Line-shape parameters for pure rotational Raman lines of D$_2$ in He

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Abstract. We review our recent experimental and theoretical studies on the spectral line shapes of D$_2$ in helium baths. We also provide the most accurate to date experimental line positions of the first pure rotational Stokes lines, $S_0(j=0-2)$, of D$_2$.

1. Introduction

We present a comparison between experimental and calculated values for the collisional line broadenings and shifts of the $S_0(0)$, $S_0(1)$ and $S_0(2)$ lines of the rotational Raman spectrum of D$_2$ in helium baths at 77, 195 and 300 K [1]. These Stokes lines were obtained by means of a stimulated Raman spectroscopy (SRS) experimental setup. Close coupling dynamical calculations were performed on the most recent ab initio H$_2$-He potential energy surface [2]. The resulting scattering matrix elements implemented in the general Hess method [3-5] allowed us to provide pressure-broadening, -shifting and Dicke coefficients from 10 K to 400 K. When comparable, experimental and calculated values show good agreement.

In addition, in the course of that work we measured [6] the wavenumbers of the $S_0(0)$, $S_0(1)$ and $S_0(2)$ pure rotational lines in D$_2$. They compare well with both previous experimental measurements [7] and theoretical results [8].

2. Experimental setup

For the acquisition of pure rotational Raman spectra we used a modified version of our SRS setup [9]. Since the frequencies of the pump and probe lasers are quite close, we worked with perpendicularly polarized beams and introduced additional polarization filtering elements instead of the usual frequency filters and dispersive optics. High-accuracy Fizeau wavemeters, with 10 MHz absolute accuracy ($3\sigma$) and 1 MHz resolution, were used to continuously monitor the wavelength of the two laser sources.

The experimental methodology consisted of systematic recordings of the spectral profiles of the D$_2$ lines in binary mixtures of the two gases at different partial pressures of He. D$_2$ pressure was kept constant for all scans (between 1 and 15 mbar, depending on the line and temperature) while helium buffer gas pressures were varied from a few mbar up to a maximum of 1200 mbar.
3. Theoretical calculations

Our analysis of the experimental profiles supported by our calculations take into account effects originating from the internal changes and effects due to the velocity changing (VC) collisions through the speed dependence of the pressure –broadening and –shifting parameters as well as the real and imaginary parts of the Dicke parameters.

Close coupling calculations were performed on the recent H₂-He potential energy surface [2] for a grid of about 255 kinetic energies from 0.1 cm⁻¹ to 1500 cm⁻¹ in order to perform the thermal average at various T. This grid in kinetic energies also allowed us to determine the speed dependence of the generalized Hess parameters: collisional width and shift and frequency of the VC collisions associated with the Dicke effect. The method of the calculations was very similar to the one used in Refs. [2,10].

These calculations helped us to analyse the recorded profiles in the regime of large Dicke narrowing. For instance, figure 1 shows a simulation of the S₀(0) line at 77 K and 1 atm. We observe that the asymmetry of the weighted sum of Lorentzian lines resulting from the speed dependence of the collisional width and shift is washed out by the velocity changing collisions (the frequency of such collisions is about 10 times larger than the collisional halfwidth). The Doppler width is also completely suppressed. Thus the final lineshape is Lorentzian with a halfwidth equal to the averaged collisional halfwidth and shifted by the (averaged) collisional shift. For the S₀(2) line, which has the greatest Doppler width, the final lineshape is a Dicke Lorentzian line with a width having a residual Dicke-narrowed Doppler component. Thus the measured width has a component which varies linearly with the pressure and another one which is inversely proportional to it [1].

Figure 1. Simulations of the D₂ S₀(0) line at T = 77 K and p = 1 atm. The black solid line is the weighted sum of Lorentzians. The dashed green line takes also into account the VC collisions. The red solid line (covered by the dashed blue line) is the simple Lorentz profile obtained with the thermally averaged values of the collisional shift and widths. The red dispersive-shape curve in the bottom part of the figure shows a difference between dashed green and red curves (it is zoomed 30 times).

4. Results

The experimental lines were fitted to Voigt profiles. A simple deconvolution allowed the removal of the well-known apparatus function and a small residual Doppler contribution, thus yielding the net collisional contribution to the profiles. The change in the wavenumber of the peak centres as the He partial pressure was varied was measured to determine the collisional shifts. Experimental and theoretical results, at 77 and 300 K, are gathered in table 1.

Table 1. Comparisons of experimental and calculated pressure broadening (first row) and pressure shifting (second row) coefficients (in 10⁻³ cm⁻¹ atm⁻¹) at selected temperatures.

|       | 77 K   | 300 K  |
|-------|--------|--------|
|       | Exp.[1] | Calc.[1] | Exp.[1] | Exp.[11] | Calc.[1] |
| S₀(0) | 0.65    | 0.65    | 1.54    | 1.69     | 1.54     |
| S₁(0) | 0.36    | 0.43    | 0.77    |          | 0.84     |
| S₂(0) | 0.54    | 0.54    | 1.07    | 1.15     | 1.05     |
|       | 0.72    | 0.74    | 0.94    |          | 0.98     |
|       | 0.85    | 0.92    | 0.84    |          | 0.90     |
|       | 0.92    |          |          |          |          |
Specific experimental details concerning the measurements of the studied D$_2$ lines position can be found in [6]. Table 2 provides a comparison of the absolute wavenumbers measured for the S$_0$(0), S$_0$(1) and S$_0$(2) pure rotational transitions of D$_2$ to those reported in the bibliography. Our measurements improve the accuracy of the previously available experimental data [7] by an order of magnitude. They are in very good agreement with the state-of-the-art ab initio calculations [8], which include both relativistic and QED corrections.

Table 2. Wavenumbers (in cm$^{-1}$) of the S$_0$(0), S$_0$(1) and S$_0$(2) pure rotational Raman lines of D$_2$. Errors in parentheses are given in units of the last significant digit and correspond to one standard deviation.

|       | Exp.[6]       | Calc.[8]       | Exp.[7]       |
|-------|---------------|----------------|---------------|
| S$_0$(0) | 179.0669(2)   | 179.06710(1)   | 179.068(2)    |
| S$_0$(1) | 297.5336(2)   | 297.53374(1)   | 297.533(3)    |
| S$_0$(2) | 414.6484(2)   | 414.64845(2)   | 414.648(2)    |

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