Spectroscopic analysis of the isotope effect in chemically assisted physical sputtering of beryllium

E. Pawelec[1], D. Borodin[2], S. Brezinsek[2], T. Dittmar[2], D. Douai[3], A. Meigs[4], A. Shaw[4]
and JET Contributors*

[1]*Institute of Physics, University of Opole, Oleska 48, 45-054 Opole, Poland;* [2]*Forschungszentrum Jülich GmbH, EURATOM Association, 52425 Jülich, Germany;* [3]*CEA, IRFM, F-13108, Saint-Paul-Lez-Durance, France;* [4]*UK Atomic Energy Authority, Culham Science Centre, Abingdon, OX14 3DB Oxfordshire, UK*

Molecules may seem as an unusual topic in the study of magnetic confined fusion (MCF) plasma. Nevertheless, in the relatively cold region where the plasma touches the vessel wall, a relatively complex chemical processes may occur, giving rise to short-living molecular species. Those molecules do not exist for long, neither are they transported far from the place of production, but can be observed and provide important knowledge about the plasma-wall interaction. In the case of the hydrogen plasma touching beryllium surface, production of beryllium hydride molecules is an important part of the erosion process [1, 2]. This Chemically Assisted Physical Sputtering (CAPS) process depends on the particle flux to the wall and on the amount of hydrogenic species present in the wall material. Increasing the beryllium wall temperature, as shown in [1], leads to the strong suppression of this part of sputtering, both diminishing the total number of beryllium atoms eroded from the vessel surface and providing much clearer data about the other, purely physical part of the sputtering process.

Erosion of beryllium wall is predominantly done by fuel, so the mass of the hydrogen isotope used in the plasma is expected to strongly impact the erosion yield. Most of the erosion data are collected from MCF machines working in deuterium, some of them also in hydrogen (and, sometimes, helium). As the isotopic composition of a burning plasma is deuterium, tritium and a small percentage of helium ash, the erosion of the beryllium wall by tritium has to be known and taken into account. To disentangle the physical sputtering and CAPS, the isotopic dependence of the molecular contribution has to be known as well. As the vibrational and rotational energy levels of moleculse depend on nuclear mass of the constituents, the isotopic dependence of the CAPS could be expected. Analysis of the influence of the molecular component on the erosion processes is largely done by appropriate modeling (see [2]) and verified experimentally mostly by optical emission spectroscopy. It can be done by measuring molecular spectra by analysis of the atomic spectra of the atoms originating from the dissociation of molecules (e.g. hydrogen/deuterium studies [3]). In the case of beryllium hydrides the low-excited A$^2\Pi$ to X$^2\Sigma^+$, $\Delta v = 0$ molecular transition at ~498 nm is very prominent in the visible radiation of the MCF fusion plasma, so its study is a method of choice in this case. Main parameters describing the beryllium hydride behavior are total intensity of the band and its shape, described by two main parameters – rotational and vibrational temperatures.

Optical transitions in molecules depend on energy levels of the optical electron(s) in a complicated Coulomb field of multiple, moving nuclear point sources. For a diatomic molecule, this analysis is done by separating the energy into three main components – electronic, vibrational and rotational contributions, with very different energy level separations. The energy of the particular level is therefore described by following equation:

$$E_{e,v,J} = E_{el} + E_{vib}(v) + E_{rot}(J)$$

The electronic part has very slight isotopic dependence, but the rotational and vibrational contributions depend strongly on the mass of the species. In the widely used approximation of a molecule as an anharmonic vibrator (Morse potential) and non-rigid rotator the energies from those two parts can be described as follows:

$$E_{vib}(v) = h\nu_e\left(v+\frac{1}{2}\right) + h\nu_e x_e\left(v+\frac{1}{2}\right)^2 + ...$$

$$E_{rot}(J) = BJ(J+1) - D[J(J+1)]^2 + ...$$

where v is the vibrational quantum number and J is the rotational quantum number, and the expansion parameters are all mass-dependent.

This polynomial expansion is an approximation, but very useful for analysis, tables and generation of the synthetic spectra from the restricted set of data taken from experiments [4]. The diatomic molecular data for BeH and BeD allow for reproducing experimental spectra with good agreement, but the dataset for BeT is much more sparse: only 4 vibrational levels, only low-level expansion coefficients especially for the A level [5], and the simulated spectrum for the JET-appropriate parameters has some very strange- looking features. Fortunately, there is a large set of transitions calculated using MARVAL and Duo codes [6] which can be obtained e.g. from Exomol site (www.exomol.com). This set contains energies, Einstein coefficients and statistical weights of every transition between rovibrational sublevels of A and X electronic levels of BeH, BeD and BeT, for vibrational quantum numbers up to 25 and rotational up to 100. This means ~700 000 transitions for each isotopologue, fortunately, many of those transitions lay outside of the chosen wavelength range, and of those within, most can be excluded by setting the minimal Einstein coefficient. In the end, to reproduce high-resolution BeH (or its isotopologue) spectrum in the 487-520 nm region there are ~7000 transitions to consider. The synthetic spectrum is created using the following procedure:

- transition and level data from *.transitions and *.states files are read to the Python numpy arrays, restricted by wavelength and transition probability
- for each transition a Gaussian line profile with the apparatus width is created and each of the profiles is multiplied by the total emissivity of the molecular line:

$$\varepsilon_{ki} = \frac{h\nu}{4\pi} A_{ki} \frac{F(v,J)}{U(T)}$$

  where A_{ki} is the Einstein coefficient, g_{tot} is the total degeneracy (containing both nuclear-spin factor and the total angular momentum), U(T) is the partition function and F(v,J) is the population of the given state with vibrational number v and rotational number J. Population is assumed to be in partial LTE state, with different temperatures for vibrational and rotational part, therefore function F(v,J) is given by:

$$F(v,J) = g_I g_J \cdot \exp\left(-\frac{E_v}{kT_{vib}}\right) \exp\left(-\frac{E_J}{kT_{rot}}\right)$$

  where the vibrational energies are defined as the minimal energy of the rotational levels with particular vibrational quantum number.

- The spectrum function is a sum of all the transition profiles with three main free parameters – total intensity of the spectrum, rotational and vibrational temperature. If needed, also the intensities of the overlapping atomic lines can be included. The background is set to zero, because the experimental spectra are background subtracted.

Contrary to the experiments described in [6,7], the spectroscopic study of BeH isotopologues in pure and mixed hydrogen plasmas were not dedicated, but piggyback ones during other JET experiments. Therefore, there is no comparable measurement of the total highly resolved band of BeH or BeT, as they would need at least the four, ideally identical, JET pulses. Larger parts of the band can be measured with lower-resolution spectrometers and the high-resolution measurements concentrated on the main peak region (mostly Q bands). There are several visible spectrometers observing JET plasma along different lines of sight, but for this study four are important – two high resolution spectrometers observing: KSRB midplane and 10 l-o-s covering outer divertor, KSRD 10 l-o-s covering the inner divertor, and low resolution spectrometers KSRA and KSRC observing the same l-o-s, respectively.

High-resolution measurements with good signal/noise ratio were obtained mostly for two lines of sight – midplane l-o-s during limiter part of the pulse (or limiter pulses), when the plasma is close to the beryllium limiter, and vertical l-o-s showing the inner strike point, where the plasma streaming along the separatrix touches the beryllium-covered tungsten.

Comparison of the low resolution spectra of for all three isotopologues is presented in the figure 1. The Q branch is slightly shifted with increasing hydrogen mass to the shorter wavelength (shift is of ~0.1 nm), the P and R branches are much more "compressed". In [1] and in [8] as a measure of the total intensity of this transition, the intensity of the background-subtracted main peak is integrated in the region of 496 nm to 499.6 nm. From the model low-resolution spectra, we could estimate that this comprises slightly more than half of the total intensity of the band, weakly depending on temperatures and the studied isotopologue. In the region of 3000 – 5000 K we could say that the ratio is lowest at 0.51 for $T_{rot} = T_{vib} =$ 5000 K for BeH and highest at 0.58 for $T_{rot} = T_{vib} = 3000$ K

Fig 1. Low-resolution experimental spectra for different isotopologues (the same pulse numbers as in Fig.3)

for BeT, which means that the possible error bar of the total intensity estimation is less than 10%.

An example of the fit results in the case of a BeD spectrum (from the same experiment as in [6]) is presented in figure 2. As can be seen, the main peak (mostly Q branches, at least up to $v = 6$) shows some discrepancy, mostly for $v = 0$ to $v=0$ transition, whereas the wings look better, though some of the peaks are slightly shifted in wavelength. The least squares fit for the full spectrum yields a pair of temperatures $T_{rot} = 3900K$ and $T_{vib} = 4500K$, with the estimated uncertainties approximately 400 K for both temperatures.
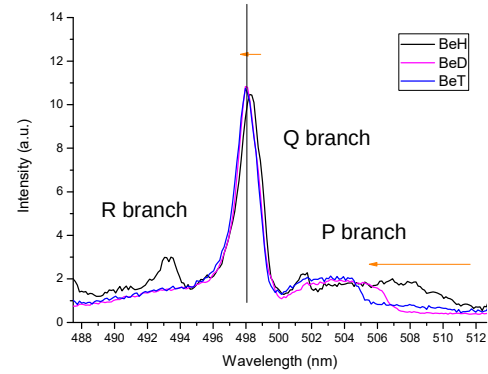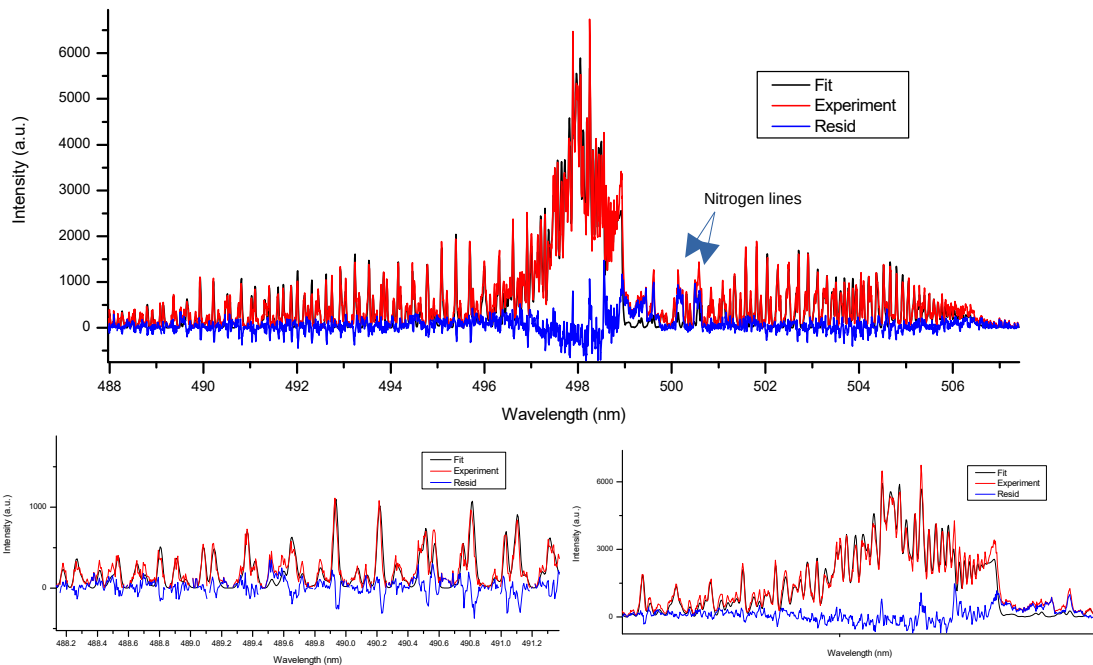
Fig 2. BeD spectrum composed from the spectra from four JET pulses with fit and residuum.

As we did not obtain the full spectrum for the other isotopologues, the fits for comparison were performed only for restricted wavelength region, the same for all three spectra – 495 to 501 nm. As can

be seen in figure 3, the differences between the high-resolution spectra measured with the midplane l-o-s and in the inner divertor are negligible. The midplane spectra have less overlapping atomic lines, which are visible in the divertor spectrum (e.g. nitrogen lines in the BeD spectrum), but the shapes of the main peaks are completely the same for both l-o-s. That's why fitting was done for the midplane spectra, and the temperatures are presented in the figure. As can be seen, the values for different isotopologues both for rotational and for vibrational temperatures agree within the estimated uncertainty, which suggests, that the molecules are created with the same internal energy distributions.

The results support the ones presented in [8] suggesting, that the CAPS in midplane is independent of the hydrogen isotope. Poster [8] shows comparison for hydrogen and deuterium, but the similarity in the tritium band shape suggests that the same is true for the third isotope as well. As the spectra measured at the inner strike point have also the same shape, the molecular contribution to the erosion process of beryllium can be assumed uniform for all the places and for all isotopologues, the only result of different plasma parameters being the total intensity of the molecular band. Note, that for the vibrational and rotational temperatures obtained from the fits to high-resolution spectra, the low-resolution conversion factor from the integrated 496.0 to 499.6 nm intensity to the total band intensity is equal to 0.52 for BeH, 0.53 for BeD and 0.54 for BeT, so the uncertainty over isotopologue is smaller than the estimated experimental errors.
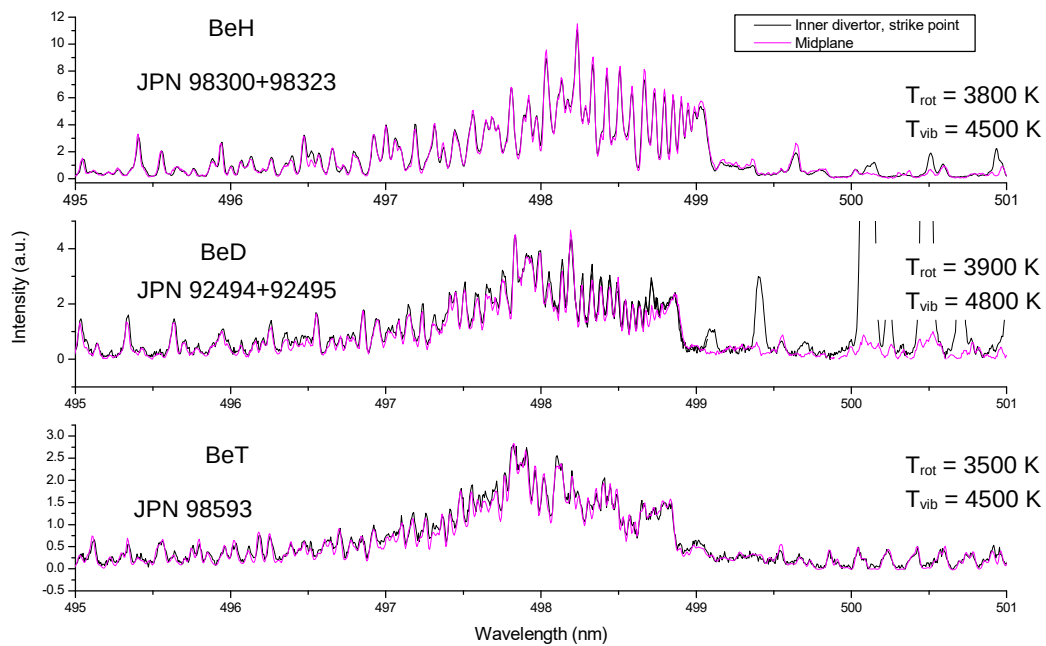
Fig 3. Main peak region of different isotopologues, comparing the midplane and divertor spectra. Vibrational and rotational temperatures obtained from the fit to midplane spectrum marked on the graph.

[1] S. Brezinsek et al, Nuclear Fusion **54** (2014) 103001 [2] D. Borodin et al, Nuclear Materials and Energy **9** (2016) 604–609 [3] K. Verhaegh et al, Plasma Phys. Control. Fusion **63** (2021) 035018. [4] C. Focsa et al, Journal of Molecular Spectroscopy **192** (1998) 348–358. [5] R.J. Le Roy et al, Journal of Molecular Spectroscopy **236** (2006) 178–188. [6] D. Darby-Lewis et al, Journal of Physics B **51** (2018) 185701 [7] G. Duxbury et al, Plasma Physics and Controlled Fusion **40** (1998) 361–370 [8] D. Borodin et al, 47th EPS Conference on Plasma Physics, Sitges, Spain 2021, P1.1029