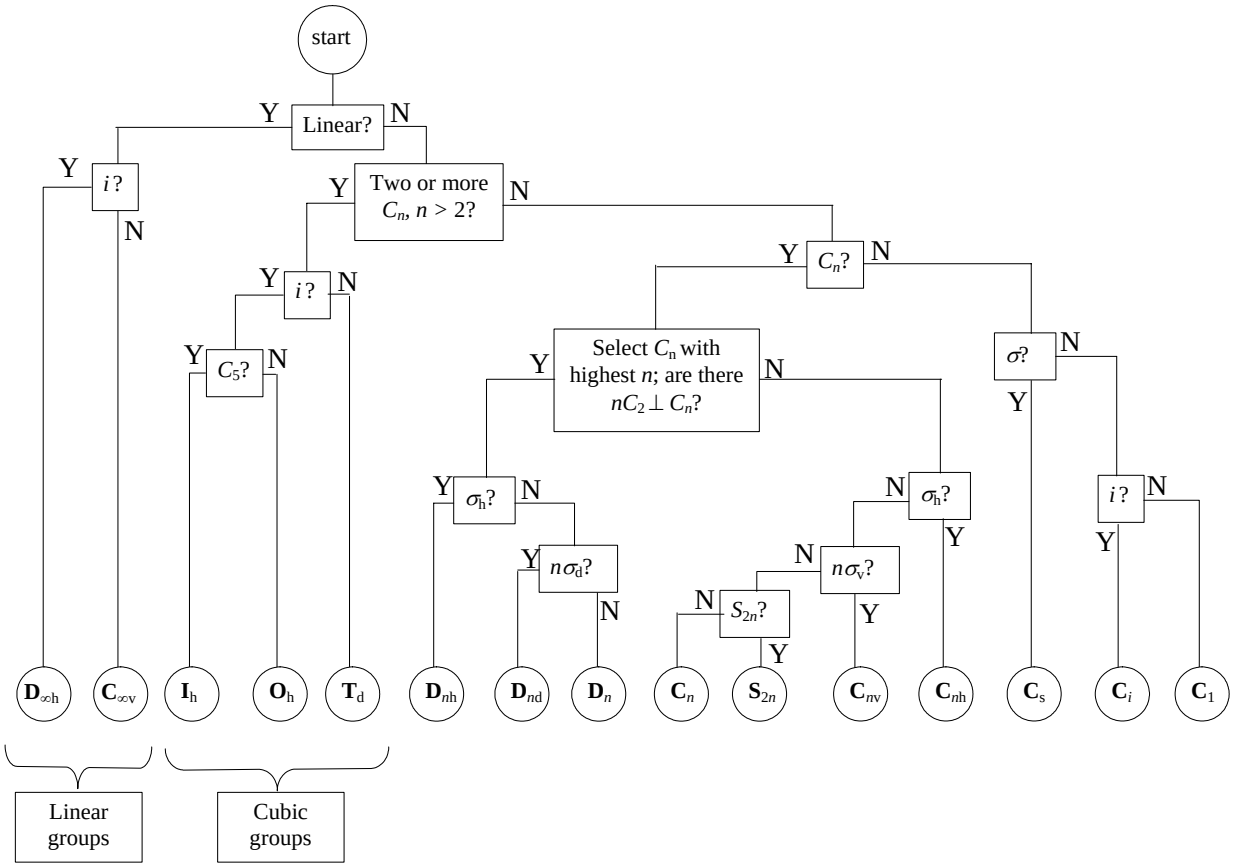
   (c) Derive the explicit forms of the molecular orbitals of H_3^+ in terms of linear combination of the 1s orbitals. Ensure that any mutually degenerate functions are orthogonal to each other.

   (d) Comment on the relevant stabilities of the species H_3 and H_3^+ in their ground states.

Useful equations:

$$a_m = \frac{1}{h}\sum_g \chi(g)\,\chi_m(g) = \frac{1}{h}\sum_c n_c\,\chi(c)\chi_m(c)$$

$$f' = \sum_g \chi_k(g)\,g(f)$$


start
Linear?
Y
N
i ?
Two or more Cn, n > 2?
Cn?
Select Cn with highest n; are there nC2 ⊥ Cn?
σ?
σh?
nσd?
nσv?
S2n?
C5?
D∞h
C∞v
Ih
Oh
Td
Dnh
Dnd
Dn
Cn
S2n
Cnv
Cnh
Cs
Ci
C1
Linear groups
Cubic groups

Determination of molecular point groups