Chemistry 543

Spring Semester 1999
First Exam
March 4, 1999

1. Given the complete orthonormal set of functions $\{\alpha,\beta,\gamma\}$ which are eigenfunctions of the z component of angular momentum I_z with eigenvalues $\hbar$, $-\hbar$, and 0, respectively. The operators I^- and I^+ have the following properties:

$$I^-\alpha = \sqrt{2}\hbar\,\gamma \qquad I^+\alpha = 0$$
$$I^-\gamma = \sqrt{2}\hbar\,\beta \qquad I^+\gamma = \sqrt{2}\hbar\,\alpha$$
$$I^-\beta = 0 \qquad I^+\beta = \sqrt{2}\hbar\,\gamma$$

a. Find the matrix representations of the operator I_z, of $I_x \equiv (I^+ + I^-)/2$ and of $I_y \equiv (I^+ - I^-)/2i$ in this basis set.

$$\mathbb{I}_z = \begin{array}{c|ccc} & \beta & \gamma & \alpha \\ \hline \beta & -1 & 0 & 0 \\ \gamma & 0 & 0 & 0 \\ \alpha & 0 & 0 & +1 \end{array}\;\hbar \qquad \mathbb{I}^+ = \begin{array}{c|ccc} & \beta & \gamma & \alpha \\ \hline \beta & 0 & 0 & 0 \\ \gamma & 1 & 0 & 0 \\ \alpha & 0 & 1 & 0 \end{array}\;\sqrt{2}\hbar \qquad \mathbb{I}^- = \begin{array}{c|ccc} & \beta & \gamma & \alpha \\ \hline \beta & 0 & 1 & 0 \\ \gamma & 0 & 0 & 1 \\ \alpha & 0 & 0 & 0 \end{array}\;\sqrt{2}\hbar$$

$\mathbb{I}_x = \frac{1}{2}(\mathbb{I}^+ + \mathbb{I}^-)$ add the matrices to get

$$\mathbb{I}_x = \frac{\sqrt{2}\hbar}{2}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

$$\mathbb{I}_y = \frac{1}{2i}(\mathbb{I}^+ - \mathbb{I}^-) = \frac{\sqrt{2}\hbar}{2i}\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}$$

b. Find the eigenvalues of I_x operator.

$$\det \frac{\sqrt{2}\hbar}{2}\begin{bmatrix} 0-\lambda & 1 & 0 \\ 1 & 0-\lambda & 1 \\ 0 & 1 & 0-\lambda \end{bmatrix} = 0 \qquad -\lambda\begin{bmatrix} -\lambda & 1 \\ 1 & -\lambda \end{bmatrix} - 1\begin{bmatrix} 1 & 1 \\ 0 & -\lambda \end{bmatrix} = 0$$

$$-\lambda(\lambda^2-1) - 1(-\lambda) = 0$$
$$\lambda^3 - 2\lambda = 0 = \lambda(\lambda^2-2)$$

Roots are $\lambda = 0$, $\lambda = \pm\sqrt{2}$

Now put back $\frac{\sqrt{2}\hbar}{2}$ factor $\Rightarrow$ Eigenvalues of I_x are 0, $+\hbar$, $-\hbar$

2. For the nuclear spin system with two inequivalent sets of nuclei, a single of spin 1/2 and three of a kind also with spin 1/2. (NMR users call this an AB_3 system.) *Determine the NMR Hamiltonian matrix in blocked-out form*, i.e., write all the non-zero elements in terms of the frequencies ν_A, ν_B, and the coupling constant J.

$$\mathcal{H}/h = -\nu_B\,(I_z(1)+I_z(2)+I_z(3)) - \nu_A\,I_z(4) + J\,(\mathbf{I}(1)+\mathbf{I}(2)+\mathbf{I}(3)) \bullet \mathbf{I}(4)$$

Couplings also exist between B and B nuclei but we ignore these, as they will not affect the spectrum. The operators I_x, I_y, I_z have the following properties:

$I_z(1)\alpha(1) = \frac{1}{2}\hbar\,\alpha(1)$ $\quad$ $I_z(1)\,\beta(1) = -\frac{1}{2}\hbar\,\beta(1)$

$I_x(1)\alpha(1) = \frac{1}{2}\hbar\,\beta(1)$ $\quad$ $I_x(1)\,\beta(1) = \frac{1}{2}\hbar\,\alpha(1)$

$I_y(1)\alpha(1) = \frac{1}{2}i\hbar\,\beta(1)$ $\quad$ $I_y(1)\,\beta(1) = -\frac{1}{2}i\hbar\,\alpha(1)$

$\alpha(1)$ and $\beta(1)$ are functions associated with particle 1.

$\mathbf{I}(1) \equiv I_x(1)\,\mathbf{i} + I_y(1)\,\mathbf{j} + I_z(1)\,\mathbf{k}$ $\quad$ **i**, **j**, and **k** are unit vectors along the x, y, and z directions.

Recall the step up and step down operators:

$$I_\pm \Psi_{I,m} = [I(I+1) - m(m\pm1)]^{1/2}\hbar\,\Psi_{I,m\pm1}$$

Remember to use as basis for your representation, the eigenfunctions of

$F_z = F_z(A) + F_z(B)$,

$F_z(B) = I_z(1)+I_z(2)+I_z(3)$.

Generate basis set grouped according to F_z values:

$F_{z_B} = 3/2$ $\quad \alpha\alpha\alpha$ $\qquad\qquad F_{z_A} = 1/2 \quad \alpha$

$1/2 \begin{cases} \alpha\alpha\beta \\ \alpha\beta\alpha \\ \beta\alpha\alpha \end{cases}$ $\qquad\qquad -\frac{1}{2} \quad \beta$

$-1/2 \begin{cases} \beta\beta\alpha \\ \beta\alpha\beta \\ \alpha\beta\beta \end{cases}$ $\qquad\qquad F_z(tot) = F_{z_A} + F_{z_B}$

$-3/2$ $\quad \beta\beta\beta$

Basis functions: products of those given on previous page numbered as follows:

① $(\frac{1}{2})(\frac{3}{2})$

$\uparrow F_{zA}$ $\uparrow F_{zB}$

② $(-\frac{1}{2})(\frac{3}{2})$

③ ④ ⑤ $(\frac{1}{2})(\frac{1}{2})$

⑥ ⑦ ⑧ $(-\frac{1}{2})(\frac{1}{2})$

⑨ ⑩ ⑪ $(\frac{1}{2})(-\frac{1}{2})$

⑫ ⑬ ⑭ $(-\frac{1}{2})(-\frac{1}{2})$

⑮ $(\frac{1}{2})(-\frac{3}{2})$

⑯ $(-\frac{1}{2})(-\frac{3}{2})$

Diagonal elements of H:

$$-(\nu_A F_{zA} + \nu_B F_{zB}) + J F_{zA} F_{zB}$$

1. $-(\frac{1}{2}\nu_A + \frac{3}{2}\nu_B) + \frac{3}{4}J$

2. $-(-\frac{1}{2}\nu_A + \frac{3}{2}\nu_B) - \frac{3}{4}J$

3, 4, 5 $-(\frac{1}{2}\nu_A + \frac{1}{2}\nu_B) + \frac{1}{4}J$

6, 7, 8 $-(-\frac{1}{2}\nu_A + \frac{1}{2}\nu_B) - \frac{1}{4}J$

9, 10, 11 $-(\frac{1}{2}\nu_A - \frac{1}{2}\nu_B) - \frac{1}{4}J$

12, 13, 14 $-(-\frac{1}{2}\nu_A - \frac{1}{2}\nu_B) + \frac{1}{4}J$

15 $-(\frac{1}{2}\nu_A - \frac{3}{2}\nu_B) - \frac{3}{4}J$

16 $-(-\frac{1}{2}\nu_A - \frac{3}{2}\nu_B) + \frac{3}{4}J$

Off-diag H matrix elements are zero unless

$\Delta F_{zB} = -1$ and $\Delta F_{zA} = +1$

or $\Delta F_{zB} = +1$ and $\Delta F_{zA} = -1$

in which case m.e. = respectively,

$$J \cdot \sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1) - \tfrac{1}{2}(\tfrac{1}{2}-1)} \cdot \sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1) + \tfrac{1}{2}(-\tfrac{1}{2}+1)} = J$$

or

$$J \cdot \sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1) + \tfrac{1}{2}(-\tfrac{1}{2}+1)} \cdot \sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1) - \tfrac{1}{2}(\tfrac{1}{2}-1)} = J$$

Zero for different F_z(tot))

A B

α ααα	β ααα	α ααβ	α αβα	α βαα	β ααβ	β αβα	β βαα	α ββα	α βαβ	α αββ	β ββα	β βαβ	β αββ	α βββ	β βββ
		0													
		J	J	J											
			0	0			0							0	
				0											
						0	0	0	0	J					
							0	J	0	J					
								0	J	0			0		
									0	0					
										0					
												0	0	J	
													0	J	0
														J	

3. The ground electronic state of O_2 is $^3\Sigma_g^-$. What are the results of the following operations on the electronic wavefunction $\Psi(^3\Sigma_g^-)$?

$-\Psi_{^3\Sigma_g^-} = I\,\Psi(^3\Sigma_g^-)$ inversion of all space-fixed coordinates through the origin

$-\Psi_{^3\Sigma_g^-} = \sigma_v\,\Psi(^3\Sigma_g^-)$ reflection of molecule-fixed electronic coordinates through a plane containing the internuclear axis

$+\Psi_{^3\Sigma_g^-} = i\,\Psi(^3\Sigma_g^-)$ inversion of molecule fixed electronic coordinates through the origin (same as inversion of space-fixed electronic coordinates)

$-\Psi_{^3\Sigma_g^-} = P_{AB}\Psi(^3\Sigma_g^-)$ the interchange of the indistinguishable nuclei A and B

$-\Psi_{^3\Sigma_g^-} = P_{12}\Psi(^3\Sigma_g^-)$ the interchange of any two electrons

always (electrons are Fermions)

For $^{16}O_2$ molecule, what are the consequences of the nuclear spin of ^{16}O being zero? Apply your discussions specifically to the ground electronic state.

^{16}O nuclei are bosons. Therefore

$P_{AB}\Psi_{^3\Sigma_g^-}\psi_{vib}\psi_{rot}\psi_{nucl\,spin} = (+)\Psi_{^3\Sigma_g^-}\psi_{vib}\psi_{rot}\psi_{nucl\,spin}$

$P_{AB}\Psi_{^3\Sigma_g^-} = -\Psi_{^3\Sigma_g^-}$

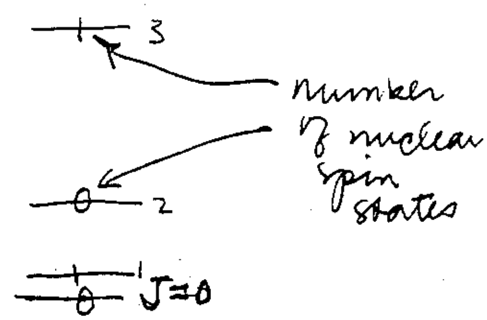
$P_{AB}\psi_{vib} = \psi_{vib}$

$P_{AB}\psi_{rot} = (-1)^J\psi_{rot}$

Since $I=0$ then only one nuclear spin state, the ortho

no. of nuclear spin states = 0 or 1

∴ only odd J states are possible



4. The potential function for ArH^+ ground state is shown below:

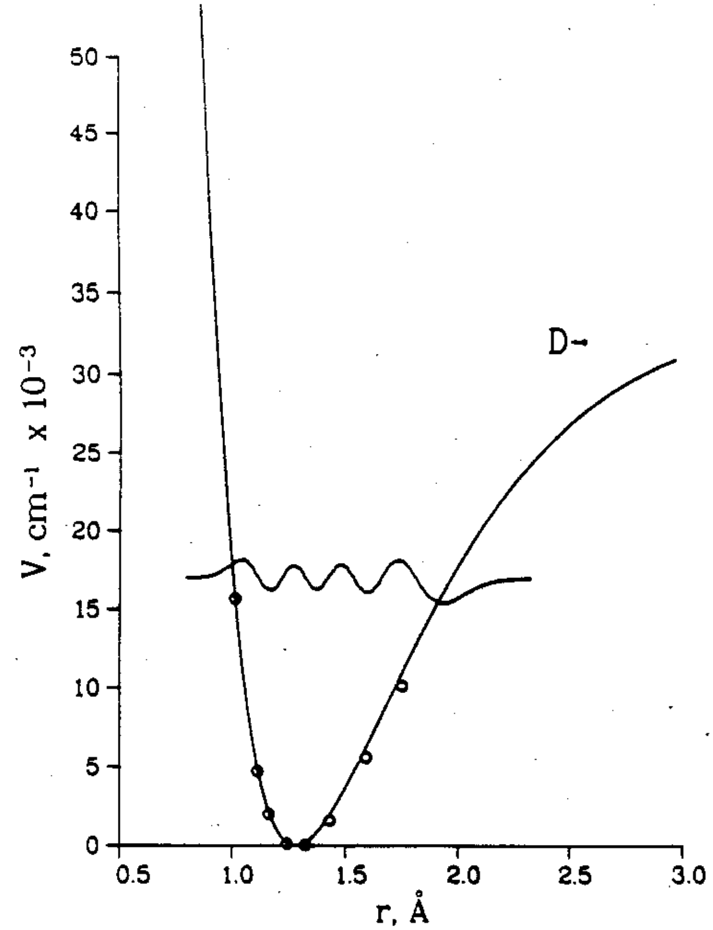


FIG. 5. Potential functions for ArH^+. The solid curve is experimental, circles correspond to points CEPA surface from Ref. (*38*).

JOURNAL OF MOLECULAR SPECTROSCOPY 131, 343–366 (1988)

Experimental Potential Functions for Open and Closed Shell Molecular Ions: Adiabatic and Nonadiabatic Corrections in $X\,^3\Sigma^-$ OH^+ and $X\,^1\Sigma^+$ ArH^+

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The points (circles) are the solutions to electronic motion calculated by Rosmus (1979). The solid curve is derived from a fit to experimental data (312 transitions from microwave, far infrared, infrared , of 5 isotopomers). One of the wavefunctions obtained by numerical solution of the nuclear motion problem is shown at the appropriate energy [Gruebele et al. (1988)] D→ refers to some asymptotic energy on the far right of the figure.

Give specific answers to the following:

a) Give the differential equation that had to be solved in order to find the circles.

b) Give the differential equation that had to be solved numerically to find the wiggly curve? Whaich particular state is this?

c) From the figure you have enough information to estimate the vibrational frequency and D_0 of ArH^+ molecule. Do it.

d) What does simple valence bond theory tell us about the stability of the ground states of the rare gas monohydrides (such as ArH) and their ions (such as ArH^+)? Explain.

④ Ar has 18 electrons, H^+ has none

a) To get the values $\overset{U(R)}{\wedge}$ for the circles need to solve the differential equation

$$\left\{ \frac{-\hbar^2}{2m} \sum_{i=1}^{18} \left(\nabla_i^2 - \frac{18e^2}{r_{iAr}} - \frac{e^2}{r_{iH}} + \sum_{\substack{j \\ j\neq i}} \frac{e^2}{r_{ij}} \right) + \frac{18e^2}{R} \right\} \cdot$$

$$\psi_{elec}(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_{18}, R) = U(R)\, \psi_{elec}(\vec{r}_1, \cdots; R)$$

for each value of R. Do this 8 times, once for each R, $1.0\,\text{Å}, \cdots, 1.75\,\text{Å}$. Choose the lowest of values of $U(R)$ at each R.

b) To find the wiggly curve, need to solve

$$\left\{ -\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dR^2} + \frac{2}{R}\frac{d}{dR} \right) + \frac{J(J+1)\hbar^2}{2\mu R^2} + V(R) \right\} F(R)$$

$$= E\, F(R)$$ This is the function of the wiggly curve

where fit $J=0$, and $V(R)$ is the set of values of V from the solid $\vee$ curve shown, presumably described by some functional form with parameters fitted to 312 data points (frequencies). From the number of nodes $= 7$ we see that this must correspond to $v = 7$, $J = 0$.

c) Since the wiggly curve is drawn at the appropriate energy (that is $17 \times 10^3\,cm^{-1}$, reading off the figure) then

$$17 \times 10^3\,cm^{-1} = (v + \tfrac{1}{2})h\nu_e + B_e J(J+1) - x_e h\nu_e (v+\tfrac{1}{2})^2$$
$$- \alpha_e (v + \tfrac{1}{2}) J(J+1) - D_e [J(J+1)]^2 + Y_{00}$$

Substitute $v = 7$, $J = 0$, neglect α_e, x_e and Y_{00},

$$17 \times 10^3 \, cm^{-1} = (7 + \tfrac{1}{2}) \, \tilde{\nu}_e$$

$$\tilde{\nu}_e \simeq 2\,270 \, cm^{-1}$$

The $D \rightarrow$ appears at $32 \times 10^3 \, cm^{-1}$, thus

$$D_e = 32 \times 10^3 \, cm^{-1}$$

$$D_0 = D_e - \tfrac{1}{2} \tilde{\nu}_e \simeq 29.7 \times 10^3 \, cm^{-1}$$

d) In Valence Bond theory the bond is formed by pairing of electron spins, one from each atom. Since Ar atom has no unpaired spins, and H atom has one ArH is predicted to be unstable. On the other hand ArH^+ can be thought of as being formed from Ar^+ and H atom which each have one unpaired spin, therefore a covalent bond can be formed making ArH^+ stable.

5. Given the following electronic wavefunction of a diatomic molecule:

$$\frac{1}{2}\left\{\pi^+(1)\,\pi'^-(2) - \pi^+(2)\pi'^-(1) - \pi^-(1)\pi'^+(2) + \pi^-(2)\pi'^+(1)\right\}$$

the π MOs being ungerade. For this electronic wavefunction, determine:

a. total parity

b. the symmetry with respect to interchange of electrons 1 and 2.

c. the symmetry with respect to inversion of electronic coordinates.

d. the symmetry with respect to interchange of the two identical nuclei.

What then is the term symbol? In each case show how you got your answers. Draw a rotational energy level diagram for this state, more or less to scale (neglecting any energy splittings due to angular momentum coupling), for identical nuclei of spin 1/2.

Label each rotational level according to:

(1) total parity

(2) the symmetry of the space part of the total wavefunction with respect to interchange of the two nuclei

(3) the total degeneracy of each rotational level.

(5) a) Parity of the state described by given electronic function can be found by seeing the result of $\sigma_v(xz)$ reflection on this function. This reflection converts ϕ to $-\phi$ and leaves r_A and r_B unchanged. Thus, since ϕ appears as $\frac{1}{\sqrt{2\pi}}e^{i\Lambda\phi}$ in the wavefunction, then reflection gives the same result as converting Λ to $-\Lambda$. Let us do this:

$$\sigma_v(xz)\psi_{elec} = \frac{1}{2}\left\{\pi^-(1)\pi'^+(2) - \pi^-(2)\pi'^+(1) - \pi^+(1)\pi'^-(2) + \pi^+(2)\pi'^-(1)\right\}$$

$= -\psi_{elec}$ so the total parity of the electronic wfn is $(-)$.

Apply P_{12} to ψ_{elec} i.e. interchanging labels (1) and (2), we get $-\psi_{elec}$. Therefore this wfn is antisym with resp. to interchange of electrons (1) and (2). This means that ψ_{elec} must be spin <u>sym</u> in order to get ψ_{total} to be antisymmetric with respect to P_{12}. This must be a <u>triplet</u> $\begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)] \end{cases}$

Since the pi MOs are ungerade (Π_u) then the state must be $u \times u$ or g. Also we see that the products are all $\pi^+\pi^-$ which means $\Lambda_{tot} = +1-1=0$

Thus, the term symbol must be $^3\Sigma_g^-$.

c) Symmetry with respect to interchange of nuclei A and B is: $P_{AB}\psi_{elec}(^3\Sigma_g^-) = -\psi_{elec}(^3\Sigma_g^-)$

~~For each rotational level J, $P_{AB}\psi_{elec}\psi_{rot} = (-)(-1)^J\psi_{elec}\psi_{rot}$~~

For each rotational level J, $= a$ for even J, s for odd J

Parity $\psi_{elec}\psi_{rot} = (-)(-1)^J\psi_{elec}\psi_{rot} = -$ for even J, $+$ for odd J

d) symmetry with respect to inversion of electronic coords is g as we have found already

e) Total degeneracy is

$(2S+1)(2J+1)(2I+1)^2$ if no nuclear spin state selectivity

but it is actually $(2S+1)(2J+1)\,I\,(2I+1)$ for para

and $(2S+1)(2J+1)(I+1)(2I+1)$ for ortho

that is, $3(2J+1)\cdot 1$ for para states, $3(2J+1)\cdot 3$ for ortho states

σ_v	P_{AB}	degeneracy		nuclear spin function
$-$	a	81	4	ortho
$+$	s	21	3	para
$-$	a	45	2	ortho
$+$	s	9	1	para
$-$	a	9	$J=0$	ortho

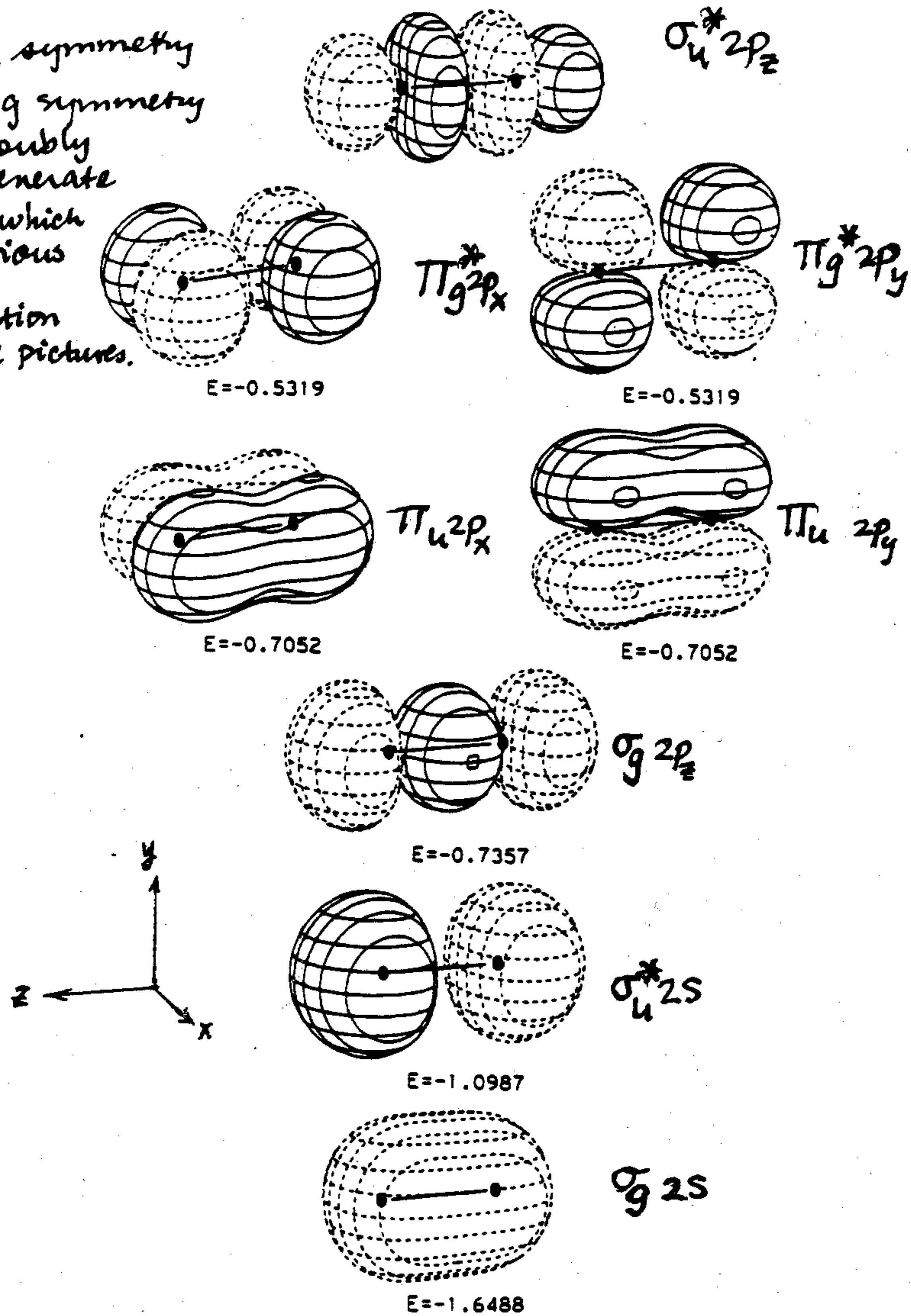
$^3\Sigma_g^-$

one $\dfrac{\alpha(A)\beta(B) - \beta(A)\alpha(B)}{\sqrt{2}}$

three $\begin{cases} \alpha(A)\alpha(B) \\ \dfrac{\alpha(A)\beta(B) + \beta(A)\alpha(B)}{\sqrt{2}} \\ \beta(A)\beta(B) \end{cases}$

6. The molecular orbitals of a diatomic molecule are shown here. Dashed lines correspond to negative values of the wavefunction. Label each one fully following the usual notation, <u>including the atomic orbitals they come from</u>.

From σ, π, symmetry
u or g symmetry
π is doubly degenerate
all of which are obvious upon inspection of the pictures.



7.

New Observations on the Visible Spectrum of Antimony Monoxide

JOURNAL OF MOLECULAR SPECTROSCOPY **130**, 382–388 (1988)

WALTER J. BALFOUR AND RAM S. RAM[1]

A summary of the observed low-lying states of SbO is given in Fig. 1. The ground electron configuration may be written

$$\cdots(z\sigma)^2(y\sigma^*)^2(xp\sigma)^2(w\pi)^4(v\pi^*)^1\!:\ X^2\Pi \qquad \text{(I)}$$

with some low-energy configurations being

$$\cdots(z\sigma)^2(y\sigma^*)^2(xp\sigma)^2(w\pi)^3(v\pi^*)^2\!:\ {}^2\Pi(3),\ {}^2\Phi,\ {}^4\Pi \qquad \text{(II)}$$

$$\cdots(z\sigma)^2(y\sigma^*)^2(xp\sigma)^1(w\pi)^4(v\pi^*)^2\!:\ {}^2\Sigma^+,\ {}^2\Sigma^-,\ {}^2\Delta,\ {}^4\Sigma^- . \qquad \text{(III)}$$

It is probable that the $(xp\sigma)$ and $(w\pi)$ orbitals are similar in energy and bonding powers . The $(w\pi)$ and $(v\pi^*)$ orbitals are relatively bonding and antibonding, respectively, so that the electron promotion from $(w\pi)$ or $(xp\sigma)$ to $(v\pi^*)$ results in a weaker bond.

Derive the given term symbols from the excited electronic configurations

For π^2 first this gives

+1	—	↑↓	↓	↑	↑	↓
−1	↑↓	—	↑	↓	↑	↓
λ	−2	+2	0	0	0	0
M_S	0	0	0	0	1	−1

$\Lambda = 2$, $S = 0$ $\qquad$ $\Lambda = 0$, $S = 0$ $\qquad$ $\Lambda = 0$, $S = 1$

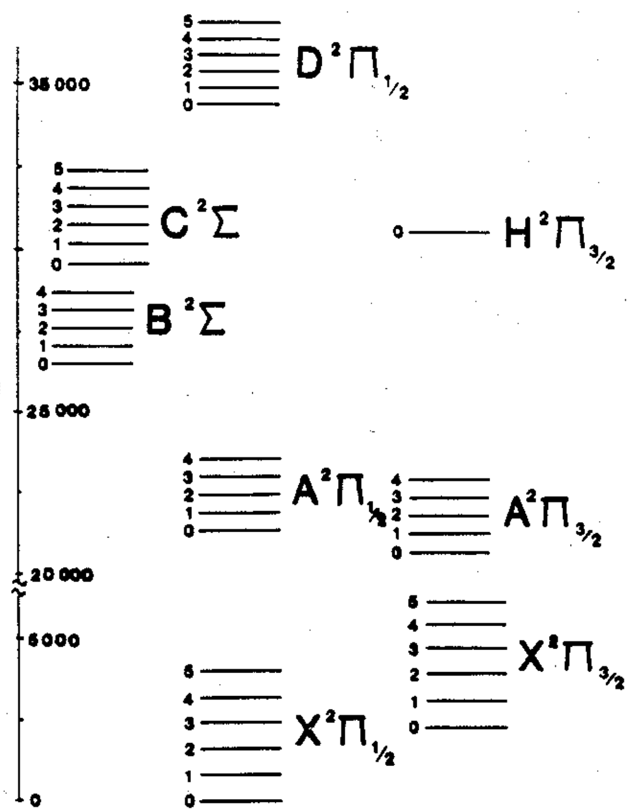


FIG. 1. Observed low-lying states of SbO (in cm^{-1}).

(II):

π^3 is like π (one hole in π^4)

$+1$	—	—	$\uparrow$	$\downarrow$
-1	$\uparrow$	$\downarrow$	—	—
λ	-1	-1	$+1$	$+1$
M_S	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$

$\Lambda = 1$
$S = 1/2$

can make all combos with π^2

$S=\frac{1}{2}$ and $\Lambda = 1+2$ or $2-1 \longrightarrow {}^2\Phi, {}^2\Pi$

$S = \frac{1}{2}$ and $\Lambda = 1+0 \longrightarrow {}^2\Pi$

$S = \frac{3}{2}$ or $\frac{1}{2}$ and $\Lambda = 1+0 \longrightarrow {}^4\Pi\ {}^2\Pi$

(III):

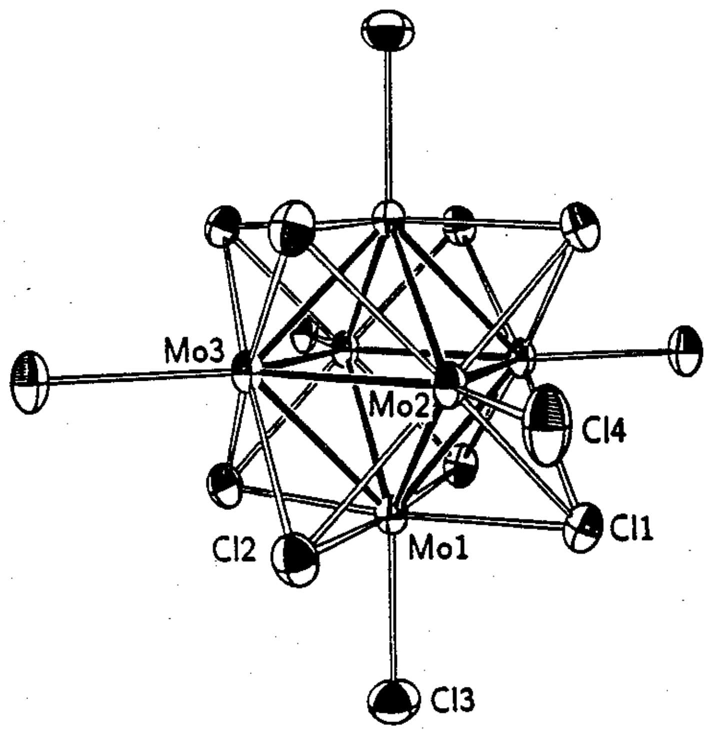
π^2 with σ^1 gives

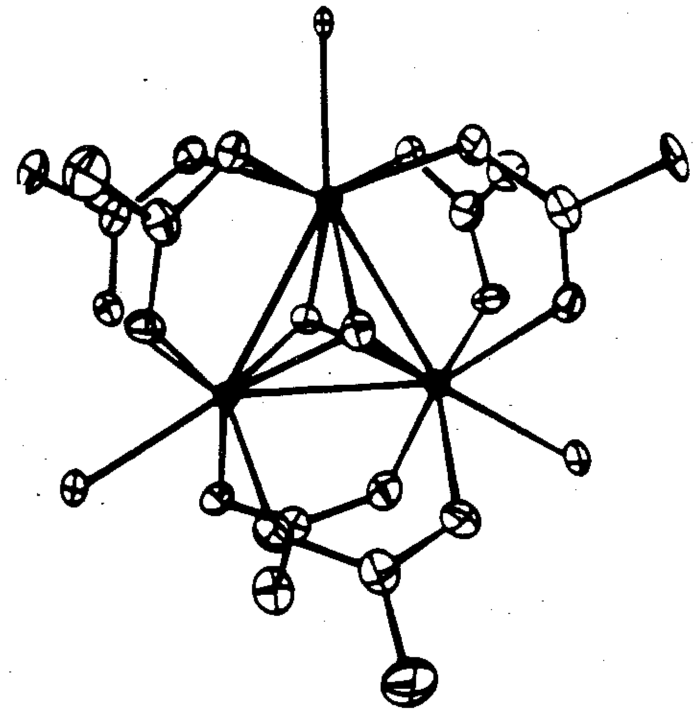
$\Lambda=2$, $S=0$	$\Lambda=0$, $S=1/2$	$\Lambda=2$, $S=1/2$	${}^2\Delta$
$\Lambda=0$, $S=0$	$\Lambda=0$, $S=\frac{1}{2}$	$\Lambda=0$, $S=\frac{1}{2}$	${}^2\Sigma^+$
$\Lambda=0$, $S=1$	$\Lambda=0$, $S=\frac{1}{2}$	$\Lambda=0$, $S=\frac{3}{2},\frac{1}{2}$	${}^4\Sigma^-, {}^2\Sigma^-$

8. Classify the following molecules according to their point group symmetry.

a. Mo_6Cl_{12}

b. $W_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$





a. O_h (D_{4h} possible if axially compressed or elongated)

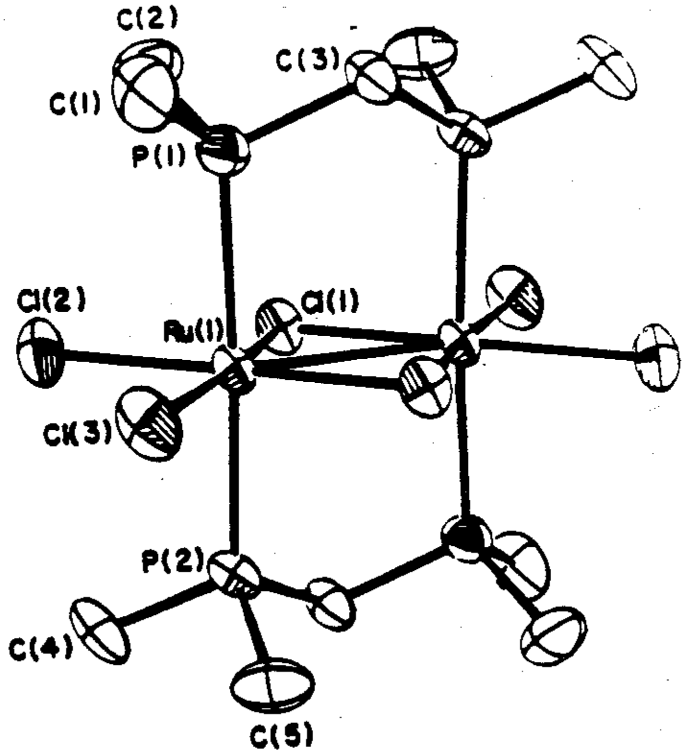
b. D_{3h} (D_{2h} possible but would require that Ru–P–C–P–Ru ~P–C–P be all in same plane

c. C_i

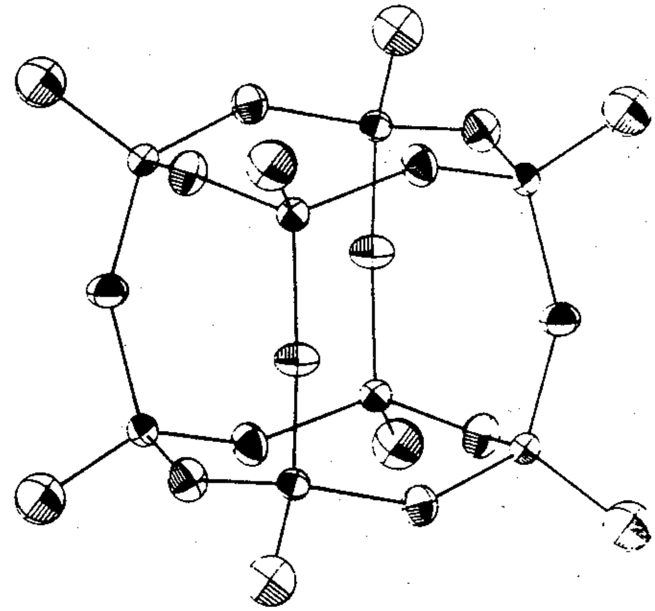
d. O_h

e. S_6

c. $Ru_2Cl_4(dmpm)_2$



d. silasesquioxane $H_8Si_8O_{12}$



e. side and end view of the $[Cr_2E_{24}]^{3-}$ anion, where E is Se or Te (not both)

Chemical Reviews, 1993, Vol. 93, No. 3 1045