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CO_2, H_2 and He Line Broadening Coefficients and Pressure Shifts for the HITRAN Database

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Motivation

The goal of this work is to increase the potential of the HITRAN database [1] towards the exploration of the Venusian atmosphere. Line-broadening coefficients, line shifts and temperature-dependence exponents of molecules of planetary interest perturbed by CO_2 have been assembled from available peer-reviewed sources, obtained from both experimental and theoretical studies or their extrapolations/interpolations. These spectroscopic data are of critical importance for the study of the atmosphere of Venus, since its atmosphere is dominated by CO_2.

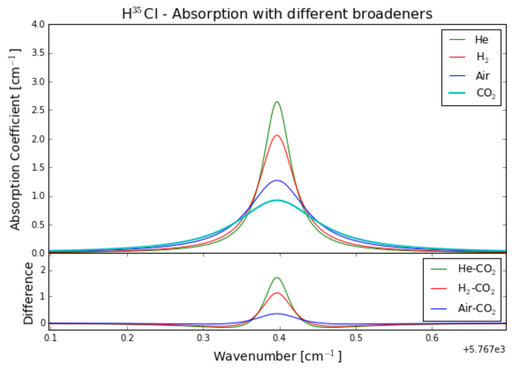

Fig. 1: Absorption coefficients of the 2-0 band R(5) transition of $H^{35}Cl$ with different broadeners. This plot was generated using the HITRAN Application Programming Interface (*HAPI*) [2]. The absorption coefficients were calculated at 296 K and 1 atm.

For example, Krasnopolsky [3] infers HCl mixing ratios in the atmosphere of Venus from the absorption signal of the 2-0 band R(5) transition of $H^{35}Cl$. Figure 1 shows the calculation of absorption coefficients for the same transition perturbed by CO_2, H_2, He and air using the HCl HITRAN files for these broadeners. Clearly, knowledge of the correct broadening parameters will facilitate an improved analysis of planetary atmospheres in general.

Constructed Datasets

The molecules investigated in this work are **SO_2, CO, HCl, HF, OCS**, which are known to exist in the atmosphere of Venus, **and C_2H_2 and NH_3**. In addition, the current study investigates pressure effects on molecular spectra in H_2 and He environments, which can be useful in the frame of studying atmospheres of gas giants.
The data collected here are used to create semi-empirical models for complete molecular data sets spanning the spectral range from microwave to UV wavelengths. Pressure broadening due to CO_2 is unfortunately only poorly understood and insufficiently studied for the majority of the molecular systems considered in this work, although new HITRAN datasets were created in each case. The data for pressure shifts are especially sparse, while these parameters are not negligible for a detailed study of the Venusian atmosphere, particularly in the near infrared. For some molecules, like CO, an extensive amount of measurements exist to build a complete database. The CO-H_2 and CO-CO_2 datasets have already been presented in Li et al. [4].

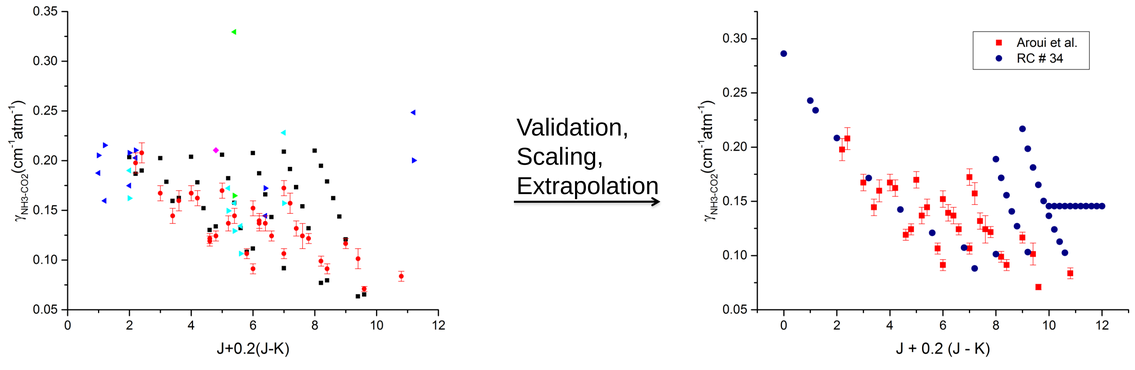

Fig. 2: NH_3 broadened by CO_2.
Left: The data retrieved from the literature from various references. Different symbols represent different studies.
Right: The newly created NH_3-CO_2 broadening dataset consists of the experimental ν_4-band data from Aroui et al. ([5], red squares) supplemented by data from a polynomial fit (blue circles) to these data. Extrapolations are denoted by custom reference codes (here: RC # 34).

As an example of a relatively complete CO_2-broadening dataset, Fig. 2 illustrates the procedure with which the new NH_3-CO_2 parameters were determined. The available broadening data were collected, scaled to HITRAN temperature and complemented with extrapolated values, which are described by a polynomial in *m* and *K*:

$$\gamma_{CO_2}(m,K) = A + B\cdot m + C\cdot K + D\cdot m^2 + E\cdot K^2$$

The quantum index m is defined by the relations m = -J, m = J-1, m = J+1 for the P-, Q- and R-branch respectively, where J is the rotational quantum number.

The data available for CO_2-broadening of SO_2 consist of only one line measured in 1962 [6]. The scaling factor between this value and the corresponding H_2 broadened width was used to scale all H_2 broadening coefficients from [7-9], which then resulted in a new CO_2-broadened dataset. The amount of data in this case is minimal and additional measurements are desirable.

Fig. 3 depicts the currently available CO_2 pressure shift parameters of HF and the data used for the final HITRAN file. No temperature-dependence studies of the HF-CO_2 system were found in the literature, although HF is abundant in the atmosphere of Venus.

Hartmann and Boulet [10] have shown that pressure shifts of diatomic molecules follow a simple scaling behavior with regard to their different vibrational bands allowing for extrapolation of a reference band to other vibrational levels. These results were used in the HF dataset and many other files.

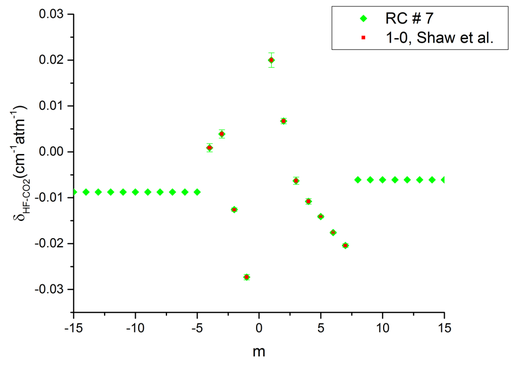

Fig. 3: The CO_2 shift data adopted in the HITRAN HF file are based entirely on 1969 measurements by Shaw and Lovell [11]. The shifts were set to constant values outside the range of low rotational quantum numbers, where no data are available.

Summary and Perspectives

The datasets which have been prepared in this paper are listed in Table 1, where δ, γ and n refer to the line shift, broadening and temperature-dependence parameters respectively. This table also details the extent of data availability for each collisional system considered in the present work. Our analysis indicates an overall trend in the effect of the three different broadeners, which is consistent for all studied molecules: CO_2-broadening seems generally greater than H_2 broadening, and H_2-broadening generally appears greater than He-broadening.
In the near future, the datasets will be placed on the HITRAN website https://hitranazure.cloudapp.net/ and soon will be moved to www.HITRAN.org.

Molecule	Parameter	Perturbed by H_2	Perturbed by He	Perturbed by CO_2
SO_2	δ	0	0	0
	γ	2	2	1
	n	1	1	0
	New Data Set?	Yes	Yes	Yes
NH_3	δ	2-3	2-3	2
	γ	3	3	2-3
	n	2-3	1	0
	New Data Set?	Yes	Yes	Yes
HF	δ	0	1	1
	γ	1	1	1-2
	n	0	1	0
	New Data Set?	Yes	Yes	Yes
HCl	δ	0	1-2	1-2
	γ	1	1-2	1-2
	n	0	0	0
	New Data Set?	Yes	Yes	Yes
OCS	δ	0	0	0
	γ	0	1	1-2
	n	0	0	0
	New Data Set?	No	Yes	Yes
C_2H_2	δ	1	1-2	0-1
	γ	3	3	1
	n	1	1	0
	New Data Set?	Yes	Yes	Yes
CO	δ	3	3	3
	γ	3	3	3
	n	3	1	3
	New Data Set?	Yes	Yes	Yes

Table 1: Data Availability:

0 = No data available,

1 = Few data available, new HITRAN file contains mostly averages,

2 = Some measurements available, allowing semi-classical extrapolations

3= Relatively complete set of measurements or calculations available - at least for room temperature.

Acknowledgments

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