We have been using the polarization labeling spectroscopy (PLS) method to study excited electronic states of diatomic alkali metal molecules accessible in one photon transitions from the molecular ground states. Our variant of the PLS method is based on a V-type optical-optical double resonance excitation scheme employing two independent laser sources. This technique elegantly surmounts the difficulty of resolving and analyzing highly congested molecular spectra. With a proper choice of frequencies and polarization of two laser beams, interacting with a given molecular sample, only transitions from a few known rovibrational levels in the ground state are observed, resulting in spectra with easily resolved and understandable rotational structure. Although the polarization spectra are Doppler-limited but the precision in determination of molecular constants and potential energy curves (PECs) from such experiments is adequate to majority of needs and fully sufficient for comparison with modern \textit{ab initio} calculations.

In this contribution we present some experimental details of our variant of the PLS technique, examples of the spectra and of their analysis leading to determination of PECs, also in cases of their irregular shapes. In particular, the results of our recent investigations on excited electronic states of NaRb and Li$_2$ will be presented.