

Assignment 7

Due November 22, 2002

Assigned problems from the text:

Chapter 19: Problems 19.5, 19.8, 19.14, 19.16, 19.18, 19.22, 19.28

Problems to turn in:

- 7.1 Go through the ten diatomics in Problem 6.1 on the last problem set, and use the MO configurations from that problem to deduce the ground electronic state term symbol for each. Don't worry about the Ω or $\Lambda + \Sigma$ values; focus on the multiplicity, the parity, the Λ value that leads to the central part of the term symbol, and the $+/-$ superscript for Σ states. (Big hint: only one of the Σ states is Σ^- .)
- 7.2 A recent paper in *Physical Review Letters* ("First Measurement of the Rotational Constants for the Homonuclear Molecular Ion He_2^+ ," L. Coman, M. Guna, L. Simons, and K. A. Hardy, *Phys. Rev. Lett.* **83**, 2715 (1999)) measured the rotational constant for He_2^+ in the $v = 3$ level of the ground electronic state through a very neat experiment that followed the ion's dissociation when it recombined with an electron. They measured the rotational constant for this vibrational level to be $6.46 \pm 0.2 \text{ cm}^{-1}$. Theory predicts $B_e = 7.221 \text{ cm}^{-1}$ and $\alpha_e = 0.224 \text{ cm}^{-1}$. Use these values to calculate B_3 and compare to their measurement. What is the ion's average bond length in the $v = 3$ level, and how does it compare to the theoretical equilibrium bond length R_e ? Finally, why do you think it has taken until 1999 for anyone to actually measure a rotational constant for this ion? See if you can list several experimental reasons as well as theoretical limitations on the types of spectroscopy experiments one can do with this ion. These measurement, by the way, were done on the ^4He molecular ion. IR absorption spectra were recorded in 1987, however, on the $^3\text{He}^4\text{He}^+$ species. Why was this isotopic species seen first? (The answer is one of the "theoretical limitations" mentioned earlier.)
- 7.3 There is all sorts of stuff out in space. Emissions have been seen in the IR as well as the microwave and visible regions that are clearly molecular in origin, and in the IR, there are many (in fact most) features for which the molecular origin is unknown. In the wavelength region from 3.2 to 3.8 μm , one such emission source, called IRAS (for "InfraRed Astronomical Source") 21282+5050 (a code number for the source), emits a series of features that look like unresolved bumps, spaced by amounts and with intensity distributions that suggest a vibrational cascade of emissions from

perhaps a single molecule. The wavelength peaks are at 3.24, 3.29, 3.34, 3.40, 3.46, 3.51, and 3.57 μm . On the assumption that these features correspond to $v = 1 \rightarrow 0$, $2 \rightarrow 1$, $3 \rightarrow 2$, etc., emissions of a single molecule, convert each wavelength to a corresponding transition wavenumber, and use a Birge–Sponer plot (see page 736 and 737 in the text) to see if this assumption has merit. Do the data fall on a straight line in such a plot? If so, what ω_e and $\omega_e x_e$ values and what dissociation energy D_e do they predict?