

Collisional broadenings and shifts in the $S_0(0)$, $S_0(1)$ and $S_0(2)$ rotational lines of HD perturbed by He.

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Helium-perturbed HD is an important system for spectroscopic studies of the atmospheres of gas giants. For instance, a proper description of the collisional perturbation of the HD spectroscopic lines is needed for the accurate determination of the D/H mass ratio [1].

This work presents a comparison of the 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 HD perturbed by He at several temperatures between 77 and 300K. For the obtention of pure rotational Raman spectra we used a Stimulated Raman Spectroscopy setup previously described [2]. 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. The experimental methodology consisted of systematic recordings of the spectral profiles of the HD lines in binary mixtures of the two gases at different partial pressures of He. HD pressure was kept approximately constant at 5 mbar for all scans, while perturber (He) pressure was varied between 50 and 500 mbar. The experimental line profiles were fitted to Voigt profiles allowing the removal of the well-known apparatus function and Doppler contribution, thus yielding the net collisional contribution to the profiles. A low pressure spectrum of pure HD was recorded between every mixture spectrum to provide a frequency calibration for the unavoidable wavemeters thermal drift allowing an accurate determination of the peak position variation as a function of the He partial pressure.

We performed the HD-He quantum-scattering calculations on a highly-accurate purely ab initio potential energy surface [3,4]. Taking advantage of the generalized Hess method [5,6] we used the scattering S-matrix to generate the parameters quantifying the collisional perturbations of the HD lines. Besides the usual shift and broadening parameters we determined the speed dependence of the broadening and shift as well as the complex frequency of the optical velocity-changing collisions.

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