Broadening of the H$_2$ ($X \rightarrow B$) transition lines in mixtures with rare gases and CF$_4$

Vadim A Alekseev$^1$ and Ralph Püttner$^2$

$^1$Institute of Physics, St.Petersburg State University, Ul’janovskaja St.1, Peterhof, 198504 St.Petersburg, Russia

$^2$Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

E-mail: alekseev@va3474.spb.edu.

Abstract. The H$_2$ ($X \rightarrow B$) transition is measured in mixtures with rare gases and CF$_4$. The rotational lines exhibit a strong dependence of the pressure broadening effect on the rotational quantum number J. At pressures of ~1 atm the collision-induced spectral width for the lines R(0) and R(1) is ~10 cm$^{-1}$ (FWHM), while for the transitions from the rotational levels with J > 3 the broadening effect is hardly visible at the spectral resolution used in the present study.

1. Introduction

The $B^1\Sigma_u^+$ state of molecular hydrogen is the lowest one which is coupled with the ground state $X^1\Sigma_u^+$ by a dipole allowed transition. The H$_2$ ($X \rightarrow B$) transition known as Lyman bands has been subject to many investigations both in absorption and in emission; the studies performed prior to 1994 are summarized in Ref. [1]. Besides the fundamental scientific interest in the benchmark system H$_2$, detailed knowledge of this transition is of prime importance also from a more applied point of view since hydrogen is the most abundant molecule in stellar atmospheres and interstellar clouds. Consequently, the emission of the H$_2$ molecule in the VUV region is observed in the spectra of many stellar objects and is one of the major sources of astrophysical information.

The shapes of spectral lines perturbed by collisions provide important information about concentration, temperature and composition of the gas surrounding the light-emitting atoms or molecules. To our knowledge, except for a brief study of the 0 $\rightarrow$ 0 and 0 $\rightarrow$ 1 bands in mixture with Ar at liquid nitrogen temperature [2], collisional effects in spectrum of the H$_2$ ($X \rightarrow B$) transition have not been studied previously. The present contribution reports on a spectroscopic study of this transition in mixtures with the rare gases He, Ne, Ar and the CF$_4$ molecule.

2. Experiment

Studies of absorption and luminescence excitation spectra of H$_2$ in mixtures with rare gases and CF$_4$ were conducted at the synchrotron radiation facility BESSY using a 10-m normal incidence monochromator [3]. The experiments were performed using a gas cell with a length of 8 cm that was separated from the ultra-high vacuum of the beamline by a LiF window. The light transmitted through
the gas cell was detected by a GaAs photodiode or by a photomultiplier tube (PMT) installed behind a quartz window that was covered with a sodium salicylate luminophore. The luminescence subsequent to the excitation by synchrotron radiation was detected via two laterally located window ports. One window was made of MgF$_2$ to record luminescence in the VUV range by using a solar blind PMT. Emission in the UV and visible spectral ranges was recorded via the second on-side window with the use of conventional PMT.

3. Results

Due to the large rotational constants, the $X \rightarrow B$ absorption spectrum consists of well separated rotational lines. Figure 1 shows a part of the high-resolution spectra of pure H$_2$ and H$_2$-Ar mixtures which includes the lines R(0) and R(1) of the 0 → 0 band and the line P(5) of the 0 → 1 band. The differences in the widths of the various lines demonstrate that the broadening effect strongly depends on the individual rotational excitation. For the R(0) line the broadening coefficient is estimated to be $\sim$10 cm$^{-1}$/atm.

![Figure 1](image.png)

**Figure 1.** Absorption spectra: H$_2$ 10 mbar (black) and H$_2$ 10 mbar + Ar 550 mbar (red).

The spectra displayed in Figure 1 were recorded using a 2400-groove/mm grating. Because of technical reasons most of spectra in the present study were recorded with a 300 grooves/mm grating. These spectra exhibit a substantially lower resolution so that the J-dependent collisional effects manifest itself in a stronger enhancement of low J transitions. Figure 2a shows an overview of the 0 → 0 band for pure H$_2$ and in a mixture with He. As can be seen in the spectra, the collision-induced enhancement of the absorption is a factor of 5 for the low-J lines R(0) and R(1) and about factor of 2 for the overlapping high-J lines P(4) and R(5). The effect also manifests itself in the luminescence excitation spectra. As is seen from Figure 2b, the relative intensities of the lines P(4) and R(5) in the normalized luminescence excitation spectra of pure H$_2$ and the H$_2$ + He mixture differ by a factor of 2. Effects on a comparable scale were observed in the mixtures with the other Rg gases and CF$_4$. Note that the shapes of the strongly broadened lines R(0) and R(1) depend on the rare gas used in the mixture. A detailed analysis of the line shapes requires results of high-resolution spectroscopic studies.
The energy separation between the lines P(J) and R(J+1) of the $0 \rightarrow 0$ band is small and for the P(4) and R(5) lines amounts only $\sim 13 \text{ cm}^{-1}$. Larger separations between these lines in the spectra of $0 \rightarrow \nu > 0$ bands opens the opportunity to study collisional effects for individual lines. For example, the spectra of $0 \rightarrow 2$ band in Figure 2c nicely illustrate that the lines P(J) are stronger enhanced by the interaction with helium (red curve) than the lines R(J+1). The $0 \rightarrow \nu > 0$ bands can be found in the energy region with $\lambda < 110 \text{ nm}$. Unfortunately, the optical absorption of Ar and Kr is very strong in this energy region so that complementary studies of mixtures with these rare gases are hampered.

In the present studies we also obtained first results on the broadening effect in pure H$_2$. The green curve in Figure 2a shows the spectrum of the $0 \rightarrow 0$ band at a pressure of 400 mbar. For reasons of comparison, this spectrum is scaled to the intensity of the overlapping lines P(4)/R5 in the low-pressure spectrum (black curve). A comparison of these two spectra clearly shows the J-dependence of the broadening effect.

**Figure 2.** a - Absorption spectra of the $0 \rightarrow 0$ band: H$_2$ 10 mbar (black), H$_2$ 10 mbar + He 1000 mbar mixture (red), and H$_2$ 400 mbar (green, the intensity is devided by a factor of 7. (see text); the overlapping lines R(0) and R(1) are saturated). The feature labelled ‘ * ’ is the line P(5) of the $0 \rightarrow 1$ band. b - Luminescence excitation spectra of the $0 \rightarrow 0$ band: H$_2$ 10 mbar (black), and H$_2$ 10 mbar + He 1000 mbar mixture (red). c - Luminescence excitation spectra of the $0 \rightarrow 2$ band: pure H$_2$ 5 mbar (black) and H$_2$ 5 mbar + Ne 1000 mbar mixture (red). For the spectra shown in panels b and c the undispersed VUV luminescence was recorded using a solar blind PMT.
4. Discussion

The present study shows that the pressure broadening effect for the rotational lines of the H\textsubscript{2} (X \rightarrow B) transition exhibits a strong dependence on the rotational quantum number J. At pressures of \~1 atm the collision-induced spectral width for the lines R(0) and R(1) is \~10 cm\textsuperscript{-1} (FWHM), while for the transitions from the rotational levels with J > 3 the broadening effect is hardly visible at the spectral resolution used in the present study.

The pressure broadening effect has been extensively studied for rotational lines in the Raman spectra of the molecular hydrogen. In these studies it has been shown that the J-dependence of the self-broadening coefficients for the Q-branch transitions with J = 1-5 is not a monotone function [4]. At room temperature the main contribution to the broadening is due to rotational-rotational (R-R) inelastic process which has the maximum probability for the J = 3 level. The self-broadening coefficient for the line Q(3) is by a factor of two larger than those for the lines Q(0) and Q(5) which are approximately equal. At high temperatures the maximum for the line Q(3) is less distinct. In mixture with He, where the resonant R-R process is absent, the broadening coefficient shows the tendency to decrease with J, except for the J = 1 level which has the smallest coefficient [5]. The observed dependence is, however, not pronounced. For all studied temperatures, the difference in the broadening coefficients for Q(0) and Q(5) is \~30 \%.

The pressure broadening coefficients for the lines in the Raman spectra of hydrogen and its mixtures with rare gases amount to \~10\textsuperscript{-3} cm\textsuperscript{-1}/atm which is a typical value for Raman spectra of other molecules as well. Consequently, a pressure of \~100 atm is required to obtain a collision-induced spectral width of \~10 cm\textsuperscript{-1}. The broadening effect for the rotational lines of electronic transitions is, however, significantly larger. For the O\textsubscript{2} (X '\Sigma\textsubscript{g} \rightarrow b '\Sigma\textsubscript{g}) magnetic dipole transition the self-broadening coefficient for the line J = 1 amount \~6\cdot10\textsuperscript{-2} cm\textsuperscript{-1}/atm and it smoothly decreases by approximately a factor of 2 up to J = 30 [6]. For the CO (X '\Sigma\textsubscript{g} \rightarrow B '\Sigma\textsubscript{g}) transition the self-broadening coefficient is one order of magnitude larger [7] and it shows, in contrast to the O\textsubscript{2} (X \rightarrow b) transition, no pronounced J-dependence of the broadening. This implies that the R-R inelastic collisions responsible for the J-dependence in the Raman spectra play only a minor role in the broadening mechanism for the CO (X \rightarrow B) transition [7]. No pronounced J-dependence of the rotational broadening coefficient was also observed for the NO (X '\Sigma\textsubscript{g} \rightarrow A '\Sigma\textsubscript{g}) [8] and the OH (X '\Sigma\textsubscript{g} \rightarrow A '\Sigma\textsubscript{g}) [9] transitions.

Comparing the broadening effect for the H\textsubscript{2} (X \rightarrow B) transition with the results from literature summarized above, two differences can be found. (i) The broadening coefficients for the H\textsubscript{2} (X \rightarrow B) lines are substantially larger than for the electronic transitions studied up to now. (ii) The J-dependence for the H\textsubscript{2} (X \rightarrow B) lines is very pronounced, with a decrease of the broadening coefficient by an order of magnitude from J = 0 to 5. The latter observation implies that the main contribution to broadening is due to R-R inelastic collisions. In this respect, the question on J-dependence of rotational relaxation rate is of significant interest. To our knowledge, rotational relaxation rates for the J-levels of the B state of molecular hydrogen are not known to date.

Experiments conducted in the course of the present study showed that the H\textsubscript{2}(B) luminescence is quenched in collisions with H\textsubscript{2}(X) and Ar. In particular, in mixture with 1000 mbar of Ar luminescence intensity is a factor of 10 weaker than in pure H\textsubscript{2} at pressure of 10 mbar. Interestingly, studies of the self-quenching process for the state $EF \ '\Sigma\textsubscript{g}^+$ in H\textsubscript{2}, which lies \~1 eV above the B state, have shown that the quenching-rate constant depends on J [10]. The J-dependence of the H\textsubscript{2}(B) quenching processes can not be excluded as well. This question requires further studies.

5. Conclusion

The present contribution mainly aims to provide first experimental results on the pressure broadening effect in the spectra of H\textsubscript{2} + Rg mixtures in the VUV region. A systematic investigation at high spectral resolution and for an extended pressure range is required to characterize the collisional
induced broadening effects in more details. A more precise data analysis, and in particular a line shape modeling, would require the knowledge of the interaction potentials for the lower and the upper state of the collision complex. The ground states of Rg-H$_2$ van-der-Waals complexes have been the subject of many experimental and theoretical studies ([11] and references therein) and are known with high accuracy. First *ab initio* calculations of Rg-H$_2$(B) interaction potentials have been performed complementary to the present experimental studies [12]. At present, the results are preliminary and are not reported here. The experimental studies of the pressure broadening effect and the *ab initio* studies of the relevant interaction potentials will be continued and the results shall be reported elsewhere.

**Acknowledgements**

We thank Prof. Dr. N. Schwentner for support of the present studies and many useful discussions. VAA acknowledges financial support from the Russian-German beamline project at BESSY.

**References**

[1] Roncin J-Y and Launay F 1994 *J. Phys. Chem. Ref. Data, Monograph* **4**
[2] Takezawa S and Iida Y 1995 *Annual Reports Gunma University* **16** 61
[3] Reichardt G, Bahrdt J, Schmidt J-S, Gudat W, Ehresmann A, Muller-Albrecht R, Molter H, Schmoranzer H, Martins M, Schwentner N and Sasaki S 2001 *Nucl. Instrum. Meth. A* 467–468 462
[4] Rahn L A, Farrow R L and Rosasco G J 1991 *Phys. Rev. A* **43** 6075
[5] Forsman J W, Bonamy J, Robert D, Berger J Ph, Saint-Loup R and Berger H 1995 *Phys. Rev. A* **52** 2652
[6] Gordon I E, Rothman L S and Toon G C 2011 *J. Quant. Spectrosc. Radiat. Transfer* **112** 2310
[7] Rosa M D, Roger L and Farrow R L J. 2001 *Quant. Spectrosc. Radiat. Transfer* **68** 363
[8] Vyrodov A O, Heinze J and Meier U E, J. 1995 *Quant. Spectrosc. Radiat. Transfer* **53** 277
[9] Kessler W J, Allen M G and Davis S 1993 *Quant. Spectrosc. Radiat. Transfer* **49** 107
[10] Niki K, Fujiwara M, Motoshima Y, Kawauchi T, Fukutani K, 2011 *Chem. Phys. Lett.* **504** 136
[11] Barletta P 2009 *Eur. Phys. J. D* **53** 33
[12] Alekseev V A 2012 *21-International Conference on Spectral Line Shapes*