Problem Set 6

Due May 2, 2006

1. Gaseous HCl is normally a 3:1 mixture of $H^{35}Cl$ and $H^{37}Cl$. The rotational energy is given, to a good approximation, by

$$E_{rot}(J) = BJ(J+1) - DJ^2(J+1)^2$$

where B, the rotational constant, is larger by a factor of 1.0015 for $H^{35}Cl$ than for $H^{37}Cl$, and the centrifugal distortion constant, D, is the same for both molecules.

- a) Derive an expression for the separation of the pure rotational absorption lines of $H^{35}Cl$ and $H^{37}Cl$ as a function of J', the J-value for the upper state ($\Delta J = J' - J'' = +1$).
- b) What is the spacing in cm^{-1} of the two lines for which $J' = 10$?

2. The "transition moment," or probability of transition, between two rotational levels in a linear molecule may be assumed to depend only on the permanent electric dipole moment of the molecule and thus to be the same for all allowed pure-rotational transitions. In the pure-rotational *emission spectrum* of $H^{35}Cl$ gas, lines at 106.0 cm^{-1} and 233.2 cm^{-1} are observed to have equal intensities. What is the temperature of the gas? The rotational constant B for $H^{35}Cl$ is 10.6 cm^{-1}.

3. In the $^{14}N_2$ molecule the ground state $X^1\Sigma_g^+$ has the following constants: $\omega_e = 2358.6$, $\omega_e x_e = 14.324$, and $B_e = 1.998$, all in units of cm^{-1}. For an excited $b'\,^1\Sigma_u^+$ state, those same constants are 760.1, 4.42, and 1.155 cm^{-1}. The term value of the transition (known as the Birge-Hopfield band system) is $T_e = 104498$ cm^{-1}.

- a) Construct a Deslandres table for the transitions between the vibrational levels $v' = 0, 1, 2, 3, 4, 5$ and $v = 0, 1, 2, 3, 4, 5$.
- b) Calculate the wavenumbers of the first few members of the R and P branches of the (0,0) band.
- c) Draw a Fortrat parabola using the variable $m = -J - 1$ for the R branch and $m = J$ for the P branch. Determine whether the band is shaded to the red or to the violet and find the position of the band head.

(more)

4. The following bands are observed in the Second Positive system of N_2 ($C\,^3\Pi_u$ – $B\,^3\Pi_g$) (units are vacuum cm^{-1}).

35,522	32,207	30,438	28,819	27,226	25,669	24,137
35,453	32,076	30,212	28,559	26,942	25,354	23,800
33,852	31,878	29,940	28,267	26,621	25,003	23,414
33,751	31,643	29,654	27,949	26,274	24,627	23,016
33,583	30,590	29,010	27,451	25,913	24,414	

Arrange these in a Deslandres table, and find values for ω_e'', $\omega_e x_e''$, ω_e', and $\omega_e x_e'$, where the primes refer to the lower electronic state and the double primes the upper state. (*Suggestion:* Look at the pattern of bands first, before doing any calculations. Do any natural groupings seem to suggest themselves? It may help to draw a "stick spectrum" of the band origins, to scale, in order to pick out patterns. Remember that bands having the same Δv fall along diagonals in the Deslandres table.)

Is there any suggestion of a cubic term in either state? If so, derive an expression for the third difference in $G_{\mathrm{v}+\frac{1}{2}}$ including terms in $\omega_e y_e(\mathrm{v}+\frac{1}{2})^3$, and estimate $\omega_e y_e$.