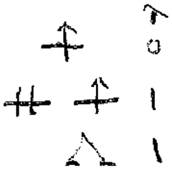
① of ⑤

Chem 776   Ass #2   out 18 Mar   IN : 1 Apr 2015

1. $\boxed{C_2}$ there are 2 configurations with similar energy. Spectral analyses (see Huber Herzberg, Diatomic Molecules, 1979) show the lowest energy states correspond to:

12e⁻



$1s\sigma_g^2\ 1s\sigma_u^2\ 2s\sigma_g^2\ 2s\sigma_u^2\ 2p\pi_u^3\ 2p\sigma_g^1$   Terms $^3\Pi_u$   states $^3\Pi_{u\,2},\ ^3\Pi_{u\,0}$

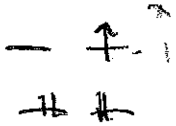
both have magnetic moments (spin = 1, orb = 1)

there are other low lying states from:

$1s\sigma_g^2\ 1s\sigma_u^2\ 2s\sigma_g^2\ 2s\sigma_u^2\ 2p\pi_u^4$   $^1\Sigma_g^+$   716 cm⁻¹ higher

Non-magnetic ($S=0$, $\Lambda=0$)

$\boxed{NO}$   — core —   — inner valence —   N-O   O L.P.



15e⁻

$O1s\sigma^2\ N1s\sigma^2\ O2s\sigma^2\ N2s\sigma^2\ 2p\sigma^2\ 2p\pi^4\ 2p\pi^{*1}$

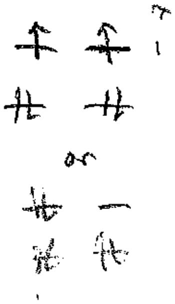
STATES

$X\ ^2\Pi_{1/2}$   $\Lambda=1$   $S=\frac{1}{2}$   $\Omega=3/2$ or $1/2$

$A\ ^2\Pi_{3/2}$   121.1 cm⁻¹ higher than the X state

both states are magnetic – spin and orbital moments

$\boxed{S_2}$   $\overbrace{1s\sigma_g^2\ 1s\sigma_u^2}^{S1s}\ \overbrace{2s\sigma_g^2\ 2s\sigma_u^2}^{S2s}\ \overbrace{2p\sigma_g^2\ 2p\pi_u^4\ 2p\pi_g^4\ 2p\sigma_u^2}^{S2p}$   $\underline{v3s}$ $3s\sigma_g^2\ 3s\sigma_u^2$



32e⁻

$3p\sigma_g^2\ 3p\pi_u^4\ 3p\pi_g^2$   term $^1\Delta_g$   states $^1\Delta_{g\,2}$

$\lambda_1=1\ \lambda_2=1$

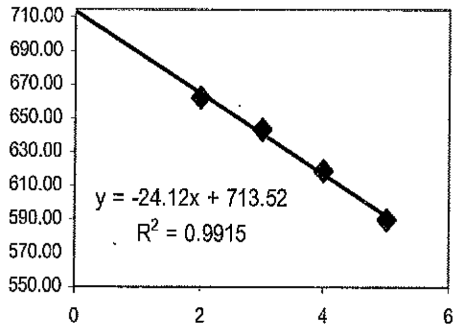
$\Lambda=0,2$   $^3\Sigma_g^-$   $^1\Sigma_g^+$   $^1\Sigma_{g\,0}^+$

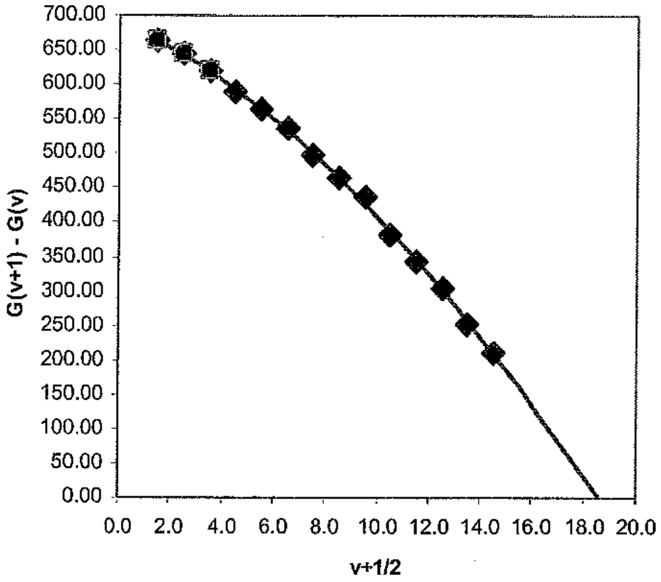
The $X\,^3\Sigma_g^-$ is the ground state   $^3\Sigma_{g\,1}^-$

The $^1\Delta_g$ and $^3\Sigma_g^-$ have magnetic moments. $^1\Sigma_g^+$ does not.
orbit   (spin)

2.(a)

$\omega_e$ from extrapolation of G(v+1)-G(v) against (v+1) for 1st 4 vib ➔ $\omega_e = 710(1)\ \text{cm}^{-1}$
$\omega_e x_e$ from slope, which is $-2\omega_e x_e$ ➔ $\omega_e x_e = 12.06\ \text{cm}^{-1}$





cubic fit (done in Sigma Plot 2000)
R = 0.9997
Standard Error of Estimate = 4.0541

| | Coefficient | Std. Error | t | P |
|---|---|---|---|---|
| y0 | 688.4812 | 7.4411 | 92.5236 | <0.0001 |
| a | -14.8302 | 3.7395 | -3.9658 | 0.0027 |
| b | -1.4746 | 0.5254 | -2.8064 | 0.0186 |
| c | 0.0148 | 0.0217 | 0.6832 | 0.5100 |

**Literature** (http://pgopher.chm.bris.ac.uk/Help/makeo2.htm)

| **State** | $T_e$ | $\omega_e$ | $\omega_e x_e$ | $\omega_e y_e$ |
|---|---|---|---|---|
| B $^3\Sigma_u^-$ | 49793.28 | 709.31 a Z | 10.65 a | -0.139 |

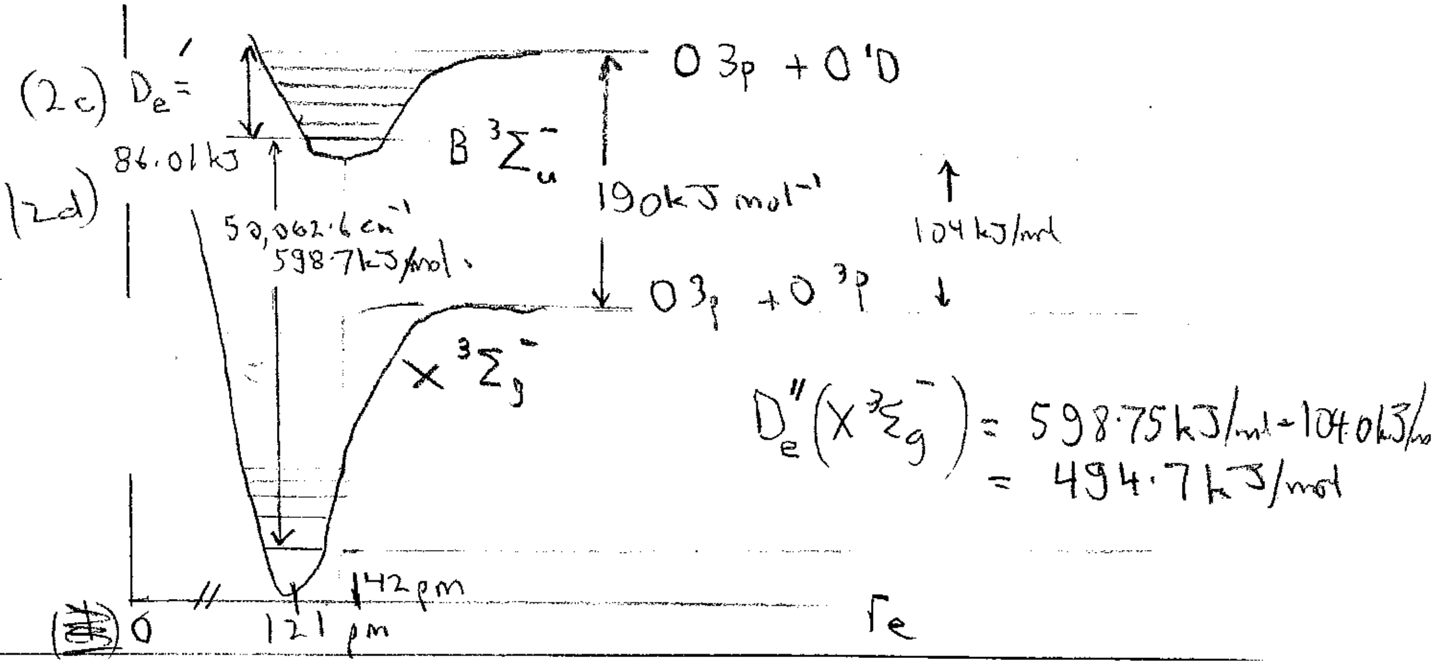
values from Huber and Herzberg (1979)

NB **pgopher** is an open source program to compute and display spectra such as the vibrational fine structure of an electronic transition from fundamental constants. Another way to do this assignment would be to manually adjust parameters in an anharmonic expression for the B state until the agreement with the measured values was satisfactory.

a) The De is obtained by SUMMING the [G(v+1) – G(v)] values in the fitted curve up to the value of v where [G(v+1) – G(v)] = 0 – this is Do = 6836 $\text{cm}^{-1}$ - then adding ½ of the estimated $\omega_e = 710(1)\ \text{cm}^{-1}$ to get the zero point energy.

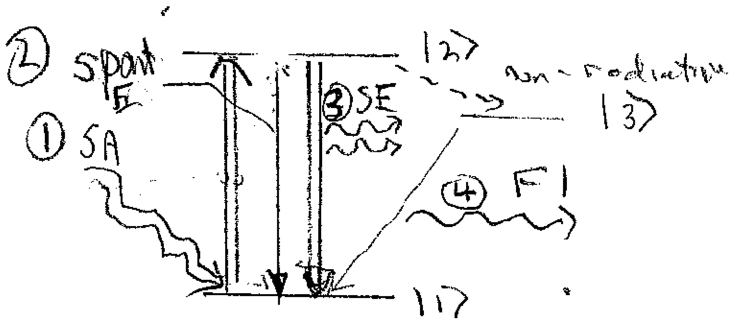
This gives $\boxed{D_e = 7191\ \text{cm}^{-1} = 86.01\ \text{kJ/mol}}$ ($1\ \text{cm}^{-1} = 11.961$ J/mol)

b) Zero point energy = $0.5 * \omega_e - 0.25 * \omega_e x_e = 0.5*710 - 0.25*12.1 = \boxed{352\ \text{cm}^{-1} = 4.19\ \text{kJ/mol}}$



$$D_e''(X\,^3\Sigma_g^-) = 598.75\,\text{kJ/mol} - 104.0\,\text{kJ/mol}$$
$$= 494.7\,\text{kJ/mol}$$

3. (a) Competing radiative processes



① (Stimulated) Absorption
② Spontaneous Emission
③ Stimulated Emission
④ Fluorescence (spont. emission at unwanted ν)

③ stimulated emission $\frac{dN_1}{dt} = N_2 \frac{B_{12}\, 8\pi h c \bar{\nu}^3}{(\exp(hc\bar{\nu}/kT) - 1)} \propto \bar{\nu}^3 \propto \nu^3$

$B_{12} \propto |\langle 2|er|1\rangle|^2$ wavenumber.

① stimulated absorption is the reverse, also $\nu^3$ dependence

②,④ spontaneous emission (either $|2\rangle \to |1\rangle$ or $|3\rangle \to |1\rangle$) are governed by the Einstein A coeff where $A \propto \nu^3 B$. Thus spontaneous emission will also vary as $\nu^3$.

(3b) Width of laser transition (CW and pulse) depends on Doppler broadening. For solids this is small. Then the natural lifetime of the transition will become the limiting factor.

(3c) Short pulse lasers (fs, as) will have a spectral linewidth determined by Heisenberg energy-time uncertainty principle

$$\Delta E \geqslant \hbar/\Delta t$$

eg a 1 fs laser pulse has a spectrum broader than the visible light spectral width

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4 ⓐ Na $^2P_{1/2} \rightarrow {}^2S_{1/2}$ $\tau = 16.4\,\text{ns}$ $\lambda = 589.6\,\text{nm}$

$\bar{\nu} = 1.696 \times 10^{6}\,\text{m}$

$$A_{21} = \tau^{-1} = (16.4 \times 10^{-9}) = 6.1 \times 10^{7}\,\text{s}^{-1}$$

$$B_{12} = A_{21} / (8\pi h c \bar{\nu}^3) = \frac{6.1 \times 10^{-7}\,\text{s}^{-1}}{8\pi(6.62 \times 10^{-34}\,\underset{\text{kg m}^2\text{s}^{-2}}{\text{J}}\,\text{s}^{-1})(3 \times 10^{8}\,\text{m/s})(1.696 \times 10^{6}\,\text{m})^3}$$

$$= 2.5 \times 10^{-2}\,\text{J m}^{-4}\,\text{s} \quad \text{units}$$

or using Engel + Reid formula (p406)

$$B_{12} = B_{21} = \frac{A_{21} c^3}{8\pi h \nu^3} = 7.50 \times 10^{20}\,\text{J}^{-1}\,\text{m}^{3}\,\text{s}^{-2}$$

4b) $$B_{12} = \frac{8\pi^3}{(4\pi\varepsilon_0) 3h^2} \mu^2 \longrightarrow \mu = \sqrt{\frac{3 B_{12} (4\pi\varepsilon_0) h^2}{8\pi^3}}$$

$$= 2.1 \times 10^{-29}\,\text{C m}$$

$$= 6.3\ \text{Debye}$$

4c) Linewidth is determined by lifetime ⇒ Lorentzian linewidth.

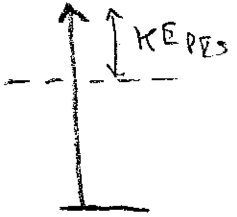
$$\sigma_0 = \frac{h\nu}{c} B = \frac{(6.6 \times 10^{-34}\,\text{J}\cdot\cancel{\text{s}^{-1}})(3.0 \times 10^{8}\,\text{m s}^{-1})}{(3.0 \times 10^{8}\,\text{m s}^{-1})(5.9 \times 10^{-7}\,\cancel{\text{m}})} (7.5 \times 10^{20}\,\text{J}^{-1}\,\text{m}^{3}\,\cancel{\text{s}^{-2}})$$

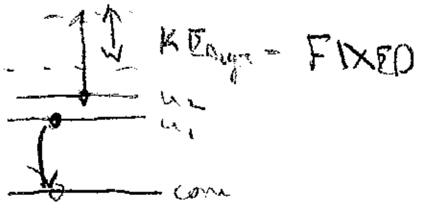
$$= 8.4 \times 10^{-7}\,\text{m}^2$$

should be $\sim 10^{-14}\,\text{m}^2$

5. ⓐ PES $KE = h\nu - BE \propto h\nu$

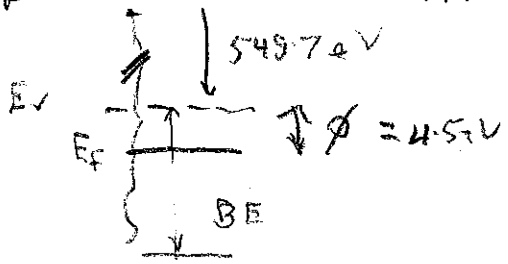
Auger $KE \cong BE_{core} - BE_{u1} - BE_{u2}$ where $BE_{u1}$ - upper levels $u_2$ that fill core hole + escape





photon energy changes - Auger occur at fixed KE independent of hν
- PES lines move KE with hν

ⓑ $h\nu\ (Al\ K\alpha) = 1486.7\ eV$



(i) $BE = 1486.7 - 549.7 - 4.5$
$= 932.5\ eV$

(ii) Cu metal $BE_{2p_{3/2}\,(L_3)} = 932.5\ eV$

(iii) atomic notation $1s^2 2s^2 2p^5 3s^2 3p^6 4s^1 3d^{10}$ ~~F~~ $Cu\ L_3\ 2p_{3/2}$ $2p^5 4s^1$ $\boxed{{}^3P_{3/2}}$

X-ray notation $K^2 L_1^2 L_3^2 L_2^3 M_1^2 M_{23}^6 N_1^1 M_4^4 M_5^6$

(iv) Cu $L_\alpha$ fluorescence decay ~~3~~ $3s\,(M_1)$ electron fills 2p hole
and Auger ~~B~~ $LM_1M_{45}$ 3s electron fills 2p hole + 3d electron is ejected (or vice - versa)

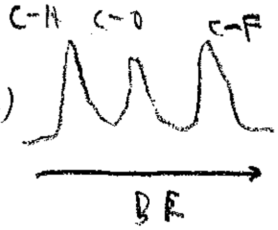
atomic notation for decay by XRF ${}^3P_{3/2} \rightarrow (3s^{-1}4s^{-1})\ {}^3S_1$ (fluorescence)

for Auger decay ${}^3P_{3/2} \rightarrow (3s^{-1}4s^{-1}3d^9)\ {}^4D_{5/2,\,3/2,\,1/2}$

X-ray notation $Cu^+ L_3 \rightarrow M_1 N_1 Cu^+$ for XRF

$Cu^+ L_3 \rightarrow M_1^{-1} N_1^{-1} M_{45}^{-1}\ Cu^{++}$ for Auger

ⓒ (i)



(ii) chemical shifts from electrostatics mostly oxidation state