Infrared spectroscopy, especially for molecular vibrations in the fingerprint region between 600 and 1,500cm􏰀1, is a powerful characterization method for bulk materials. However, molecular fingerprinting at the nanoscale level still remains a significant challenge, due to weak light–matter interaction between micron-wavelengthed infrared light and nano-sized molecules. Here we demonstrate molecular fingerprinting at the nanoscale level using our specially designed graphene plasmonic structure on CaF2 nanofilm. This structure not only avoids the plasmon–phonon hybridization, but also provides in situ electrically-tunable graphene plasmon covering the entire molecular fingerprint region, which was previously unattainable. In addition, undisturbed and highly confined graphene plasmon offers simultaneous detection of in-plane and out-of-plane vibrational modes with ultrahigh detection sensitivity down to the sub-monolayer level, significantly pushing the current detection limit of far-field mid-infrared spectroscopies.