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5.80 Small-Molecule Spectroscopy and Dynamics
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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
Spring 1978

Problem Set #3

1. See Problem Set #3, 1976, Question #1.
2. See Problem Set #3, 1976, Question #2.
3. See Problem Set #3, 1976, Question #3.
4. See Problem Set #3, 1976, Question #4.
5. See Problem Set #3, 1976, Question #5.
6. See Problem Set #3, 1976, Question #6.
7. See Problem Set #3, 1976, Question #7.
8. See Problem Set #3, 1976, Question #8.
9. 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 that 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:

$$T_e'' = 0 \text{ cm}^{-1}$$

$$D_e'' = 10,000 \text{ cm}^{-1}$$

$$R_e'' = 1.44 \times 10^{-8} \text{ cm}^{-1}$$

$$\omega_e'' = 582 \text{ cm}^{-1}$$

$$T_e' = 10,000 \text{ cm}^{-1}$$

$$D_e' = 5,000 \text{ cm}^{-1}$$

$$R_e' = 1.8 \times 10^{-8} \text{ cm}^{-1}$$

$$\omega_e' = 329 \text{ cm}^{-1}$$

and determine the two strongest transitions originating from $v' = 27$. 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 bands in this system which possess significant intensity;
 - (ii) The long and short wavelength limits of strong bands from $v' = 27$;
 - (iii) The region(s) of x where the electronic transition moment is sampled for the (27, 27) band.
 - (iv) The wavelength region in which erratic intensity variations will occur.