8.7: The Negative Hydrogen Ion

The word "ion" in the gas phase is often thought of as the positively charged remnant of an atom that has lost one or more electrons. However, any electrically charged atom (or molecule or radical), whether positively charged (as a result of loss of an electron) or negatively charged (having an additional electron) can correctly be called an "ion". In this section, we are interested in the negative hydrogen ion, H^-, a bound system consisting of a proton and two electrons.

The formation of such an ion can be qualitatively described, in classical terms, as follows. A hydrogen atom, consisting of a proton and an electron, is approached by a second electron. The electric field of the second electron (which falls off with distance as r^{-2}) induces a dipole moment in the neutral hydrogen atom, with the two electrons then being at opposite sides of the proton. The induced dipole moment is proportional to the electric field of the polarizing electron, and hence to r^{-2}. The second electron now finds itself immersed in the electric field of the dipole that it has itself induced in the neutral H atom, and can be captured by it. The field of the dipole falls is proportional to p/r^3, where p, the induced dipole moment, is already proportional to r^{-2}. Thus the force between the neutral (but dipolar) hydrogen atom and the intruding second electron falls off as r^{-5}, and the second electron moves in a potential varying as r^{-4}. Because of this, the energy level structure of H^- is very different from that of H. In H, the potential falls off as r^{-1}, which results in the familiar infinite Rydberg series of levels. For a potential of the form r^{-n}, if $n > 1$ the Schrödinger equation predicts a *finite* number of bound levels below the ionization limit, and, in the case of H^-, there is just *one* bound level, and it is a mere $0.7\ \mathrm{eV}$ below the ionization limit. The $0.7\ \mathrm{eV}$ can be called the *ionization potential* of the H^- ion or the *electron affinity* of the H atom. Perhaps the latter term is preferable, because it is a little odd to refer to removing an electron from the H^- ion (so that it is then no longer an ion) as "ionization"! As Professor Joad might have said: "It all depends what you mean by 'ionization'". In any case, an electron can easily be removed from H^- either by a mild collision or by any photon of (vacuum) wavelength shorter than about $1771\ \mathrm{nm}$.

In the solar atmosphere, most hydrogen atoms are neutral and have the electron in the $n = 1$ shell (K shell). Only a few are in the form of H^+ or H^-. (I am not sure offhand which is more numerous, H^+ or H^- − that would make a good lunchtime discussion.) But because H^- is so readily stripped of an electron by almost any old photon, H^- makes an appreciable contribution to the continuous opacity of the solar atmosphere. The continuous absorption can be either by "bf" (bound-free) transitions or so-called "ff" (free-free) transitions. In the latter case the second electron is unbound, but it swerves in the field of the dipole that it has itself induced in the neutral H atom.