ADVANCED PHYSICS LABORATORY – PHYSICS 441/442 - ATOMIC AND MOLECULAR SPECTROSCOPY

These notes clarify the assignment of the vibrational peaks in the measured spectrum of molecular nitrogen; see Figure 1. The observed transitions are commonly known as the First Positive System (positive means that they pertain to neutral N_2). They involve the blue and yellow potential energy curves shown in Figure 2 [from A. Lofthus and P. H. Krupenie, Phys. Chem. Ref. Data **6**, 113 (1977)].

In the range 570-620 nm, the almost periodic pattern corresponds to transitions from the nth level of the upper $B^3\Pi_g$ band to the $(n\text{-}4)$th level of the lower $A^3\Sigma_u^+$ band whereas, in the 620-680 nm range, the transitions are from the upper nth to the lower $(n-3)$th level. Note that the repeating pattern is not perfectly periodic because the potentials are not purely harmonic.

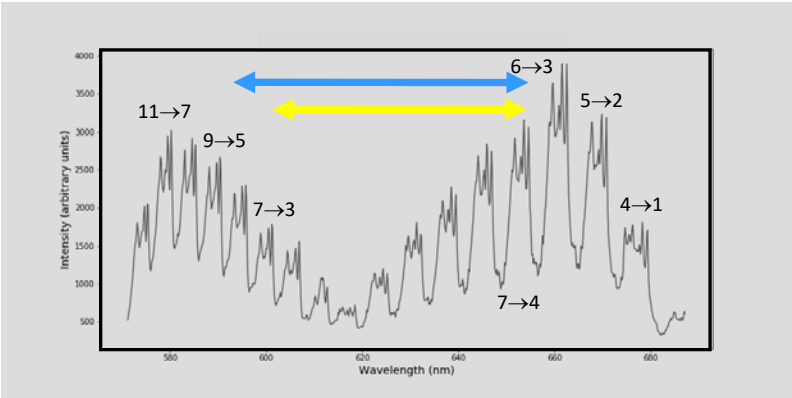

Fig. 1 – Spectrum of molecular nitrogen.

Using these assignments, we obtain from the data $\approx 1590\ \text{cm}^{-1}$ for the frequency separation between the two lowest $B^3\Pi_g$ levels (blue potential curve). This value, indicated by the blue arrow in Figure 1, accounts also for the separation between the observed two broad features in the spectrum. We note that this value is much smaller than that for the ground state of the molecule, which is $\approx 2360\ \text{cm}^{-1}$.

Since the frequency of the repeating pattern is $\approx 160\ \text{cm}^{-1}$, the data can be used to obtain $\approx 1430\ \text{cm}^{-1}$ for the separation between the two lowest $A^3\Sigma_u^+$ levels (yellow arrow in Figure 1).

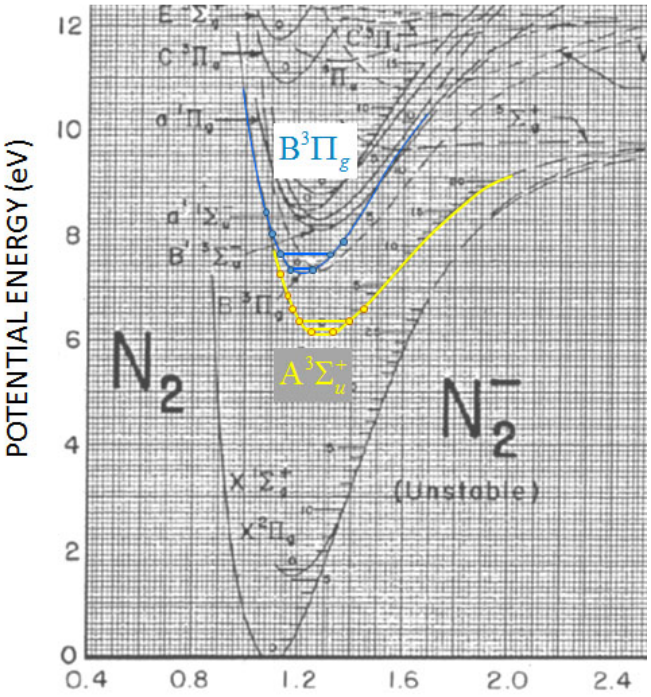

Fig. 2 - Potential Energy Curves for N_2 and its unstable ionized form.