Molecular Astrophysics 8 (2017) 1–18

Contents lists available at ScienceDirect

Molecular Astrophysics

journal homepage: www.elsevier.com/locate/molap

Review Article

Laboratory spectra of hot molecules: Data needs for hot super-Earth exoplanets

Jonathan Tennyson*, Sergei N. Yurchenko

Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

ARTICLE INFO

Article history:
Received 5 March 2017
Revised 17 May 2017
Accepted 19 May 2017
Available online 19 May 2017

Keywords:
Super-Earth
Lava-planets
Absorption Intensities
FTIR spectroscopy
Line lists
Transit spectroscopy
Exoplanets

ABSTRACT

The majority of stars are now thought to support exoplanets. Many of those exoplanets discovered thus far are categorized as rocky objects with an atmosphere. Most of these objects are however hot due to their short orbital period. Models suggest that water is the dominant species in their atmospheres. The hot temperatures are expected to turn these atmospheres into a (high pressure) steam bath containing remains of melted rock. The spectroscopy of these hot rocky objects will be very different from that of cooler objects or hot gas giants. Molecules suggested to be important for the spectroscopy of these objects are reviewed together with the current status of the corresponding spectroscopic data. Perspectives of building a comprehensive database of linelist/cross sections applicable for atmospheric models of rocky super-Earths as part of the ExoMol project are discussed. The quantum-mechanical approaches used in linelist productions and their challenges are summarized.

1. Introduction

There are vast areas of the Universe thinly populated by molecules which are cold. However, there are also huge numbers of important astronomical bodies which support hot or highly-excited molecules. It is the spectroscopic demands of studying these hot regimes we focus on in this review. We will pay particular attention to the demands on laboratory spectroscopy of a recently identified class of exoplanets known as hot rocky super-Earths or, more colourfully, lava and magma planets. These planets orbit so close to their host stars that they have apparent temperatures such that their rocky surface should melt or even vaporise. Little is known about these planets at present: much of the information discussed below is derived from models rather than observation.

Of course hot and cold are relative terms; here we will take room temperature ($T \sim 300$ K) as the norm which means, for example, that so-called cool stars which typically have temperatures in the 2000–4000 K range are definitely hot. Much of the cold interstellar medium is not thermalised and excitation, for example by energetic photons, can lead to highly excited molecules. This can be seen, for example, from maser emissions involving transitions between highly excited states, which is observed from a range of molecules from a variety of interstellar environments (Gray, 2012). Similarly the coma of comets are inherently cold but when bathed in sunlight can be observed to emit from very high-lying energy levels (Barber et al., 2009; Dello Russo et al., 2005, 2004).

Turning to the consideration of exoplanets. At the present it even remains unclear how to conclusively identify which planets of a few to ten Earth masses are actually rocky (Tasker et al., 2017). From density observations some of them appear to be rocky (silicate-rich), or with a fraction of ice/iron in the interior. Others suggest a structure and composition more similar to gas giants like Neptune. Density alone is not a reliable parameter to distinguish among the various cases. In addition to there is a class of ultra-short period (USP) exoplanets which are thought to be undergoing extreme evaporation of their atmosphers due to their close proximity to their host star (Gillon et al., 2014, 2012; Oberst et al., 2017; Sanchis-Ojeda et al., 2014). These objects are undoubtedly hot but as yet there are no mass measurements for USP planets. Spectroscopic investigations of atmospheres of super-earths and related exoplanets holds out the best prospect of learning about these alien worlds. The prospects of observing the atmospheric composition for the transiting planets around bright stars make us confident we will be in a much better position in a few years time with the launch of the James Webb space telescope (JWST) and future dedicated exoplanet-characterization missions.

From the laboratory perspective, the observation of hot or highly excited molecules places immense demands on the spec-

* Corresponding author.
E-mail address: j.tennyson@ucl.ac.uk (J. Tennyson).

http://dx.doi.org/10.1016/j.molap.2017.05.002

troscopic data required to model or interpret these species. As discussed below, a comprehensive list of spectroscopic transitions, a line list, for a single molecule can contain significantly more than 10^{10} lines. This volume of data points to theory as the main source of these line lists (Tennyson, 2012).

A line list consists of an extensive list of transition frequencies and transition probabilities, usually augmented by other properties such as lower state energies, degeneracy factors and partition functions to give the temperature dependence of the line and, ideally, pressure-broadening parameters to give the line shape. For radiative transport models of the atmospheres of hot bodies, completeness of the the line list to give the opacity of the species is more important than high ("spectroscopic") accuracy for individual line positions. This is also true for retrievals of molecular abundances in exoplanets based on the use of transit spectroscopy which, thus far, has largely been performed using observations with fairly low resolving power ($R < 3000$) (Tinetti et al., 2013). However, the situation is rather different with the high-dispersion spectroscopy developed by Snellen and co-workers (Birkby et al., 2013, 2017; Brogi et al., 2014; de Kok et al., 2013; Snellen, 2014), which is complementary to transit spectroscopy. This technique tracks the Doppler shifts of a large number of spectroscopic lines of a given species, by cross-correlating them to the reference lab data on the line positions. This exciting but challenging technique requires precise frequencies with $R \geq 100{,}000$, as well as a good spectroscopic coverage (hot transitions), available laboratory data is not always precise enough for this technique to work (Hoeijmakers et al., 2015a).

This review is organised as follows. First we summarise what is known about hot rocky super-Earth exoplanets. We then consider the laboratory techniques being used to provide spectroscopic data to probe the atmospheres of these bodies and others with similar temperatures. In the following section we summarise the spectroscopic data available making recommendations for the best line list to use for studies of hot bodies. Molecules for which little data appears to be available are identified. Finally we consider other issues associated with spectroscopic characterization of lava planets and prospects for the future.

2. Hot rocky super-Earths

As of the end of 2016 there are well over 100 detected exoplanets which are classified as hot super-Earths. These planets are ones which are considered to be rocky, that is with terrestrial-like masses and/or radii, see e.g. Seager et al. (2007), and which are hot enough for, at least on their dayside, their rock to melt (Kite et al., 2016). Only a handful of these planets are amenable to spectroscopic characterization with current techniques (Madhusudhan et al., 2016), which makes these few objects the ones suitable for atmospheric follow-up observations. All these rocky planets have very short orbits, meaning that they are close to their star and hence have hot atmospheres ($T \gg 300$ K). Some of these planets are evaporating with water vapour as a major constituent of the atmosphere (Barclay et al., 2013a; Batalha et al., 2011; Borucki et al., 2013; David et al., 2016; Leger et al., 2009; Madhusudhan and Redfield, 2015). The atmospheres of these planets are thought to have a lot in common with the young Earth (Alfvén and Arrhenius, 1974) and the atmosphere of a rocky planet immediately after a major impact planet is expected to be similar (Lupu et al., 2014). However, we note that as they are generally tidally-locked to their host star, hot rocky super-Earths will generally have significant day-night temperature gradients (Demory et al., 2016).

According to the NASA Exoplanets Archive (exoplanetarchive.ipac.caltech.edu), key hot exoplanets with masses and radii in the rocky-planet range include CoRoT-7b, Kepler-10b, Kepler-78b, Kepler-97b, Kepler-99b, Kepler-102b, Kepler-131c, Kepler-406b, Kepler-406c, and WASP-47e, with Kepler-36b and Kepler-93b being slightly cooler than 1673 K (Batalha et al., 2011; Carter et al., 2012; Dai et al., 2015; Hatzes et al., 2011; Howard et al., 2013; Leger et al., 2009; Moutou et al., 2013; Pepe et al., 2013; Weiss and Marcy, 2014). Most of the rocky exoplanets that have so far been studied are characterized by the high temperature of their atmospheres, e.g., about 1500 K in Kepler-36b and Kepler-93b, 2474 ± 71 K in CoRoT-7b Leger et al. (2011), 2360 ± 300 K in 55 Cnc e (Demory et al., 2012; Tsiaras et al., 2016), and around 3000 K in Kepler-10b (Kite et al., 2016). Somewhat cooler but still hot rocky planets include temperatures of 700 K in Kepler-37b (Barclay et al., 2013b), 750 K in Kepler-62b (Borucki et al., 2013), 580 K in Kepler-62c (Borucki et al., 2013), and 400–500 K in GJ 1214b (Bean et al., 2010; Charbonneau et al., 2009; Howe and Burrows, 2012).

If the main constituent of these atmospheres is steam, it will heat the surface of a planet to (and above) the melting point of rock (Zahnle et al., 1988). For example, the continental crust of a rocky super-Earth should melt at about 1200 K (Sawyer et al., 2011), while a bulk silicate Earth at roughly 2000 K (Schaefer et al., 2012). The gases are released from the rock as it heats up and melts, including silica and other rock-forming elements, and is then dissolved in steam (Fegley et al., 2016). The main greenhouse gases in the atmospheres of hot rocky super-Earths are steam (from vaporising water and hydrated minerals) and carbon dioxide (from vaporising carbonate rocks), which lead to development of a massive steam atmosphere closely linked to magma ocean at the planetary surface (Abe and Matsui, 1988; Elkins-Tanton and Seager, 2008; Fegley et al., 2016; Kasting, 1988; Lebrun et al., 2013; Matsui and Abe, 1986; Zahnle et al., 1988).

At temperatures up to 3000 K, and prior to significant volatile loss, the atmospheres of rocky super-Earth are thought to be dominated by $\mathbf{H_2O}$ and $\mathbf{CO_2}$[1] for pressures above 1 bar, see Schaefer et al. (2012). These objects will necessarily have spectroscopic signatures which differ from those of cooler planets. At present interpretation of such signature is severely impacted by the lack of the corresponding spectroscopic data. For example, recent analysis of the transit spectrum of 55 Cnc e by Tsiaras et al. (2016) between 1.125 and 1.65 μm made a tentative detection of hydrogen cyanide (**HCN**) in the atmosphere but could not rule out the possibility that this signature is actually in part or fully due to acetylene (**HCCH**) because of the lack of suitable laboratory data on the hot spectrum of HCCH. The massive number of potential absorbers in the atmosphere of these hot objects also have a direct effect on the planetary albedo (Kasting, 1988) as well as the cooling and hence evolution of the young hot objects; comprehensive data is also crucial to model these processes.

Atmospheric retrievals for hot Jupiter exoplanets such as HD 209458b, GJ 1214b and HD 189733b (Sing et al., 2016) show that transit observations can help to establish the bulk composition of a planet. However, it is only with good predictions of likely atmospheric composition allied to a comprehensive database of spectral signatures and proper radiative transfer treatment that the observed spectra can be deciphered. The completeness of the opacities plays a special role in such retrievals: missing or incomplete lab data when analysing transit data will lead to overestimates of the corresponding absorbing components.

The typical compositions of steam atmospheres have been considered by Schaefer et al. (2012), with an example for low atmospheric pressure shown in Fig. 1. The chemical processes on these objects are very similar to the young Earth (Mars or Venus) and have been studied in great detail. The major gases in steam atmospheres (equilibrated chemistry) with pressures above 1 bar and surface temperatures above 2000 K are predicted to be H_2O, CO_2,

[1] Molecules thought to be important for the spectroscopy of hot super-Earths are given in bold when first mentioned.