



Notes

Diode-laser measurements of N₂-broadening coefficients in the ν_{10} band of allene at low temperatures



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ABSTRACT

Using a tunable diode-laser spectrometer, we have measured the N₂-broadening coefficients of allene for 5 lines in the ν_{10} fundamental band near 11 μm at five low temperatures ranging from 167.7 K to 259.7 K. The collisional halfwidths have been obtained by fitting the spectral lineshapes with the Voigt and the Rautian profiles. For these lines, the n parameter of the temperature dependence has been determined giving respectively mean values of 0.651 (0.038) and 0.612 (0.027) for the Voigt and Rautian models.

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1. Introduction

The goal of this note is to determine the n parameter of the temperature dependence for the N₂-broadening of allene lines. This work is the following part of our previous studies concerning the broadening coefficients of allene: the first has been devoted to the N₂-broadening at room temperature [1] and the second to the self-broadening with its temperature dependence [2].

For that, we have recorded, by diode-laser spectroscopy, five lines in the ν_{10} band of allene at five low temperatures (167.7 K, 188.7 K, 204.7 K, 223.7 K, and 259.7 K). The diode-laser spectrometer used in this study has been described in details elsewhere [1,3]. Here, we only resume the experimental conditions. The spectra with a range of approximately 0.15 cm^{-1} have been obtained with one PbSnTe diode-laser with a resolution of about $5 \times 10^{-4} \text{cm}^{-1}$. The allene (CH₂CCH₂) sample in natural abundance has been provided by Sigma-Aldrich Company with a stated purity of 97% and has been contained in a cell working at low temperatures (from room temperature to

77 K with a stability of about 0.1 K). This cell has also been described in details elsewhere [4]; it has an optical path of 40.43 cm and has been cooled down at five temperatures. The pressure of allene has varied between 0.4 and 1.1 mbar and the N₂ pressure between 10 and 35 mbar. These pressures have been measured by two MKS baratron gauges with a full scale readings of 12 and 120 mbar. The relative wavenumber calibration was obtained by introducing in the laser beam a confocal étalon with a free spectral range of 0.007958 cm^{-1} . To correct the slightly nonlinear tuning of the diode-laser radiation, the spectra have been linearized in wavenumber with a constant step of about $7 \times 10^{-5} \text{cm}^{-1}$ by means of a cubic spline technique. The assignments and wavenumbers of the measured lines of allene are taken from Refs. [5,6]. Fig. 1 shows an example of the recorded spectra for the ^pP(20,1) line at 824.6672 cm^{-1} and for a temperature of 204.7 K.

Data reduction was achieved using the same method as applied previously (see for instance Ref. [7]), fitting the experimental lineshapes with the Voigt profile [8,9] and the Rautian model [10]. The small instrumental distortions were taken into account as previously [11,12] through use of an effective Doppler width instead of the true Doppler width. For each line, the Voigt profile involves three adjustable parameters: the line center ν_0 , the collisional

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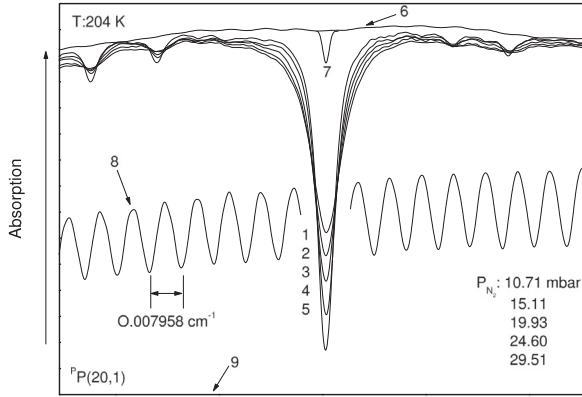


Fig. 1. Example of the spectra obtained for the ${}^{\text{P}}\text{P}(20,1)$ line in the ν_{10} band of C_3H_4 at 204.7 K: (1–5) broadened line at 10.71, 15.11, 19.93, 24.60, and 29.51 mbar of C_3H_4 ; (6) diode-laser emission profile recorded with an empty cell; (7) low-pressure C_3H_4 line (observed Doppler line); (8) confocal étalon fringes; and (9) 0% transmission level.

Table 1

N_2 -broadening coefficients γ_0 for the lines in the ν_{10} of C_3H_4 (allene) from the fits of Voigt and Rautian profiles.

Temperature (K)	Line	ν (cm^{-1})	γ_0 ($10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$)	
			Voigt	Rautian
259.65	${}^{\text{P}}\text{P}(10,2)$	821.5702 ^a	129.7 ± 6.9 ^b	130.6 ± 5.5
	${}^{\text{P}}\text{P}(11,4)$	801.8150	133.4 ± 6.2	134.0 ± 5.4
	${}^{\text{P}}\text{P}(12,4)$	801.2217	130.0 ± 6.7	131.0 ± 5.5
	${}^{\text{P}}\text{P}(15,2)$	818.5522	119.1 ± 6.8	120.4 ± 5.6
	${}^{\text{P}}\text{P}(20,1)$	824.6672	121.0 ± 6.4	121.8 ± 5.6
223.65	${}^{\text{P}}\text{P}(10,2)$	821.5702	140.4 ± 7.2	141.4 ± 6.0
	${}^{\text{P}}\text{P}(11,4)$	801.8150	147.1 ± 5.5	147.6 ± 6.4
	${}^{\text{P}}\text{P}(12,4)$	801.2217	141.1 ± 6.4	141.7 ± 5.5
	${}^{\text{P}}\text{P}(15,2)$	818.5522	130.5 ± 6.5	131.7 ± 5.5
	${}^{\text{P}}\text{P}(20,1)$	824.6672	130.8 ± 6.3	131.5 ± 5.7
204.65	${}^{\text{P}}\text{P}(10,2)$	821.5702	149.4 ± 7.1	151.8 ± 5.9
	${}^{\text{P}}\text{P}(11,4)$	801.8150	153.6 ± 6.0	154.2 ± 5.1
	${}^{\text{P}}\text{P}(12,4)$	801.2217	151.5 ± 5.5	152.1 ± 5.9
	${}^{\text{P}}\text{P}(15,2)$	818.5522	140.2 ± 6.8	141.3 ± 6.0
	${}^{\text{P}}\text{P}(20,1)$	824.6672	139.6 ± 6.7	140.6 ± 6.0
188.65	${}^{\text{P}}\text{P}(10,2)$	821.5702	158.2 ± 7.4	159.0 ± 6.6
	${}^{\text{P}}\text{P}(11,4)$	801.8150	161.6 ± 6.9	162.2 ± 6.2
	${}^{\text{P}}\text{P}(12,4)$	801.2217	157.3 ± 7.3	158.0 ± 5.9
	${}^{\text{P}}\text{P}(15,2)$	818.5522	148.7 ± 5.1	149.7 ± 6.2
	${}^{\text{P}}\text{P}(20,1)$	824.6672	146.0 ± 6.1	146.8 ± 6.0
167.65	${}^{\text{P}}\text{P}(10,2)$	821.5702	169.0 ± 7.4	170.5 ± 7.1
	${}^{\text{P}}\text{P}(11,4)$	801.8150	174.7 ± 7.5	175.8 ± 6.8
	${}^{\text{P}}\text{P}(12,4)$	801.2217	170.4 ± 7.5	171.2 ± 7.3
	${}^{\text{P}}\text{P}(15,2)$	818.5522	156.5 ± 7.2	157.8 ± 6.8
	${}^{\text{P}}\text{P}(20,1)$	824.6672	157.9 ± 7.3	159.0 ± 6.6

^a Line wavenumbers are taken from Refs. [5,6].

^b The experimental uncertainties given are twice the standard deviation from the linear fit, plus an additional 3% of γ_0 .

half-width at half maximum (HWHM) γ_c and an intensity factor. For the Rautian profile, we have one more: the collisional narrowing parameter β_c . However, as can be seen in Fig. 1, the spectra of allene are dense and many weak lines are close to the studied line. A very precise line profile analysis is thus difficult. It is the reason why we do not use other more elaborated models such as the

Speed Dependent Hard Collision profile (SDHC). In addition as shown in our previous study of allene at room temperature [1], the SDHC model gives very weak differences in the determination of the collisional broadening coefficients γ_0 . Furthermore, as this additional parameter β_c is very sensitive to small baseline uncertainties and strongly varies from one record to another, we have preferred

to constrain β_c to its theoretical value. $\beta_c = P \times \beta_0^{\text{diff}}$ where P is the gas pressure and β_0^{diff} is the dynamical friction parameter deduced from

$$\beta_0^{\text{diff}} = \frac{k_B T}{2\pi c m D_{12}}. \quad (1)$$

Here, m is the molecular mass of C_3H_4 and D_{12} is the mass diffusion coefficient for the $\text{C}_3\text{H}_4 + \text{N}_2$ system calculated following [13]. The used values β_0^{diff} are 61.29, 55.12, 51.39, 47.26 and $41.64 \times 10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$ respectively at 167.7, 188.7, 204.7, 223.7, and 259.7 K. For each studied line, we have obtained, by individual fits, the observed HWHM γ_{obs} (in cm^{-1}) for five pressures of nitrogen with the same partial pressure of allene (C_3H_4). In the determination of the broadening coefficient γ_0 , we have systematically considered the small self-broadening contribution derived from the allene self-broadening coefficients [2] and the knowledge of the constant partial pressure of allene in the gas mixture. From an unconstrained linear least-squares procedure of $\gamma_c (= \gamma_{\text{obs}} - \gamma_{\text{self}})$ versus $P (= P_{\text{tot}} - P_{\text{allene}})$, we have deduced the N_2 -broadening coefficients γ_0 (in $\text{cm}^{-1} \text{ atm}^{-1}$).

Table 1 lists the N_2 -broadening coefficients obtained with the Voigt and the Rautian profiles for the five considered lines in the ν_{10} band of C_3H_4 at the five low temperatures. The given uncertainties are twice the statistical error derived from the linear least-squares fit plus 3% of γ_0 to take into account all experimental errors. The main contributions to the quoted experimental errors arise from perturbations due to interfering lines, the baseline location, the line shape model and the nonlinear tuning of

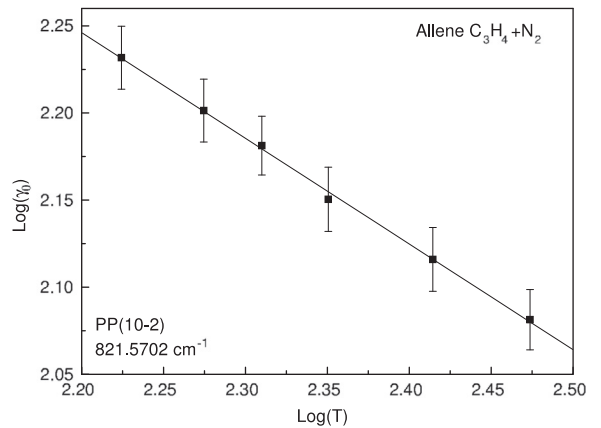


Fig. 2. N_2 -broadening coefficients (in $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$) of the ${}^{\text{P}}\text{P}(10,2)$ line in the ν_{10} band of allene versus temperature (in K) in log–log scales. The γ_0 coefficients given here have been deduced from the Rautian profile.

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