HIGH-RESOLUTION PRESSURE-BROADENING PARAMETERS FOR ROVIBRONIC TRANSITIONS IN EXOMOLECULES

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Spectroscopic studies of extrasolar planets simultaneously in visible and infrared regions constitute the main goal of next-generation space missions, such as the James Webb Space Telescope (JWST) launched late 2021 and Atmospheric Remote-sensing Infrared Exoplanet Large-survey (ARIEL) adopted by the European Space Agency for launch in 2029 [1]. Analyses of the recorded spectra will strongly rely on a new and important source of information: high-resolution line-shape parameters for rovibrational and rovibronic transitions, in particular line-broadening parameters [2] which contribute to absorption in atmospheric transparency windows and spectral wings and influence the continuum modelling. Given elevated temperatures, optically active species to be considered include not solely already detected and expected ”exotic” molecules but also molecular ions. Moreover, because of a wide variety of exoplanet atmospheres to be probed, various perturbers should be taken into account: hydrogen and helium, as for gas giants, but also carbon dioxide, nitrogen, oxygen, water vapor, carbon monoxide, nitric monoxide, methane and ammonia. Thus, a large amount of line-shape data for ”exotic” molecular pairs is required.

Extensive line lists of positions and intensities for over 90 ”exomolecules” are provided by the ExoMol database [3] and molecular species relevant to the Earth's and planetary atmospheres are included in specialized databases, such as HITRAN [4], GEISA [5], TheoReTS [6], MoLList [7], etc. Although air-broadening and air-induced shift coefficients for vibration bands are generally available in HITRAN for ”standard” atmospheric molecules and within temperature ranges of atmospheric interest, pressure broadening and shifting parameters as well as their temperature dependence for required exomolecules are extremely scarce or (more often) completely missing. In addition, the specific conditions of hot atmospheres and chemical reactions occurring in them are hardly reproducible in laboratory, so that experimental studies of line-shape parameters are also deficient. The only alternative to produce the large amount of essential but missing data on line-shape parameters is offered, therefore, by theoretical approaches.

Whereas the pressure broadening and pressure-induced shift of molecular spectral lines corresponding to pure rotational and vibrotational transitions have been extensively addressed by theoreticians, these parameters for transitions involving a change in electronic state have received much less attention. We present a theoretical study of collisional broadening of rovibronic lines in the framework of phase-shift theory developed for atoms but applicable also to molecules because of high transition energies and common line-shape features conformed by electronic absorption spectra. We start by a general analysis for arbitrary molecular partners which is conducted in terms of a dimensionless parameter depending on 12-6 Lennard-Jones parameters describing the intermolecular interactions in the ground and excited electronic absorber's states. The mean-thermal-velocity approximation as well as the Maxwell-Boltzmann average over velocities are considered. The latter allows, in particular, addressing the validity of the traditional power law for widths and shifts. To check the validity of the theory, after having computed the required potential-energy surfaces, we present practical computations of linewidths and shifts at various temperatures for some representative molecular pairs and compare them to available measurements. The influence of the trajectory model for the relative molecular motion and the role of the Lennard-Jones form for the isotropic intermolecular potential representation are discussed. Concluding remarks outline some prospectives of improvements.

[1] https://arielmission.space/
[2] J.J. Fortney et al., arXiv:1905.07064 (2019).
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[4] T. Delahaye et al., J Mol Spectrosc 380, 111510 (2021).
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[6] A.V. Nikitin et al., J Mol Spectrosc 327, 138 (2016).
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