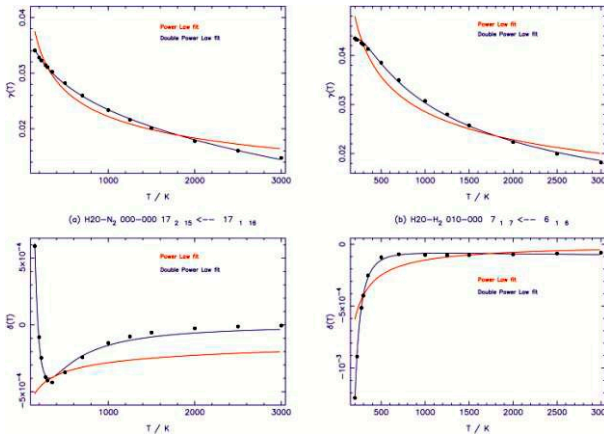


On the temperature dependence of half-widths and line shifts for molecular transitions in the microwave and infrared regions

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An expression was developed that correctly models the temperature dependence of the half-width over large temperature ranges and the temperature dependence of the line shift, even for cases where the line shift changes sign. The expression was derived from the expansion of the collisional cross-sections in a series of powers of the relative velocity of the radiator and perturber. Cutting off at two terms yields a complex double power law (DPL) expression, where the real and imaginary parts describe the temperature dependence of the half-width and line shift, respectively. Data were collected for more than 100 thousand transitions and the standard power law expression for the half-width and line shift were compared with the new double power law expression. It is shown that the double power law works well for all transitions, even those that exhibit unusual structure, which the standard power law cannot model. The DPL expression gives better results than the standard power law for all transitions studied and the DPL model gives good results for the temperature dependence of the line shift when it changes sign. The figure below shows examples of power law and double power law fits to 2 transitions: the $17_{215} \leftarrow 17_{118}$ rotation band transition of H_2O in collision with N_2 and the $7_{17} \leftarrow 6_{16}$ ν_2 band transition of H_2O in collision with H_2 . The DPL model for the temperature dependence of the line shift was compared with the linear model, which is currently used on the HITRAN database. In all cases the DPL model gave much better results than the linear model no matter what temperature range was considered. The new formalism allows a substantial reduction in the number of parameters that need to be stored in databases and the same expression can be utilized in radiative transfer and simulation codes for both the half-width and line shift.



Calculation of half widths and line shifts of H₂O–N₂ collision system using the modified complex Robert–Bonamy formalism

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Water vapor is the principal absorber of infrared radiation in the Earth's atmosphere. Knowing the line shape parameters for water vapor is crucial to understanding remote sensing measurements. In this work, semi-classical line shape calculations using the Modified Complex Robert–Bonamy (MCRB) [1,2] formalism were performed to determine the half-width (γ) and the line shift (δ) for the H₂O–N₂ collision system at several temperatures. The MCRB calculations use an exact trajectory model [3], include all complex terms, a potential composed of electrostatic, atom–atom (expanded to 20th order and 4th rank), London dispersion and induction components, and explicit integration of the velocity integral. While most parameters in the potential are well known, the coefficients of the atom–atom potential need to be adjusted to reproduce a set of well-chosen half-width and line shift data.

The data were selected by applying an intercomparison procedure on the experimental H₂O–N₂ database (8235 transitions). These data were further refined by applying the Group of Transition rules (family of transitions [4] and Ma's rules [5]). First, the variation in the half-width as a function of atom–atom coefficients was studied. Then, changes are made to the atom–atom coefficients, new MCRB calculations made, and the calculated half widths and line shifts are compared to the experimental data. This procedure is iterated until the final standard deviation of the percent difference between the selected data and calculated data are a minimum.

[1] J. Phys. France, 1979, 40 (10), 923.

[2] J. Quant. Spectrosc. Radiat. Transfer, 2007, 103 (3), 588.

[3] J. Quant. Spectrosc. Radiat. Transfer, 2012, 113 (11), 951.

[4] J. Quant. Spectrosc. Radiat. Transfer, 1996, 56 (2), 263.

[5] Mol. Phys., 2011, 109 (2), 1925.

High accuracy ab initio DMS and extra high accuracy PES for sub-percent calculation of line intensities

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Calculation of rotation–vibration line intensities with sub-percent accuracy has recently become a standard requirement for the applications in retrieval and monitoring of gases in the Earth's atmosphere and potentially in the atmospheres of exoplanets. A major factor in the accurate calculation of line intensities is the requirement for the high accuracy ab initio Dipole Moment Surface (DMS) (e.g. references [1,2]). We present here the newly developed DMS surfaces for H₂O [3], HCN [4] and O₃[5] molecules and the results of the line intensities calculations using these surfaces.

In this talk we also demonstrate that the change from "good" potential energy surface (PES) to "excellent" PES, used for the line intensities calculations is also very important. Sometimes the change in intensities reach up to 1 or 2 percent. By "good" we mean here, for example, the PES with a standard deviation of 0.025 cm⁻¹ [6] and by "excellent" the PES with the standard deviation 0.011 cm⁻¹ [7]. Details of studies on H₂O [3], O₃ [5], HCN [4] and CO₂[2] molecules will be presented in the talk.

[1] L. Lodi, J. Tennyson and O.L. Polyansky, *J. Chem.Phys.*, **135**, 034113 (2011)

[2] O.L. Polyansky, K. Bielska, M. Ghysels, L. Lodi, N.F. Zobov, J.T. Hodges and J.Tennyson, *Physical Review Letters* **114**, 243001(2015)

[3] E.K. Conway, A.A. Kyuberis, O.L. Polyansky, J. Tennyson, N.F. Zobov , *J. Chem. Phys.*, submitted[1]

[4] V.Yu. Makhnev, A.A. Kyuberis, N.F. Zobov, L. Lodi, J. Tennyson and O.L. Polyansky, *J. Mol. Spectrosc.* (in preparation)

[5] O.L. Polyansky, N.F. Zobov, I.I. Mizus, A.A. Kyuberis, L. Lodi, J.Tennyson , *JQSRT*, **210**, 127 (2018)

[6] I.I. Bubukina, N.F. Zobov, O.L.Polyansky, S.I. Shirin, S.N. Yurchenko, *Optics and Spectroscopy*, **110**, 160, (2011)

[7] I.I. Mizus, A.A. Kyuberis, N.F. Zobov, V.Y. Makhnev, O.L.Polyansky and J. Tennyson, *Phyl. Trans. R. Soc A*, **376**, 20170149(2018)

Line shape parameters from first principles: investigation of the S and O branches in the H₂-He system

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Hydrogen molecule is the most abundant molecule in the Universe. It is investigated in various physical fields, ranging from astrophysics and the analysis of gas giants' atmospheres [1,2], to ultra-accurate measurements in molecular spectroscopy [3,4,5], and even in the search for physics beyond Standard Model [6]. Recently [7] it was pointed out, that the available data regarding the line-shape parameters of hydrogen is rather sparse. The development of experimental techniques in molecular spectroscopy requires a sub-percent accuracy of the theoretical calculations. It is believed that fully quantum calculations, based on the close-coupling scheme, could fulfill such requirements.

The collisional system of hydrogen molecule and helium atom is a perfect benchmark system for performing complex, *ab initio* investigation line-shape parameters. It involves only four electrons, allowing researchers to calculate the potential energy surface of such system with highly accurate methods of quantum chemistry. Moreover, because of the small mass of the system and large rotational constant of the hydrogen molecule, the dynamical calculations can be performed in reasonable computational time.

Using the recently reported ultra-accurate potential energy surface for the H₂-He system [8], we performed close-coupling calculations of generalized cross sections for lines of the S and O branches. We investigated 60 lines in total, for vibrational bands from 0-0 to 0-5 and rotational levels up to j=5. Generalized spectroscopic cross sections were obtained from S-matrix elements for a wide range of kinetic energies (from 0.1 to 9000 cm⁻¹). The cross sections were later averaged over the relative speed distribution of the colliding pair, leading to the final line-shape parameters: pressure broadening and shifting coefficients and real and imaginary part of the Dicke contribution to the Hess profile. The parameters are obtained for 17 temperatures, ranging from 5 to 2000 K. This is the first complex investigation of the S and O branches in the H₂-He system using *ab initio* methods.

[1] Icarus, 1989, 81, 429

[2] Icarus, 1995, 114, 328

[3] J Mol Spectrosc., 2014, 300, 55

[4] Astrophys. J., 2012, 749, 76

[5] J Quant Spectrosc Radiat Transf. 2018, 213, 41

[6] J Mol Spectrosc., 2016, 320, 1

[7] J Quant Spectrosc Radiat Transf. 2016, 177, 75

[8] J Quant Spectrosc Radiat Transf. 2017, 202, 308