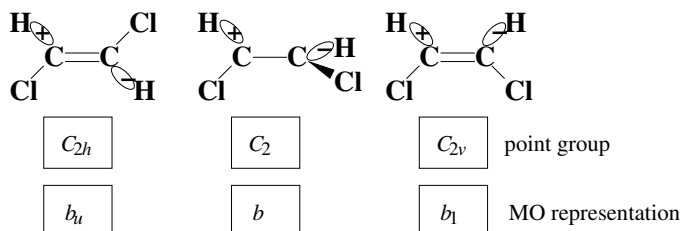


1. One of the symmetry molecular orbitals for the C—H bonds in dichloroethene is drawn below as the molecule isomerizes from *trans* to *cis*. Fill in the blanks below for the point group of the molecule and the representation of the orbital at these three geometries. Let the two carbons lie along the  $x$  axis in each case.



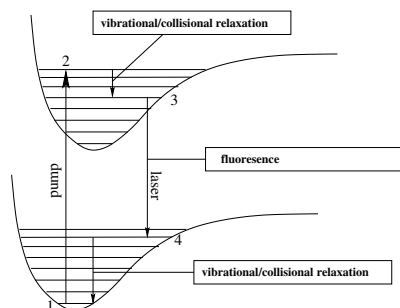
2. For the molecular ion  $\text{Be}_2^+$ :

(a) write the MO configuration and term symbol for the ground electronic state  $X$ ;

**Solution:**  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u$ ,  $X^2\Sigma_u^+$ .

(b) form an excited state  $A$  by promoting the highest energy electron to the lowest energy unoccupied MO, and determine if the transition  $X \rightarrow A$  is allowed or forbidden by electric dipole selection rules. **Solution:** The  $A$  excited state will be  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g$ ,  $A^2\Sigma_g^+$ . The transition  $X \rightarrow A$  is **allowed** because  $\Sigma_u^+ \otimes \Sigma_g^+ = \Sigma_u^+$  which is the representation for the function  $z$ .

3. In a typical liquid dye laser, a dissolved compound is excited from a low energy state 1 to an upper state 2 by an energy source called the “pump.” Some energy is lost to reach state 3, and the laser radiation is released by the allowed transition  $3 \rightarrow 4$ . Identify any energetic process (photoionization, level-crossing, etc.) that could be responsible for each of the three energy-loss steps  $2 \rightarrow 3$ ,  $3 \rightarrow 4$ , and  $4 \rightarrow 1$ , in the boxes provided below.



4. Write an expression that would determine the tunnelling probability of the  $v = 1$  harmonic oscillator wavefunction, *i.e.*, the probability density that lies in the tunnelling region. **Solution:** We need the wavefunction for  $v = 1$  and the limits for the

integral:

$$\eta_1(R) = A_{v=1} H_{v=1}(y) e^{-y^2/2} = \left(\frac{k\mu}{\hbar^2}\right)^{1/8} \left(\frac{1}{2\sqrt{\pi}}\right)^{1/2} (2y) e^{-y^2/2}$$

where  $y = (R - R_e) \left(\frac{k\mu}{\hbar^2}\right)^{1/4}$ . The tunnelling region lies outside the range where  $U(R) = \frac{1}{2}k(R - R_e)^2 = E_{v=1} = 3\omega_e/2$ , which corresponds to  $R = R_e \pm \sqrt{3\omega_e/k}$ . We can either integrate from *infity* to  $R_1 \equiv R_e - \sqrt{3\omega_e/k}$  and from  $R_2 \equiv R_e + \sqrt{3\omega_e/k}$  to  $\infty$ , or equivalently we can find the probability in the classically allowed region, and subtract this from 1 to get the probability in the classically forbidden (tunnelling) region:

$$1 - \int_{R_1}^{R_2} \eta_1(R)^2 dR.$$

5. Using your best judgement, put the following in order of **increasing value** of the vibrational constant  $\omega_e$ :

(a)  $^{31}\text{P}^{34}\text{S}$       (b)  $^{31}\text{P}_2^+$       (c)  $^{31}\text{P}^{14}\text{N}$       (d)  $^{31}\text{P}^{32}\text{S}$       (e)  $^{31}\text{P}_2$

**Solution:** The PN and  $\text{P}_2$  have the same valence electron arrangement as  $\text{N}_2$  and so will also have triple bonds, nominally, by filling  $\sigma$  and  $\pi$  bonding orbitals of the valence  $2p$  or  $3p$  atomic orbitals. The extra electron in PS goes into an antibonding orbital, weakening the bond and leading to lower  $k$  and lower  $\omega_e$ . In  $\text{P}_2^+$ , an electron is removed from a bonding orbital, which also leads to lower  $k$  and lower  $\omega_e$ . Between  $\text{P}_2$  and PN, PN has the stronger bond (smaller N atom) and lower reduced mass, so in terms of  $\omega_e$ ,  $c > e > (a, b, d)$ . We also know that  $a < d$  because the bonding will be almost identical in the two, but  $\mu_{^{31}\text{P}^{34}\text{S}} > \mu_{^{31}\text{P}^{32}\text{S}}$ . It turns out (but you are not responsible for knowing) that removal of the bonding electron in  $\text{P}_2^+$  has a greater effect on  $k$  than adding the antibonding electron in PS, so the final ordering is  $\boxed{b < a < d < e < c}$ .