Line-shapes analysis with ultra-high accuracy

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Abstract. We present analysis of the R7 Q8 O₂ B-band rovibronic transition measured with ultra-high signal-to-noise ratio by Pound-Drever-Hall-locked frequency-stabilized cavity-ring-down spectroscopy. For line-shape calculations ab initio spirit approach was used based on numerical solution of the proper transport/relaxation equation. Consequences for spectroscopic determination of the Boltzmann constant as well as precise determination of the line position in the Doppler limited spectroscopy are indicated.

1. Introduction
Dynamic development of experimental techniques of high resolution molecular spectroscopy allows to obtain molecular spectra with an extremely high signal-to-noise ratio. Even relatively weak molecular transition can be measured with a signal-to-noise ratio exceeding \( 2 \times 10^5 \) [1]. To analyze so accurate experimental data it is necessary to use theory allowing line shape calculation with a similar accuracy. Such theory [2] must take into account a number of effects such as Doppler and collisional broadening and shift of the spectral line, Dicke narrowing [3], the speed dependence of collisional broadening and shifting [4]. The description of molecular collisions should be based on realistic potential energy surface.

2. Line-shape analysis
Starting from the first principles simple analytical expressions [5, 6, 7] describing the shape of the spectral line can not be obtained in general case. Realistic spectral line-shape calculations require to solve a proper transport/relaxation kinetic equation [2, 8, 9]. Numerical methods usually used for this purpose fail when the collisional effects are small comparing to the Doppler broadening [10, 11].

We present here application of an efficient iterative approach to this problem allowing the line-shape calculations [11] in a wide range of pressure and temperature of an investigated gas sample. In this approach we decompose the operators and functions from the transport/relaxation equation in the Burnett basis, what allows to convert the integral equation into the algebraic problem. Then we used the iterative technique to solve it [11].

It was shown that use of a collisional operator obtained from even very simple description of interaction between colliding molecules can lead to a very good fit quality of the calculated profile to the measured spectra. Residuals obtained from such a fit correspond to signal-to-noise ratio approaching \( 10^5 \). In our study we assumed that speed dependence of collisional broadening and shifting is described by a hypergeometric function [4]. We analyse several line-shape models including speed-dependent Blackmore profile (SDhBP) [12], speed-dependent
billiard ball profile (SD\textsubscript{BBP}) \[9\], exact speed-dependent Galatry profile (eSD\textsubscript{GP}) \[9\], and speed-dependent Nelkin-Ghatak profile (SD\textsubscript{NGP}) \[13\].

In Fig. 1 we present residuals obtained from the fits with SD\textsubscript{BBP}, eSD\textsubscript{GP}, SD\textsubscript{NGP}. All three profiles have the same number of fitted parameters. The best quality of the fit was obtained for SD\textsubscript{BBP}. Noticeably worse quality of the fit can be seen in case of SD\textsubscript{NGP}. Using SD\textsubscript{BBP} we were able to reach 3 kHz precision of determination of the line position in the Doppler limited spectroscopy. Such precision is crucial to test quantum calculations of molecular energy levels and search a new physics beyond the Standard Model \[14\]. We also found that when SD\textsubscript{BBP} and SD\textsubscript{NGP} were used for Doppler width determination the results differed by 166 kHz what corresponds to relative difference about $3 \times 10^{-4}$. These results demonstrates that more advanced models, like SD\textsubscript{BBP}, need to be used to eliminate additional systematic errors originating from oversimplified description of molecular collisions. At the moment, these systematic errors give the largest contribution to the error budget for the spectroscopic determination of the Boltzmann constant \[15, 16\]. More details about this research can be found in Ref. \[11\].

3. Conclusion
We showed that experimental spectra can be fitted with high quality corresponding to signal-to-noise ratio approaching $10^5$ level with SD\textsubscript{BBP}. Presented approach can be used to minimize systematic errors in spectroscopic determination of the Boltzmann constant. As was indicated in Ref. \[17\] both speed-dependent effects and velocity changing collision can affect this kind of experiments. At present for data analysis in the Doppler width thermometry, leading experimental groups \[15, 16\] use profile \[18\] equivalent to SD\textsubscript{NGP} or its simplifications, what can lead to some errors. Finally, improvement in line position determination is important for tests of the fundamental theories of interactions in molecular systems \[14\].
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