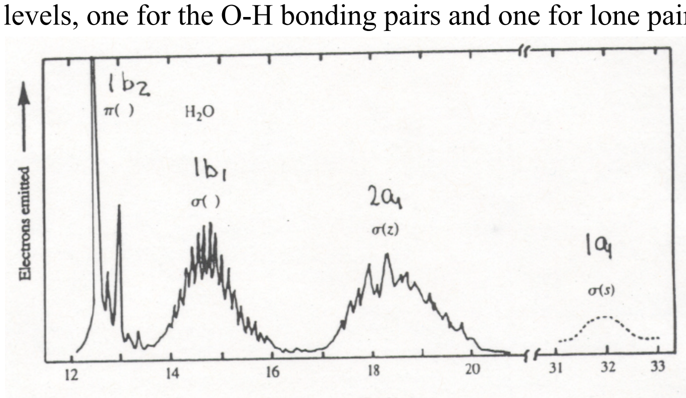
Inorganic Chemistry Cumulative Exam

Neal Mankad, 3 October 2019

1. At standard conditions (1 atm, 273.15 K), most elements are solids in pure form.
    a. Only the noble gases and five other elements are gaseous at standard conditions. What are those five elements?
    b. There are only two elements in the periodic table that are liquids at standard conditions. One is mercury (Hg). What is the other?
    c. Given that elemental Au (Z = 79) is a solid at standard conditions with melting point 1337 K, it might seem surprising that Hg (Z = 80) is a liquid with melting point 234 K. Provide a reasonable explanation for the anomalously low melting point of elemental Hg.
2. Irradiation of the octahedral complex $Cr(CO)_6$ with ultraviolet radiation ejects one CO ligand and produces $Cr(CO)_5$ as a transient intermediate. This species has been trapped in a cryogenic matrix and studied by vibrational spectroscopy at temperatures between 4.2 K and 10 K.
    a. Two possible structures for $Cr(CO)_5$ were considered by researchers initially. One has C_{4v} symmetry and the other has D_{3h} symmetry. Draw both structures.
    b. For each structure, determine the Mulliken symbols of the C≡O stretching combinations.
    c. In a classic 1971 study, Turner and coworkers[1] found that $Cr(CO)_5$ exhibits *three* peaks in the C≡O stretching region of its IR spectrum: 2093 cm^{-1}, 1966 cm^{-1}, and 1936 cm^{-1}. On the basis of this data, predict whether $Cr(CO)_5$ adopts a C_{4v} or D_{3h} structure.
    d. In 1974, Ozin and coworkers[2] determined that the 2093-cm^{-1} peak originally attributed to $Cr(CO)_5$ actually arose from an impurity. Using isotopic labeling studies, they were able to confirm that $Cr(CO)_5$ actually has just *two* peaks in the C≡O stretching region of its IR spectrum: 1962 cm^{-1} and 1933 cm^{-1}. On the basis of this new information, predict whether $Cr(CO)_5$ adopts a C_{4v} or D_{3h} structure.
3. As shown below, the valence electrons of water (H_2O) occupy _four_ different energy levels with ionization energies of approximately 12.5, 14.7, 18.1, and 32 eV.
    a. Show that the molecular orbital description of H_2O is consistent with this data.
    b. Discuss the shortcomings of other descriptions involving the population of _two_ valence energy levels, one for the O-H bonding pairs and one for lone pairs.



4. Several molybdenum complexes are shown below.

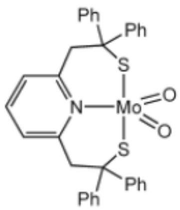
---

[1] M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (**1971**).

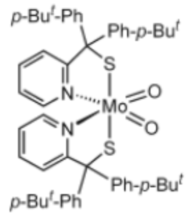
[2] E. P. Kündig and G. A. Ozin, *J. Am. Chem. Soc.*, 3820 (**1974**).

a. Which complexes are expected to be paramagnetic, and which are diamagnetic?

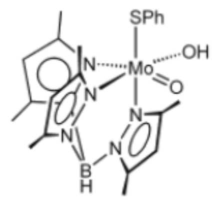
b. The ethene dithiolate (edt) ligands shown in complexes **31** and **32** is a canonical example of a "redox non-innocent" ligand. Explain what is meant by the term, "redox non-innocent". Discuss the concept with representative cases exhibiting redox innocence compared with non-innocence.



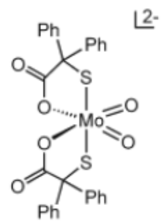
10



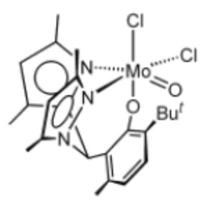
11



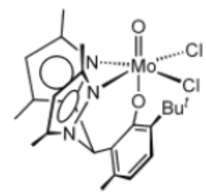
12



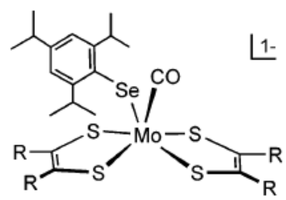
13



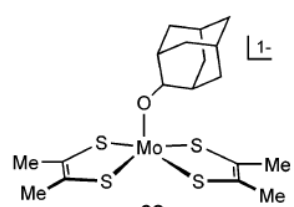
14



15



31



32

Character table for C_{2v} point group

	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Character table for C_{4v} point group

	E	$2C_4$ (z)	C_2	$2\sigma_v$	$2\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)

Character table for D_{3h} point group

	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	linear, rotations	quadratic
A'_1	1	1	1	1	1	1		x^2+y^2, z^2
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)