The interaction between molecule and alumina is of great interest in catalysis, soil chemistry and atmospheric chemistry. In this study, the adsorption of piperidine gas molecule on the hydrated alumina (0001) surface was investigated in the ambient environment by a surface selective spectroscopic technique, vibration broad bandwidth sum frequency generation (BBSFG) spectroscopy. The interfacial vibrational signature of the CH\textsubscript{2} symmetric stretch of piperidine adsorbed at the alumina (0001) surface obtained by BBSFG was used as a sensitive spectroscopic probe reflecting the information about the adsorption mechanism. Results show that the SFG frequency of the interfacial CH\textsubscript{2} symmetric stretching mode of piperidine at the alumina surface is comparable to that of the hydrogen-bonded piperidine at the air-water interface, but different from that of the non-hydrogen-bonded piperidine (neat piperidine) and the protonated piperidine (piperidium) at the air-liquid interface. This allows us to make a reasonable conclusion that piperidine is adsorbed on the alumina surface through hydrogen bonding between alumina and piperidine.