Terahertz spectroscopy of single Ce@C$_{82}$ molecules using sub-nm scale gap electrodes

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Terahertz (THz) spectroscopy is a powerful tool for clarifying electronic structures and vibrational dynamics of various kinds of molecules. However, it is a great challenge to greatly exceed the diffraction limit [1] and perform single molecule spectroscopy, because there is a huge size difference (a factor of $\sim 10^5$) between the THz wavelength ($\sim 100 \mu$m) and the size of single molecules ($\sim 1$ nm).

In this work, we propose a novel method for performing THz spectroscopy on single molecules. THz vibrational spectra of a single Ce@C$_{82}$ molecule have been measured by using a single molecule transistor (SMT) geometry, which consists of a single molecule and metal nanogap electrodes, as a THz detector. The inset of Fig. 1(b) shows an SEM image of a fabricated Ce@C$_{82}$ SMT structure. We created a sub-nm gap in a metal nanojunction by using electromigration. By using the nanogap electrode as a THz antenna, this sample structure allows us to overcome the diffraction limit and focus THz radiation onto a single molecule. Figure 1(a) shows the Coulomb stability diagram of a Ce@C$_{82}$ SMT. The crossing pattern indicates that we capture a single molecule in the nanogap. THz signal of a single Ce@C$_{82}$ molecule was obtained by measuring the THz-induced photocurrent in the SMT sample. Figure 1(b) shows the obtained THz spectra of a single Ce@C$_{82}$ molecule. Broad photocurrent peaks appear around 50 cm$^{-1}$ and 110 cm$^{-1}$. Although the origin of these peaks is not clear at present, we think it is related with dynamical motion of the encapsulated Ce atom in the C$_{82}$ cage [2]. This is the first successful measurement of THz spectra of a single molecule.


![Fig. 1](image-url)