MOLECULAR OXYGEN MICROWAVE SPECTRUM COMPREHENSIVE STUDIES FOR ATMOSPHERIC APPLICATIONS

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The weak magnetic dipole fine structure lines of molecular oxygen are widely used in microwave radiometric atmospheric measurements for the temperature or pressure distribution retrieving. The accuracy of determining the atmospheric parameters depends on the accuracy of the absorption and radiative transfer model used and, in particular, on the underlying spectroscopic parameters of the molecular lines and the continuum. We report results of the state-of-the-art high-accuracy comprehensive studies of the molecular oxygen microwave spectrum.

Studies were carried out in three main directions: 1) line shape and parameters of the individual lines 2) the shape of the spectrum in general, considering collisional coupling effect strongly manifesting in the microwave spectrum and "dry" non-resonant absorption, and 3) refinement of the radiative transfer models and testing them using radiometry measurements data.

In the first direction, fine structure lines are studied individually, extending the range of rotational quantum number N up to N=43. A temperature interval of about 120 K centered at room temperature is considered, a wide pressure range (0.02–1500 Torr) is covered by three different spectrometers having complementary abilities¹ validating each other within the experimental uncertainties. Signal-to-noise ratio of the experimental recordings reached about 20000 allowing investigation of speed-dependence (SD) of pressure broadening. As a result, the following parameters were measured or refined: line centers (sub-kHz uncertainty)², pressure shifting, pressure broadening and its' speed-dependence³ coefficients (including their temperature dependencies). Speed-dependent broadening was studied in frames of widely used quadratic approximating function⁴. Rotational dependence of the speed-averaged

¹10.1016/j.jms.2012.06.010 A.F. Krupnov, M.Yu. Tretyakov, S.P. Belov, G.Yu. Golubiatnikov, V.V. Parshin, M.A. Koshelev, D.S. Makarov, and E.A. Serov, Accurate broadband rotational BWO-based spectroscopy, J. Molec. Spectrosc. 280, 110–118 (2012)

²10.1016/j.jqsrt.2021.108001 M.A. Koshelev, G.Yu. Golubiatnikov, I.N. Vilkov, M.Yu. Tretyakov, Molecular oxygen fine structure with sub-kHz accuracy. J. Quant. Spectrosc. Radiat. Transfer. 278, 108001 (2022)

 $^{^{3}}$ 10.1016/j.jqsrt.2023.108493 M.A. Koshelev, I.N. Vilkov, T.A. Galanina, E.A. Serov, D.S. Makarov, M.Yu. Tretyakov, Temperature behavior of collisional parameters of oxygen fine-structure lines: O₂– O₂ case. J. Quant. Spectrosc. Rad. Trans. 298, 108493 (2023)

 $^{^{4}10.1063/1.468342}$ F. Rohart, H. Mader, H.W. Nicolaisen, Speed dependence of rotational relaxation induced by foreign gas collisions: studies on CH₃F by millimeter wave coherent transients. J. Chem. Phys. 101, 6475–6486 (1994)

pressure broadening γ_0 and speed-dependence parameter γ_2 were measured for both O_2 and N_2 perturber molecules. It was demonstrated that the single power law is suitable for both $\gamma_0(T)$ and $\gamma_2(T)$ within the studied temperature range. It was found that the corresponding temperature exponents n_{γ_0} and n_{γ_2} showed significantly different rotational dependence, which also depends on a collisional perturber. Experimental results for the 118-GHz line are well confirmed by the quantum scattering calculations⁵. Intensity of the 118-GHz line was determined with the subpercent uncertainty, which allowed assigning a higher intensity accuracy category to all fine structure lines.

In the second direction, the collisional coupling effect was studied at pressures near 1 atm on the basis of the 60-GHz band profiles recorded in natural and artificial air. Two approaches were used to model the absorption and obtain the corresponding parameters: the perturbative one, leading to the line-by-line description of the 60-GHz band, and the one based on the ECS formalism⁶. Both approaches use the data on the lines' intensities, central frequencies, and widths as *a priori* information. For both models, corresponding mixing parameters were obtained giving average obs.-calc. relative difference below 0.3%. ECS approach has shown better agreement with the 60-GHz band far wings, including the Debye absorption.

Results of the brightness temperature calculation using radiative transder model (with included developed microwave oxygen spectrum models) and the meteosounders data on the atmosphere pressure, temperature and humidity profiles were compared to the measurement results. Model based on the ECS formalism showed better reproducing of the brightness temperature yet requiring greater computation resources⁷.

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 $^{^{5}10.1063/5.0063006}$ M. Gancewski, H. Jozwiak, E. Quintas-Sanchez, R. Dawes, F. Thibault, P. Wcislo, Fully quantum calculations of O₂–N₂ scattering using a new potential energy surface: Collisional perturbations of the oxygen 118 GHz fine structure line. J. Chem. Phys. 155(12), 124307 (2021)

⁶10.1016/j.jqsrt.2019.106798 D.S. Makarov, M.Yu. Tretyakov, P.W. Rosenkranz, Revision of the 60-GHz Atmospheric Oxygen Absorption Band Models for Practical Use. J. Quant. Spectrosc. Rad. Trans. 242, 106798 (2020)

⁷10.3390/rs14236042 M.V. Belikovich, D.S. Makarov, E.A. Serov, M.Yu. Kulikov, A.M. Feigin, Validation of Atmospheric Absorption Models within the 20–60 GHz Band by Simultaneous Radiosonde and Microwave Observations: The Advantage of Using ECS Formalism. Remote Sensing 14, 6042 (2022)