Study of Manganese-bearing molecules

Progress towards line lists for MnH, MnF & MnCl

Maire N. Gorman[1,2], Emily R. Ingman[1], Jamie Dumayne[1], Sergey N. Yurchenko[2] & Jonathan Tennyson[2]

[1] Department of Physics, University of Aberystwyth
[2] Department of Physics, University College London

mng2@aber.ac.uk

Introduction

In this poster we present progress on the calculation of theoretical line lists for the various isotoplogues of the diatomic molecules of MnH, MnF and MnCl as part of the ExoMol project (Tennyson and Yurchenko, 2012). A line list is simply a list of wavelengths with associated intensities. At present none of these molecules have been detected in space and to the best of our knowledge there are no line lists available in literature.

Given that the cosmic abundance of Chromium and Manganese are relatively similar and also the applications of CrH in modelling of L type dwarfs, it does beg the question of why MnH has not been observed to date (Kirkpatrick et al., 1999; Anders and Grevesse, 1989). Given the problems astronomers have experienced using the existing linelists for CrH and FeH to successfully model observed L dwarf spectra the possibility that MnH is accountable for at least some of the discrepancies in opacity can now be investigated (Lyubchik et al., 2007).

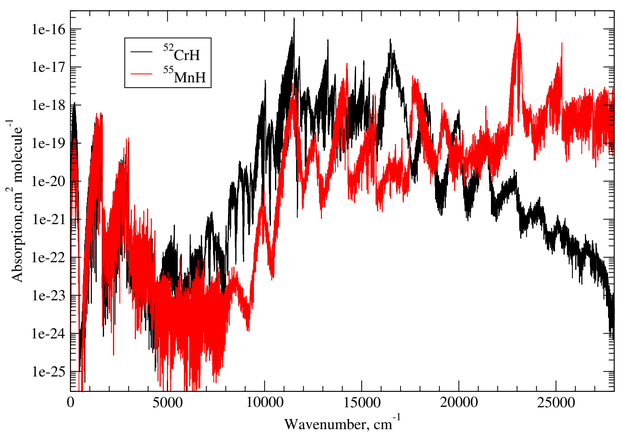

Figure 1: Comparison of absorption spectra simulated at 1500 K (Gaussian HWHM of 1.0) for CrH and MnH using ExoMol linelists.

The group led by Lucy Ziurys undertake sub-millimetre experimental studies on both established and potentially interesting astronomical molecules have worked on both MnCl and MnF (Sheridan and Ziurys, 2003; Halfen and Ziurys, 2005). They have recently confirmed the detection of AlF and have also searched for MgF and CaF in IRC+10216 in which the NaCl, KCl and AlCl have also been detected (Ziurys et al., 1994; Cernicharo and Guelin, 1987).

Methodology

The methodology used to calculate these line lists is that of the ExoMol group in which high-level quantum chemistry calculations (here MRCI as implemented in the MOLPRO program)are refined by use of available experimental energies. For more detail of the methodology please see the attached document hand out or contact **mng2@aber.ac.uk**.

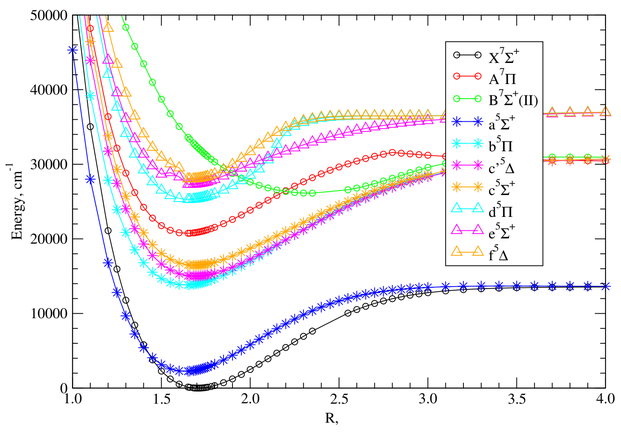

Figure 2: *Ab initio* PECs used in the construction of the linelist for MnH. These PECs have been calculated using a cc-pVQZ basis set at MRCI level of theory.

Manganese Hydride, MnH

For MnH, an extensive range of MRCI calculations have been performed for the 15 low-lying electronic states of MnH including, for the first time the nonuplet states of $g^9\Pi$ and $h^9\Sigma^+$. The r_e values of both the $a^5\Sigma^+$ and $X^7\Sigma^+$ have been found to be consistent with previous experimental studies. For the first time, electronic angular momenta and spin-orbit couplings have been calculated for MnH for couplings acting between the 15 low-lying electronic states. The spin-orbit couplings were found to vary between 40 cm^{-1} and 275 cm^{-1}. These results are important in the context of creating accurate linelists.

For the $^7\Pi$ states, it was found that for the $A^7\Pi$ state, the PEC underwent a dramatic change in character from been anti-bonding to bonding in nature when an increased active space was used. This is very important as naively, one could undertake MRCI calculations using a lower active space for one $^7\Pi$ state and obtain a PEC which seems continuous and reasonable in character.

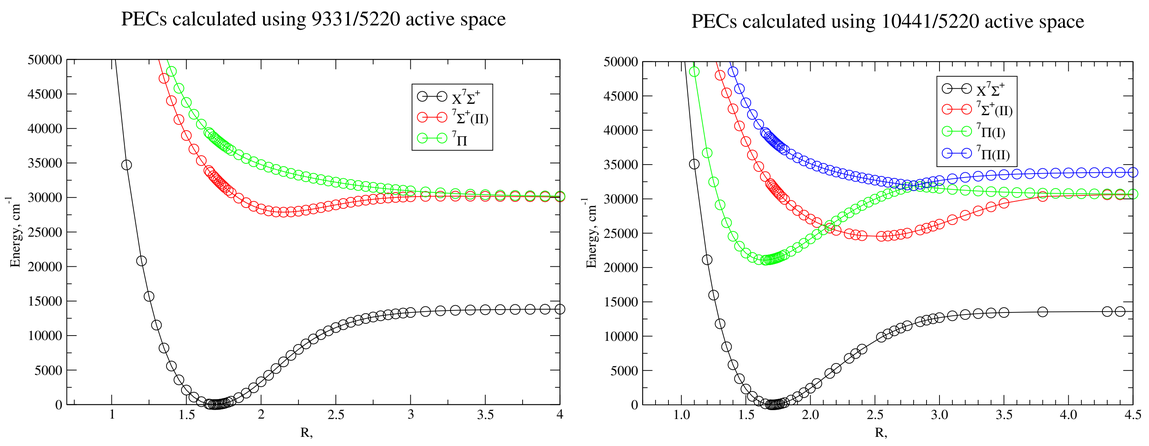

Figure 3: Comparison of PECs calculated at MRCI level using cc-pVQZ basis set for low-lying septuplet states using two different active spaces as defined within the C_{2v} symmetry framework used by MOLPRO.

These MRCI calculations have then been used to create a line list for MnH in which the PECs for the $X^7\Sigma^+$, $A^7\Pi$, $a^5\Sigma^+$, $b^5\Pi$, $c^5\Sigma^+$, $d^5\Pi$ and $e^5\Sigma^+$ states have been refined using available experimental data (Gordon et al., 2005; Gengler et al., 2007; Balfour et al., 1990, 1992). This line list includes has a coverage up to $J = 60$, $\nu = 20$ and 32, 000 cm^{-1}. We have compared our partition function to that calculated by Sauval and Tatum (1984) and found that for temperatures between 300 K and 5000 K it is 20-25% greater indicating our model is more complete.

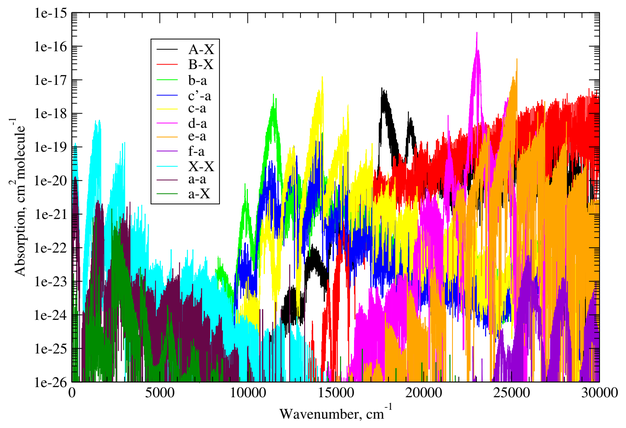

Figure 4: Simulated Absorption spectra (Gaussian HWHM of 1.0) at 1500 K for bands of the ^{55}MnH isotopomer.

It has been postulated that CrH could be used for the so-called "deuterium-test" by Pavlenko et al. (2008). Figure 5 shows that, if MnH was to be detected in L-type dwarfs, with a resolution of 50 the shift between MnH and MnD could be observed.

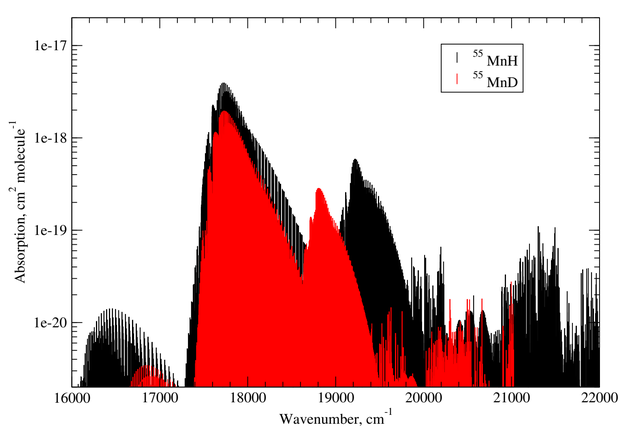

Figure 5: Simulated Absorption spectra (Gaussian HWHM of 1.0) at 1500 K for ^{55}MnH and ^{55}MnD.

Manganese Fluoride & Manganese Chloride

As was done for MnH, a comprehensive program of *ab initio* calculations has been undertaken: PECs and DMCs have been produced for the 10 low-lying states of these molecules at the MRCI level of theory using cc-pVQZ basis set. Previously, to the best of our knowledge only Koukounas et al. (2004) and Nhat et al. (2012) have performed calculations on these molecules.

At present, for both molecules, calculations of the $A^7\Pi$ states have proved to be troublesome which corroborates the work of Koukounas et al. (2004). Thankfully, for MnF the correct bonding behaviour for this state has been obtained at CASSCF level of theory. We plan to refine this PEC using the experimental data of Launila et al. (1993) and also use the available experimental data for the $X^7\Sigma^+$, $a^5\Sigma^+$, $b^5\Pi$, $c^5\Sigma^+$, $d^5\Pi$ and $e^5\Sigma^+$ states (Sheridan and Ziurys, 2003; Launila, 1992; Launila and Simard, 1992a,b; Simard and Launila, 1994) to produce a refined multi-electronic state line list for MnF.

For MnCl there is only experimental data available for the ground $X^7\Sigma^+$ by Halfen and Ziurys (2005): hence we plan to produce a refined line list for this state and un-refined multi-electronic state line list. In this poster we present ground state spectra for both MnF and MnCl using unrefined *ab initio* PECs.

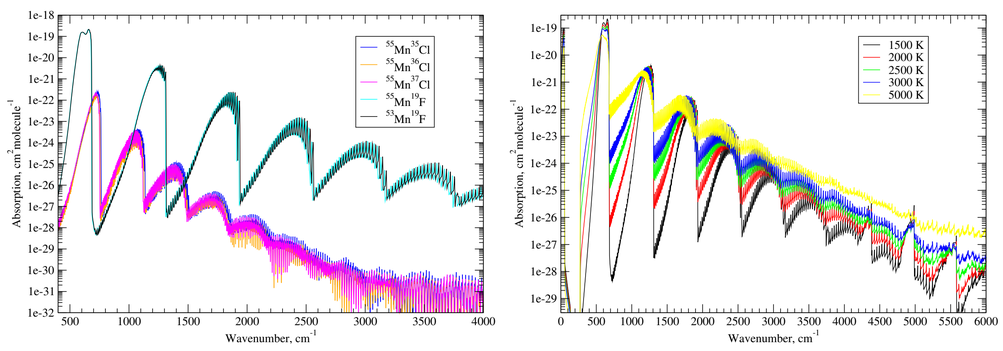

Figure 6: Simulated absorption spectra (Gaussian HWHM of 1.0) for a) various isotopologues of MnCl and MnF (at 1500 K) and b) for various temperatures for ^{55}Mn^{19}F.

Further Research

For all molecules we would be interested to hear from any experimentalists who could provide us with more experimental measurements for different electronic systems (in particular for MnCl) and higher vibrational coverage which would hence allow us to refine our PECs, and hence our linelists to greater level of certainty. We are also interested in collaborating with astronomers on detecting these molecules in space.

Acknowledgements

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