1. interaction rayonnement – syst. at, mol., detection des photons, absorption: baisse du flux de photons, emission: detection de photons emises
interet : renseignements sur – structure electronique, type d'atome
– propriétés moléculaires, comme cte de rot (mom. d'inertie, distance d'eq pour diatomiques,
– cte de raideur pour vibrations

2 mesure 'à distance', important pour astrophysique

2. 1 a) $1s^2 2s^2 2p^6 3s^2 = [Ne]3s^2$ $l_1 = l_2 = 0 \Rightarrow L = 0$, $s_1 = s_2 = \frac{1}{2} \Rightarrow S = 0$, $\cancel{1}$ $^1S_0$
couches fermés $[Ne]$ ne contribuent pas car $L = S = 0$

1 b) $l_1 = l_2 = 0 \Rightarrow$ 1 orbital spatiale, ϕ_{3s} et 2 electrons equivalents α, β

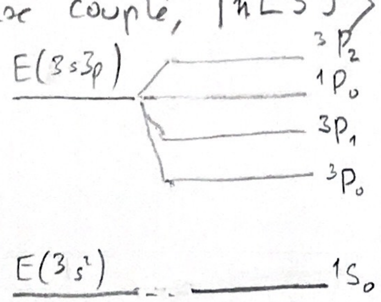
$$|D\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{3s}(1)\alpha(1) & \phi_{3s}(1)\beta(1) \\ \phi_{3s}(2)\alpha(2) & \phi_{3s}(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left(\phi_{3s}(1)\alpha(1)\,\phi_{3s}(2)\beta(2) - \phi_{3s}(1)\beta(1)\,\phi_{3s}(2)\alpha(2)\right)$$

1 c)
$$S_z|D\rangle = s_z^{(1)}|D\rangle + s_z^{(2)}|D\rangle = \frac{\hbar}{2}\frac{1}{\sqrt{2}}\left(\phi_{3s}(1)\alpha(1)\,\phi_{3s}(2)\beta(2)\right) + \frac{\hbar}{2}\frac{1}{\sqrt{2}}\left(\phi_{3s}(1)\beta(1)\,\phi_{3s}(2)\alpha(2)\right)$$
$$+\left(-\frac{\hbar}{2}\right)\frac{1}{\sqrt{2}}\left(\phi_{3s}(1)\alpha(1)\,\phi_{3s}(2)\beta(2)\right) - \frac{\hbar}{2}\frac{1}{\sqrt{2}}\left(\phi_{3s}(1)\beta(1)\,\phi_{3s}(2)\beta(2)\right)$$
$$= 0$$

val. propre de S_z : $M_S = 0$, ok car $S = 0$ donc $M_s = 0$

1 d) $[Ne]3s^1 3p^1$ $l_1 = 0$, $l_2 = 1$, $\Rightarrow L = 1$ $s_1 = \frac{1}{2}$, $s_2 = \frac{1}{2} \Rightarrow S = 0, 1$
$L = 1$, $S = 0$, $J = 1$: $^1P_1$;
$L = 1$, $S = 1$, $J = 0, 1, 2$: $^3P_0$, $^3P_1$, $^3P_2$

2.5 e) base couplé, $|nLSJ\rangle$:



$\Delta E(^1P_1) = \frac{A}{2}(1 \cdot 2 - 1 \cdot 2 - 0) = 0$
$\Delta E(^3P_0) = \frac{A}{2}(0 - 1 \cdot 2 - 1 \cdot 2) = -2A$
$\Delta E(^3P_1) = \frac{A}{2}(1 \cdot 2 - 1 \cdot 2 - 1 \cdot 2) = -A$
$\Delta E(^3P_2) = \frac{A}{2}(2 \cdot 3 - 1 \cdot 2 - 1 \cdot 2) = A$
$\Delta E(^1S_0) = 0$

0.5 f) seul transition possible: $^1P_1 \longrightarrow {}^1S_0$ $(\Delta S = 0)$

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3. 1 a) $1s^2 2s^2 2p^6 3s^2 3p^2$ $\quad l_1 = 1,\ l_2 = 1 \Rightarrow L = 0, 1, 2.$

$s_1 = \frac{1}{2},\ s_2 = \frac{1}{2} \Rightarrow S = 0, 1$

p^2 elec. equivalents, donc : $L = 0, S = 0, \Rightarrow J = 0$ $\quad {}^1S_0$

$L = 1, S = 1. \Rightarrow J = 0, 1, 2$ $\quad {}^3P_{0,1,2}$

$L = 2, S = 0 \Rightarrow J = 2$ $\quad {}^1D_2$

etat fond. : ${}^3P$ (max. S)

2.5 b)

$\Delta E({}^1S_0) = \frac{A}{2}(0 - 0 - 0) = 0$

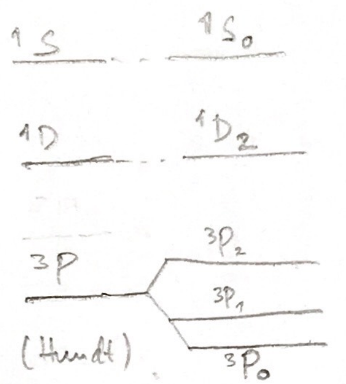
$\Delta E({}^3P_0) = \frac{A}{2}(0 - 1\cdot 2 - 1\cdot 2) = -2A$

$\Delta E({}^3P_1) = \frac{A}{2}(1\cdot 2 - 1\cdot 2 - 1\cdot 2) = -A$

$\Delta E({}^3P_2) = \frac{A}{2}(2\cdot 3 - 1\cdot 2 - 1\cdot 2) = A$

$\Delta E({}^1D_2) = \frac{A}{2}(2\cdot 3 - 2\cdot 3 - 0) = 0$

0.5 c)



2.5 d)

$\Delta E_z({}^1S_0) = 0$ car seul $M_J = 0$

$\Delta E_z({}^3P_0) = 0$ car seul $M_J = 0$

$\Delta E_z({}^3P_1) = \omega_0\left(1 + \frac{1\cdot 2 + 1\cdot 2 - 1\cdot 2}{2\cdot 1\cdot 2}\right) = \frac{3\omega_0}{2} M_J \quad (M_J = 0, \pm 1)$

$\Delta E_z({}^3P_2) = \omega_0\left(1 + \frac{2\cdot 3 + 1\cdot 2 - 1\cdot 2}{2\cdot 2\cdot 3}\right) = \frac{3\omega_0}{2} M_J \quad (M_J = 0, \pm 1, \pm 2)$

$\Delta E_z({}^1D_2) = \omega_0\left(1 + \frac{2\cdot 3 + 0 - 2\cdot 3}{2\cdot 2\cdot 3}\right) = \omega_0 M_J \quad (M_J = 0, \pm 1, \pm 2)$

0.5 e) nombre de Zeeman-niveaux donne valeur de J car nbr. de niveaux = 2J+1

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4. 0.5 a) raies correspond à des transitions rotationnells associés à la trans. vib.

$J \rightarrow J+1$ (raie "P"), $J \rightarrow J-1$ (raie "R")

0.5 b) energie de la trans. vibrationnelle se trouve au centre: $E_{centre} = \frac{1}{2}(0.3151 + 0.3192) = 0.31715$ eV

1 c) $\Delta E \approx 0.0022$ eV (br. R), $\Delta E \approx 0.0019$ eV (br. P)

$\Delta E_{moy} \approx 0.002$ eV $= 2B$ (différence: distortion centrifuge)

$B \approx 0.001$ eV $= 1.6 \cdot 10^{-22}$ J

$$r_0 = \left(\frac{\hbar^2}{2\mu B}\right)^{1/2} = \left(\frac{h^2}{8\pi^2 \mu \cdot B}\right)^{1/2} = \left(\frac{(6.6 \cdot 10^{-34})^2 \, J^2 \cdot sec^2}{8\pi^2 \cdot 1.66 \cdot 10^{-27} \, kg \cdot 1.6 \cdot 10^{-21} \, J}\right)^{1/2}$$

$$= \left(\frac{(6.6 \cdot 10^{-34})^2 \cdot \frac{kg \cdot m^2}{sec^2} \cdot sec^2}{8\pi^2 \cdot 1.66 \cdot 10^{-27} \, kg \cdot 1.6 \cdot 10^{-22}}\right)^{1/2} = 1.4 \cdot 10^{-10} \, m$$

2 d) max. d'intensité pour branche "P" pour $2 \rightarrow 3$

$$N_J = N_0 (2J+1) e^{-\frac{BJ(J+1)}{kT}}$$

max pour: $\frac{dN_J}{dJ} = 0$, $\frac{dN}{dJ} = N_0 2 \cdot e^{-\frac{BJ(J+1)}{kT}} - N_0 (2J+1) \frac{B}{kT} (2J+1) e^{-\frac{BJ(J+1)}{kT}}$

$$= N_0 e^{-\frac{BJ(J+1)}{kT}} \underbrace{\left(2 - \frac{B}{kT}(2J+1)^2\right)}_{=0}$$

$$\frac{B}{kT}(2J+1)^2 = 2$$

$$T = \frac{B}{2k}(2J+1)^2$$

$$= \frac{25}{2} B/k_B$$

(pour $J_{max} = 2$)

$$= \frac{36}{2} \frac{B}{k_B}$$

(pour $J_{max} \sim 2.5$)

$$T = \frac{25}{2} \cdot \frac{1.6 \cdot 10^{-22} \, J}{1.3 \cdot 10^{-23} \, J} \cdot K$$

$= \frac{25}{2} \cdot 12.3$ K ≈ 153 K ($J_m = 2$)

$\approx \frac{36}{2} \cdot 12.3$ K ≈ 221 K ($J_m \approx 2.5$)

$\boxed{4}$

total: 20