

EXPERIMENTAL STUDY OF DEVIATION FROM LORENTZIAN SHAPE OF COLLISIONAL BROADENED SPECTRAL LINES IN MILLIMETER AND SUBMILLIMETER WAVE BANDS

GUERMAN Yu. GOLUBYATNIKOV, VLADIMIR N. MARKOV, *Applied Physics Institute of RAS, 46 Ul'yanova str., GSP-120, Nizhny Novgorod 603600, Russia*; ANTONIO GUARNIERI and HEINRICH J. MÄDER, *Institut für Physikalische Chemie der Universität Kiel, Olshausenstr. 40, D-24098 Kiel*.

Experimental deviations from Lorentzian line shape of collisional broadened pure rotational CO ($J=1\leftarrow 0$, $J=5\leftarrow 4$) molecular lines have been observed. The deviations are effects of narrowing and asymmetry in the spectral line core. Measurements were performed by a RAD (radio-spectrometer with acoustic detector) spectrometer with a signal-to-noise ratio ~ 1000 . While the fit error of the line profile to Lorentzian shape was within 0.5 %, an error of line broadening parameters exceeded 4 % for different shape models and lengths of line record. Pickett's model^a gave a much better residue between experimental and fitted data for CO lines, but the broadening parameter was more dependable on gas pressure and also had dependence on the length of line record.

To clear up an origin of deviation from Lorentzian profile, either it is due to speed-dependent like effects or apparatus ones, accurate testings of receiving part of spectrometer was performed by using a resonance curve of Fabry-Perot resonator as etalon. There was no discrepancy exceeding the noise observed between resonance curve shape and simple Lorentzian model. By variation of a length of gas absorption cell revealed dependence of spectral line profile on wall collisions. That is not simple line broadening^b but distortion of Lorentzian line shape near its core: line "narrowing" and central line shifting as well. This effect was quite similar to speed-dependent effects for collision of absorber molecules CO with heavy buffer molecules as Kr, Xe. Since the most recent papers dealing with line shape consider mainly the speed-dependent effects, it seems worth the influence of wall collisions on the line shape to be discussed.

^aH.M. Pickett, Effects of velocity averaging on the shape of absorption lines, *J. Chem. Phys.* **73**(12), 6090-6094, 1980.

^bM. Danos, S. Geschwind, Broadening of Microwave Absorption Lines Due to Wall Collision, *Phys. Rev.* **91**(5), 1159-1162, 1953.