Low-pressure verification of collisional coupling models of the molecular oxygen 60-GHz band

D. S. Makarov, M. A. Koshelev, I. N. Vilkov, and M. Yu. Tretyakov

Institute of Applied Physics, Russian Academy of Sciences, Uljanova str, 46, 603950, Nizhniy Novgorod, Russia, Tel.: +7(831)4164866, E-mail: dmak@appl.sci-nnov.ru

The collisional coupling (or line mixing) effect is a redistribution of the spectral intensity between overlapping lines in comparison to the sum of solitary profiles of the considered lines. One of the most important spectra influenced by the collisional coupling in mm-submm waverange is the molecular oxygen absorption band near 60 GHz. This band is formed by a large number of fine structure lines. At pressure near 1 atm, the band is observed as a single profile which is noticeably dissimilar to the sum of Van Vleck-Weisskopf profiles of the constituting lines [1].

Modeling of this band has a long history [1-6]. There are two approaches accounting for line mixing by different ways. The Energy Correction Sudden (ECS) model [6] deals with full semi-empiric rotational relaxation matrix calculation and direct inversion of the matrix in spectral function (see, e.g., equation (1) in [6]). Millimeter-wave Propagation Model (MPM) [1,4,5], being well-known and widely used for atmosphere remote sensing applications, uses perturbation theory approach instead of direct matrix inversion and simplified rotational relaxation matrix. The perturbation approach was recently extended from first to second order terms [5].

Both models were built based on the measurements made at atmosphere pressure where all lines are merged together. Earlier, mixing between well-resolved profiles of the molecular oxygen fine-structure lines was never observed and analyzed (the only exception is 1- line at 118.75 GHz which is far from the band and therefore weakly coupled with other lines, so that mixing effect is clearly noticed only at high pressure [7]). This was the reason for the attempt of verification of both MPM and ECS models at low pressures.

By means of spectrometer with radioacoustic detection of absorption [8] several recordings of two close fine-structure lines denoted as 9- and 3+ at pressures from 2 to 18 Torr and temperature -34 C were made. The distance between line centers is ~123 MHz which provides noticeable profile overlapping at 18 Torr. Treatment of the obtained profiles by means of fitting the sum of two lorentz model functions (taking into account the features of the spectrometer [8]) to the measured absorption profile has shown noticeable difference in half-widths of both lines in comparison to known value [1]. At the same time, comparison of the measured absorption profile against ones calculated (i.e. not fitted to the experimental data) using MPM and ECS models has shown good and almost equal coincidence between measured and calculated profiles. Thus we can conclude that collisional coupling of spectral lines makes noticeable contribution into absorption profile even at low pressures and can be taken into account with both models.

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