Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Spectroscopy 243 (2007) 155–161
Journal of MOLECULAR SPECTROSCOPY
www.elsevier.com/locate/jms

Pressure broadening and shifting parameters for the spectral lines in the fundamental vibration–rotation bands of HBr and HI in mixtures with rare gases

A.V. Domanskaya [a,*], M.O. Bulanin [a], K. Kerl [b], C. Maul [b]

[a] V.A. Fock Institute of Physics, St. Petersburg University, Peterhof, 198504 St. Petersburg, Russia
[b] Institut für Physikalische und Theoretische Chemie der Technischen Unversität Braunschweig, D-38106 Braunschweig, Germany

Received 28 December 2006; in revised form 5 February 2007
Available online 16 February 2007

Abstract

We report measurements of the line broadening and shifting coefficients in the $(1 \leftarrow 0)$ fundamental absorption bands of the HBr and HI molecules in mixtures with rare gases He, Ne, Ar, Kr, and Xe. Comparison is given with the published data on other HHal–Rg systems. The measured line shifts are separated into terms symmetric and asymmetric in the line number m. The magnitudes of the symmetric shifts change in a regular manner in the series of rare gases and reach perturber-specific asymptotic values at higher $|m|$. It is found that the asymptotic values of the symmetric line shifts linearly correlate with the respective C_6 potential energy constants and that the slopes of these correlations are proportional to the vibrational ground state dipole moments squared of the hydrogen halide molecules.

Keywords: Infrared spectra; Diatomic molecules; Pressure broadening; Pressure shift

1. Introduction

Hydrogen halide (HHal) molecules are traditionally popular molecular probes widely used in the studies of the collision-induced spectral perturbations, of intermolecular interactions in pure gases, gas mixtures, and condensed systems, and for reconstruction of the potential energy surfaces (PES) of van der Waals complexes. Still, the interaction-induced effects involving heavier members of the HHal family received relatively little attention, so that the available experimental data on the line broadening and shifting in the IR spectra of HBr and HI remained sparse.

The first measurement of the self-broadening coefficients determined using the curve-of-growth method applied to the isotopically unresolved fundamental band of HBr was published by Babrov [1]. Close values for the R_1-branch lines were later obtained with a better resolution by Séoudi et al. [2], who demonstrated that the $H^{79}Br$ and $H^{81}Br$ isotopomers yield, as expected, essentially identical results and also reported the line broadening coefficients for the $HBr–CO_2$ system. Chou et al. [3] measured self-broadening for the $R_2(7)$ and $P_2(2)$ first vibrational overtone lines of $H^{79}Br$ by a diode laser spectroscopy technique. Foreign gas-induced broadening and shifting parameters for the fundamental band lines of HBr in mixtures with Ar, Xe, and with a few molecular buffer gases were tabulated by Rank and co-workers [4], but have not been verified since publication. First estimates of self-broadening in the fundamental band of HI were published by Ameer and Benesch [5]. We reported recently the self-broadening and shifts for many lines in the fundamental and first two overtone bands of HI [6,7]. To the best of our knowledge, the above references exhaust presently available sources of information on the collision-induced spectral line parameters for these molecules.

---

* Corresponding author. Fax: +7 812 428 72 40.
E-mail address: domav@yandex.ru (A.V. Domanskaya).

0022-2852/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2007.02.015

We report in this work the results of the FTIR measurements of the line broadening and shifting coefficients for the spectral lines in the vibration–rotation ($1 \leftarrow 0$) fundamental bands of the HBr and HI molecules in presence of all rare gas (Rg) perturbers. Whenever possible, we compare our results with the data available from the literature on other HHal–Rg systems.

2. Experimental

The experimental technique was essentially the same as used in our previous studies [8,9] and would be only briefly described here. The instrument used was a Bruker IFS 120HR interferometer operated at the spectral resolutions in the range 0.005–0.05 cm^{-1}, depending on the sample gas pressures. Sub-atmospheric pressures of HBr and HI were measured with MKS Baratron capacitance gauges, higher pressures of the perturber gases were measured with Bourdon gauges. Two high-pressure stainless steel gas cells were used of 9.6 and 2.9 cm path lengths. To prevent gradual decomposition of hydrogen iodide, the interiors of the cells were protected by a fluorinated polymer coating [9]. Rare gases of the stated purities He 4.6, Ar 5.0, Kr 5.0, Xe 4.0 (Linde), and Ne 5.0 (Ingas AE) were used as supplied. After discarding the first portion of the gas and pumping out the lecture bottle frozen by liquid nitrogen, HBr 2.8 (Air Liquide) was used without further purification. Samples of HI were prepared by dehydration of the hydroiodic acid (Fluka, p.a.) with phosphoric anhydride and purified by a trap-to-trap distillation. Our measurements were carried out at 298 ± 1 K.

3. Results and discussion

Small intensity of the HI fundamental band, particularly of its P_1-branch, required using relatively high partial pressures of the hydrogen iodide gas (up to 600 mbar). Self-broadening and self-shifting contributions in the spectra of HI–Rg mixtures were accounted for by using the results of Ref. 7. The fundamental band of HBr is about two orders of magnitude stronger compared to that of HI, which allowed using much lower partial pressures (a few mbar) of the HBr gas, making self-pressure contributions negligible in the HBr–Rg gas mixtures. No traces of the hyperfine structure appear in the domain of pressures used in our experiments and the spectral line shapes can be adequately fitted with the Lorentzian profiles. The same applies to the $H^{127}I$ lines having a more wide-spread hyperfine structure that collapses already under sub-atmospheric pressures into single features of about 0.04 cm^{-1} FWHM for the $R_1(0)$ and $P_1(1)$ lines [6,10]. Representative line shape fits to the measured $P_1(4)$ lines of the $H^{81}Br$ and $H^{79}Br$ isotopomers are depicted in Fig. 1. The Lorentzian fits appear good even in the most unfavourable case of a minimal light perturber pressure, $p(\mathrm{He}) = 360$ mbar. The Doppler HWHH widths near the band centres are, respectively, 0.0017 cm^{-1} and 0.0012 cm^{-1} for HBr and HI, well below the determined line widths. No statistically meaningful line asymmetries or the Dicke collisional narrowing were detected at the conditions of our experiments.

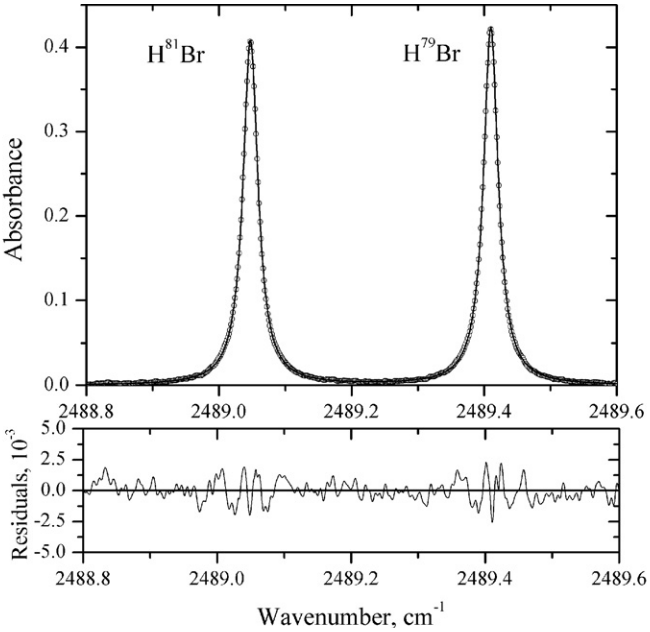

Fig. 1. An example of the Lorentzian fits to the $H^{81}Br$ and $H^{79}Br$ $P_1(4)$ line profiles broadened by 360 mbar of He.

Line widths and shifts scale in a linear manner with the perturber pressures, as noted many times before. The least-squares values of the pressure broadening (γ) and shifting (δ) coefficients for each spectral line were determined from the slopes of such linear dependencies. The standard deviation provided by linear regression accounts not only for the quality of lorentzian fits but for pressure uncertainties as well because the data points belong to the mixtures with different pressures of both perturber and absorber.

In agreement with earlier findings [2], the widths and shifts were found to be within the experimental uncertainties the same for $H^{81}Br$ and $H^{79}Br$. In what follows, we present data for hydrogen bromide averaged over both isotopomers. The measured broadening and shifting coefficients for the lines in the ($1 \leftarrow 0$) bands of HBr and HI are collected in Tables 1 and 2.

3.1. Line broadening

It becomes possible to compare the Rg-induced line broadening parameters in the ($1 \leftarrow 0$) bands for the whole family of the HHal molecules by invoking the published data for the HCl–Rg and HF–Rg gas mixtures. It was customary to plot the γ values versus the line numbers m ($m = J + 1$ in the R-branch and $m = -J$ in the P-branch). However, such plots often appear hardly illustrative, because many data points corresponding to different HHal species overlap. Collisional narrowing and line shape asymmetries were observed in several HF–Rg systems [11–14],