

SpS1-Laboratory spectroscopy of small molecules

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This contribution focuses on the study of ‘cool’ sources with surface temperatures in the range of about 500 – 4000 K. In this temperature range spectra are dominated by strong molecular absorption and the tools of modern chemical physics can be applied to compute the molecular opacities needed to simulate the observed spectral energy distributions. (See Bernath (2005) for an introduction to molecular spectroscopy including line intensities and Bernath (2009) for a recent astronomical review article.)

1. Hot H₂O, CH₄ and NH₃

The vibration-rotation and pure rotational lines of H₂O and OH appear strongly in cool oxygen-rich objects. The dominant carbon-containing molecule is CO at high temperatures and CH₄ for cooler objects, such as T-type brown dwarfs and ‘hot Jupiter’ extrasolar planets. For nitrogen, N₂ is the high temperature molecular form, but NH₃ appears in T dwarfs and is predicted to be the distinguishing feature for very cool brown dwarfs (‘Y’-type) with surface temperatures below about 700 K.

Excellent high resolution ground-based spectra of the Sun are available from the Kitt Peak Fourier transform spectrometer (FTS) and from low earth orbit with the Advanced Composition Explorer (ACE) FTS. The spectra are dominated by the strong first overtone and fundamental vibration-rotation bands of CO. The Meinel bands (OH vibration-rotation bands) near 3 μm are also strong and the OH pure rotational lines are prominent at longer wavelengths. The vibration-rotation bands of CH and NH can be seen at 3 μm and pure rotational lines of NH are also present.

A new very high signal-to-noise solar atlas in the 750 – 4400 cm^{-1} region has recently been prepared by Hase *et al.* (2009) from ACE satellite observations. Based on ACE, ATMOS and laboratory spectra, the analysis of OH has recently been improved by Bernath & Colin (2009) and similar work is underway for CH and NH.

At 5800 K, the Sun’s photosphere is too hot for water to exist, but by 3900 K the concentration of OH and H₂O are equal. A large number of unassigned lines were noticed in two Kitt Peak sunspot atlases; it was suspected that these lines were due to hot water but the available laboratory data were inadequate to confirm this. Comparison of a new laboratory emission spectrum of H₂O at 1800 K with the sunspot absorption spectrum identified most of the unassigned sunspot lines as H₂O lines. Wallace *et al.* (1995) proved that there is ‘water on the Sun’. Through variational calculations of the energy levels using a high quality *ab initio* potential energy surface, Polyansky *et al.* (1997) were able to assign most of the strong lines.

The water emission in the 500–13 000 cm^{-1} spectral region was recorded with a high-resolution FTS using an oxy-acetylene torch as a source. Work on this 3000 K spectrum of H₂O has just finished with the publication by Zobov *et al.* (2008) of the last paper in the series. The latest water linelist of Barber *et al.* (2006) contains more than 500 million lines and is recommended for simulation of spectral energy distributions of cool stars, brown dwarfs and extrasolar planets.

The situation for CH₄ is much less satisfactory than for H₂O although Nassar & Bernath (2003) have published hot emission spectra and there is considerable theoretical activity, for example by Warbier *et al.* (2009) A similar situation exists for NH₃ with calculations underway, for instance, by Huang *et al.* (2008)

We have decided to take an empirical approach to determine new linelists for hot CH₄ and NH₃. A reasonably complete list of line positions, line strengths and lower state energy levels is needed. We have therefore begun to record spectra of hot NH₃ and CH₄ over a wide range of temperatures and to calibrate the line positions and strengths using the HITRAN database

of Rothman *et al.* (2009) Empirical lower state energies are determined from the temperature dependence of the line intensities.

2. Metal hydrides

The only metal hydride seen clearly in the solar photosphere spectrum is MgH, detected via the $A^2\Pi-X^2\Sigma^+$ transition. Sunspot spectra convincingly show lines of the visible and near infrared electronic transitions of AlH, MgH, CaH and FeH. Both the $A^2\Pi-X^2\Sigma^+$ and $B'^2\Sigma^+-X^2\Sigma^+$ electronic transitions of MgH can be seen in sunspot spectra. Shayesteh *et al.* (2003) completed a set of MgH observations in the infrared and visible that had led earlier in 2003 to the discovery of the linear MgH₂ molecule. From the MgH B–X observations, Shayesteh *et al.* (2007) determined all bound ground state levels with spectroscopic precision and obtained a very precise dissociation energy of 11104.7 cm⁻¹.

The most important application of the spectroscopy of metal hydrides is in the classification of L-type dwarfs as discussed by Kirkpatrick (2005). The FeH $F^4\Delta-X^4\Delta$ electronic transition near 1 μm and the $E^4\Pi-A^4\Pi$ transition near 1.58 μm are seen strongly along with the $A^6\Sigma^+-X^6\Sigma^+$ transition of CrH near 861 nm. Dulick *et al.* (2003) prepared a linelist for the F–X transition of FeH, Burrows *et al.* (2002) prepared one for CrH and Burrows *et al.* (2005) for TiH (which has not been detected yet in L-dwarfs) by extrapolating laboratory observations and using line intensities based on *ab initio* calculations. These molecular opacities are in modest agreement with observations, but high resolution comparisons indicate that improvements are needed.

References

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