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 Oral

A quantum study of argon induced line mixing in ammonia doublets

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We have calculated, diagonal and off-diagonal, generalized spectroscopic cross sections for a few lines of ammonia perturbed by argon. For relative kinetic energies up to 900 cm^{-1} , we employed the close coupling method, while for larger kinetic energies and up to 1800 cm^{-1} , the coupled states approximation, as implemented in the MOLSCAT code¹ was preferred. The covered relative kinetic energies range allowed us to compute thermal averages for various relevant temperatures. Dynamical calculations, treating the NH_3 monomer as a rigid body, were performed using two different NH_3 - Ar potential energy surfaces^{2,3}. A pure rotational symmetrized basis set⁴ $|j k \epsilon\rangle$ with the corresponding energy levels and thus including the ortho-para species and the inversion motion, has been used. Line couplings within inversion doublets belonging to the ν_4 band are deduced from mathematical transformations of the obtained cross sections. In particular, we paid attention to $^{\text{P}}\text{P}(j, k)_{\text{s/a}}$ transitions for which the intra-doublet separation $\Delta\sigma_{\text{s/a}}$ is very small (see Table 1). Despite the approximation that neglects any vibrational dependence the preliminary results are very encouraging when compared with experimental parameters at room temperature available in the literature⁵. Table 1 gathers selected results obtained with the semi-empirical PES of Schmuttenmaer *et al.*². Very similar results are obtained when using the fully ab initio potential energy surface of Loreau *et al.*³.

Table 1: Line coupling coefficients, in $10^{-3}\text{ cm}^{-1}\text{ atm}^{-1}$, within the inversion doublets at selected temperatures.

Line	$\Delta\sigma\text{ (cm}^{-1}\text{)}$	77 K	193 K	296 K	Exp. (296 K)
$^{\text{P}}\text{P}(3, 3)_{\text{s/a}}$	0.275	26.21	11.0	7.23	4.6
$^{\text{P}}\text{P}(5, 2)_{\text{s/a}}$	1.244	5.52	2.51	1.76	
$^{\text{P}}\text{P}(5, 5)_{\text{s/a}}$	0.245	49.8	21.35	13.99	14.9
$^{\text{P}}\text{P}(4, 2)_{\text{s/a}}$	0.769	7.8	3.65	2.56	
$^{\text{P}}\text{P}(6, 5)_{\text{s/a}}$	0.545	32.68	13.87	8.93	6.0
$^{\text{P}}\text{P}(8, 8)_{\text{s/a}}$	0.210	78.11	35.08	23.37	24.7

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