ANSWERS TO MIDTERM EXAMINATION

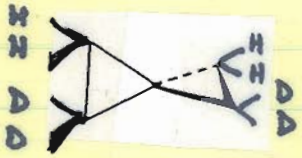
1. CHEM*3870 SAMPLE ANSWERS

(a) SF_5Cl

(2) C_{4v}

dipole moment Yes

(b) $C_5H_4D_4$



(2) C_2

dipole moment Yes

(c) bicyclo[3.3.3]undecane

(2)

C_{3h}

dipole moment No

(d) twistane

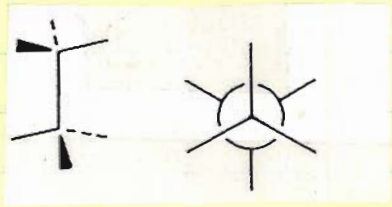
D_2

(2)

dipole moment No

(e) staggered ethane

(2)



D_{3d}

dipole moment No

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(Only molecules belonging to the $C_1, C_s, C_n, C_{nv}, C_{\infty v}$ point groups can have permanent electric dipole moments.)

2. (a) S_4^1

$S_4^2 = C_2$ (2)

S_4^3

$S_4^4 = E$

(b)

	E	S_4^1	S_4^3	C_2^1
E	E	S_4^1	S_4^3	C_2^1
S_4^1	S_4^1	C_2	E	S_4^3
S_4^3	S_4^3	E	C_2	S_4^1
C_2^1	C_2^1	S_4^3	S_4^1	E

(3)

(c) GROUP IS ABELIAN.
THUS EACH ELEMENT IS
IN A CLASS BY ITSELF. (2)

(d) ONLY PROPER SUBGROUP

	E	C_2
E	E	C_2
C_2	C_2	E

(1)

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T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

3.

(a)

	E
A_1	1
A_2	1
E	2
T_1	3
T_2	3
	4

(2)

l_i $\quad i$ RUNS OVER IRR. REP.

$$\sum_i l_i^2 = (1)^2 + (1)^2 + (2)^2 + (3)^2 + (3)^2$$
$$= 24$$
$$h = 24 \quad \text{ORDER OF GROUP}$$

1	E
8	C_3
3	C_2
6	S_4
6	σ_d
24	

(b) TAKE ONE (OR MORE) OF THE IRREDUCIBLE REPRESENTATIONS AS EXAMPLES.

e.g. A_1 $\quad (1)^2 + 8(1)^2 + 3(1)^2 + 6(1)^2 + 6(1)^2 = 24 = h$

(2) E $\quad (2)^2 + 8(-1)^2 + 3(2)^2 + 6(0)^2 + 6(0)^2 = 24 = h$

T_2 $\quad (3)^2 + 8(0)^2 + 3(-1)^2 + 6(-1)^2 + 6(1)^2 = 24 = h$

(c) TAKE TWO IRREDUCIBLE REPRESENTATIONS (2)

e.g. T_1 and T_2

$$1(3)(3) + 8(0)(0) + 3(-1)(-1) + 6(1)(-1) + 6(-1)(1)$$
$$= 9 + 3 - 6 - 6 = 0$$

(d)

Γ_{RED}	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
	6	0	2	0	2

3. (CONTINUED) $a_i = \frac{1}{h}\sum \chi(R)\chi_i(R)$

(5)

$$a_{A_1} = \frac{1}{24}(6\cdot1\cdot1 + 8\cdot0\cdot1 + 3\cdot1\cdot2 + 6\cdot0\cdot1 + 6\cdot2\cdot1) = \frac{1}{24}(6+6+12) = 1$$

$$a_{A_2} = \frac{1}{24}(6\cdot1\cdot1 + 8\cdot0\cdot1 + 3\cdot1\cdot2 + 6\cdot0\cdot(-1) + 6\cdot2\cdot(-1)) = \frac{1}{24}(6+6-12) = 0$$

$$a_E = \frac{1}{24}(6\cdot2\cdot1 + 8\cdot0\cdot(-1) + 3(2)(2) + 0 + 0) = \frac{1}{24}(12+12) = 1$$

$$a_{T_1} = \frac{1}{24}(6\cdot3\cdot1 + 0 + 3(2)(-1) + 0 + 2(-1)6) = \frac{1}{24}(18-6-12) = 0$$

$$a_{T_2} = \frac{1}{24}(6\cdot3\cdot1 + 0 + 3(2)(-1) + 0 + 6(2)(1)) = \frac{1}{24}(18-6+12) = 1$$

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$$\Gamma_{RED} = A_1 \oplus E + T_2$$

4. $$\varepsilon_{J,v} = BJ(J+1) + (v+\tfrac{1}{2})\partial_e - (v+\tfrac{1}{2})^2 \chi_e \partial_e$$

ASSUME B CONSTANT IN $v''=0$ AND $v'=1$

$$\Delta\varepsilon = \varepsilon_{J',v'=1} - \varepsilon_{J'',v''=0}$$

$$= B J'(J'+1) + \frac{3}{2}\partial_e - \frac{9}{4}\chi_e\partial_e - \left[BJ''(J''+1) + \frac{1}{2}\partial_e - \frac{1}{4}\chi_e\partial_e \right]$$

(4)

$v'=1 \longleftarrow v''=0$

✓ ✓

$$\Delta\varepsilon = \partial_e(1-2\chi_e) + B(J'-J'')(J'+J''+1)$$

NOW SPECIALIZE FURTHER FOR $\Delta J = +1$ AND $\Delta J = -1$

$\Delta J = +1 \quad J' = J'' + 1$

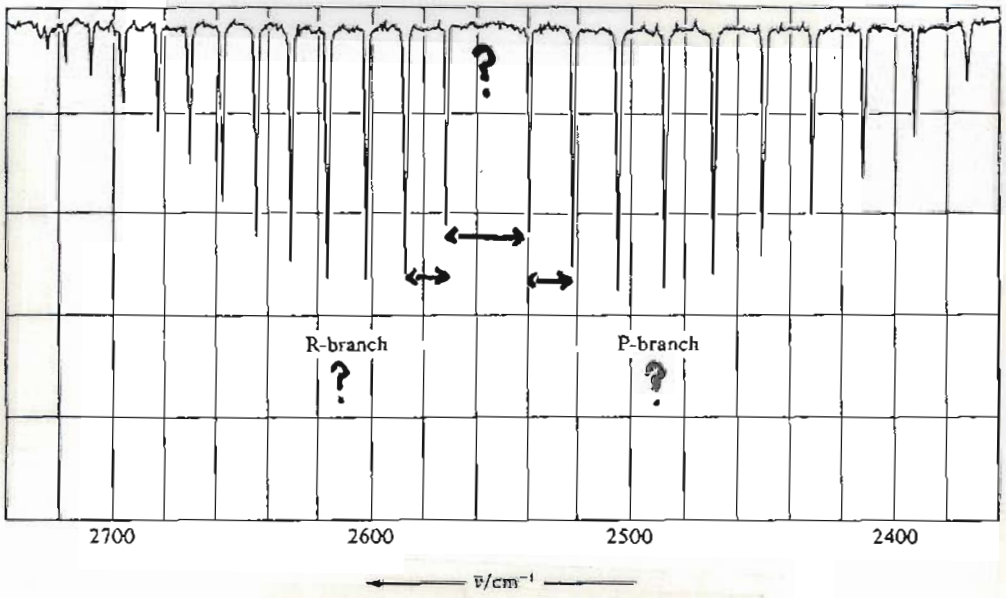
$J' - J'' = +1$

$\Delta \varepsilon = \nu_e(1 - 2x_e) + 2B(J'' + 1)$ ✓

$\Delta J = -1 \quad J'' = J' + 1$

$J' - J'' = -1$

$\Delta \varepsilon = \nu_e(1 - 2x_e) - 2B(J' + 1)$ ✓



The rotational-vibrational spectrum of the $0 \rightarrow 1$ vibrational transition of HBr(*g*).

(b) ✓ R $\Delta J = +1$

✓ P $\Delta J = -1$

✓ Q $\Delta J = 0$ FORBIDDEN NO TRANSITION

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✓ - SEPARATION ~ 2B EXCEPT 4B ACROSS MISSING $\Delta J = 0$ LINE

- SOME DISTORTION, SMALLER SEPARATION HIGH J

✓ - INTENSITIES - BOLTZMANN DIST^N OVER ROT. LEVELS

ROT. $(2J+1)$ DEGENERACY $J=0$ NOT MOST POPULATE

4. (c) FRANCK-CONDON

vertical transitions - nuclei do not relax as electronic

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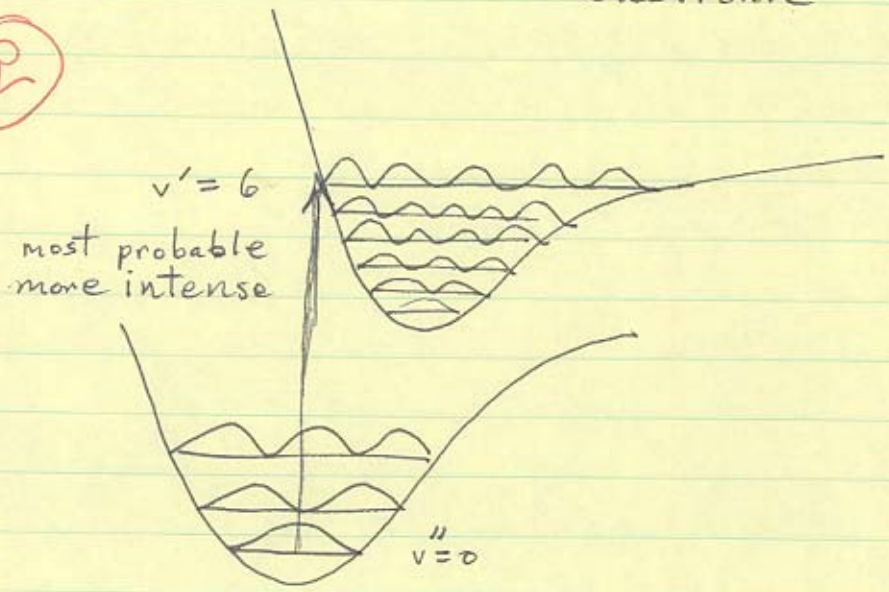

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