5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
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**Problem Set #3**

1. See Problem Set # 3, 1976, # 2.
2. See Problem Set # 3, 1976, # 5.
3. See Problem Set # 3, 1976, # 6.
4. See Problem Set # 3, 1976, # 7.
5. See Problem Set # 3, 1976, # 8.
6. The classical statement of the Franck-Condon principle is that, in an electronic transition, an electron jumps before the nuclei can alter their positions and momenta. In wave mechanics, position and momenta are not sharply defined for an energy eigenstate, yet we persist in drawing diagrams with vertical lines connecting turning points and using these diagrams to predict the strongest transitions. See J. Tellinghuisen, *Phys. Rev. Lett.* **34**, 1137 (1975) and *Chem. Phys. Lett.* **29**, 359 (1974).

   (a) Explicitly translate the classical statement into wave mechanical language. Explain why an overlap integral for a pair of vibrational wavefunctions should be large if the classical Franck-Condon conditions are satisfied. Note that a function which is analogous to the classical momentum

   $$p(x) = (2\mu)^{1/2}\,[E - V(x)]^{1/2}$$

   determines how fast the vibrational wavefunction oscillates. Explain what will happen if the two vibrational wavefunctions oscillate in phase over a small range of $x$ but have a random phase relationship elsewhere. Is the in-phase relationship satisfied anywhere in addition to near turning points?

   (b) Draw two Morse curves defined by the following constants:

   | | |
   |---|---|
   | $T_e'' = 0\ \text{cm}^{-1}$ | $T_e' = 10,000\ \text{cm}^{-1}$ |
   | $D_e'' = 10,000\ \text{cm}^{-1}$ | $D_e' = 5,000\ \text{cm}^{-1}$ |
   | $R_e'' = 1.44 \times 10^{-8}\ \text{cm}^{-1}$ | $R_e' = 1.54 \times 10^{-8}\ \text{cm}^{-1}$ |
   | $\omega_e'' = 582\ \text{cm}^{-1}$ | $\omega_e' = 308\ \text{cm}^{-1}$ |

   and determine the two strongest transitions originating from $v' = 19$. Use a reduced mass of $\mu = 6.857$ amu.

(c) Plot $V'(x) - V''(x)$ vs. $x$. Use this curve to determine:

(i) The long and short wavelength limits of all bound-bound transitions in this system which possess significant intensity;

(ii) The long and short wavelength limits of strong bands from $v' = 19$;

(iii) Plot the x-value(s) sampled vs. transition energy for the progression of bands ($v' = 19$, $v''$) for $v'' = 0$ through the maximum $v''$ level that can be reached via non-negligible Franck-Condon factor from $v' = 19$.

(iv) The wavelength region(s) in which erratic intensity variations occur. Which $v'$ levels participate in such transitions?