



Fig. 6 Evolution of the  $I(\theta_e)$  MFPAD for the  $\chi = 0^\circ$  orientation, featuring the parallel transition, across the energy region scanned by the H15–H21 harmonics, corresponding to the shape resonance of the  $\text{NO}^+(\text{c}^3\Pi)$  ionic state. The 3D plots are based on the Legendre polynomial fit of the measured  $F_{\text{LN}}$  functions (see Fig. 5).

the influence of the electron-ion scattering process including dynamic electronic correlation.

## 5. Molecular polarimetry: an *in situ* tool for polarization analysis in high-order harmonic spectroscopy (HHS)

High-harmonic spectroscopy of unaligned  $\text{SF}_6$  molecules<sup>38,44,65</sup> pertains to recent experimental and theoretical studies aimed at the extension of this ultrafast metrology to polyatomic molecules,<sup>32,66–70</sup> with a focus on the role of non-adiabatic multi-electron dynamics and coherent superposition of multiple channels. Different HHS methods were combined to characterize HHG from the  $\text{SF}_6$  generation medium,<sup>44</sup> among which the investigation of the spectral dependence of the parameters describing the polarization ellipse of the XUV harmonics. Optical polarimetry measurements based on Malus' law, in terms of the ellipse orientation and the upper bound ellipticity  $\varepsilon_{\text{ub}}$ , showed unprecedented values ranging between 0.8 and 0.6 for harmonics H13 to H17 for an ellipticity  $\varepsilon_{\text{fun}} = 0.2$  of the 800 nm driving laser.<sup>38</sup> The produced elliptically polarized HHG source was subsequently used to measure photoelectron circular dichroism (PECD)<sup>71</sup> on chiral molecules,<sup>38</sup> *i.e.*, to characterize the electron emission forward/backward asymmetry along the propagation direction of the light. Such measurements should provide the  $s_3$  Stokes parameter, if the PECD is calibrated independently and if the contribution of each HH can be resolved in the photoelectron spectra.

We applied the MP method to the analysis of the APT generated in  $\text{SF}_6$  by an elliptically polarized driving IR laser, with the goal of probing the complete polarization state of each HH composing the APT, expressed in terms of the  $s_1$ ,  $s_2$ ,  $s_3$  Stokes parameters, or the  $(\psi, \varepsilon, P)$  quantities characterizing the polarization ellipse and the degree of polarization  $P$ . The analysis of the measured  $I(\chi, \gamma)$  histograms and the  $s_3 \times F_{11}(\theta_e)$  functions for the dominant DPI process (eqn(5)) induced by the H15–H21 major harmonics proceeds along the lines described in Section 2.

For the extraction of the  $s_3$  Stokes parameters, we rely on the reference  $F_{11}(\theta_e)$  functions which were measured on the DESIRS beamline at SOLEIL at the same photon energies,<sup>62</sup> and are well predicted by MCSCI calculations:<sup>45</sup> for each harmonic, the  $s_3$  value is obtained as the ratio between the  $s_3 \times F_{11}(\theta_e)$  curve and the reference  $F_{11}(\theta_e)$  function at the corresponding photon energy.  $s_1$  and  $s_2$  are