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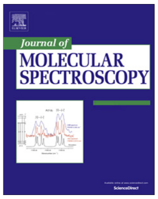

Temperature dependence of self-broadening of allene in the ν_{10} band

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ABSTRACT

Using a tunable diode-laser spectrometer, we have measured self-broadening coefficients of allene for 4 lines in the ν_{10} fundamental band near 11 μm for three low temperatures (178.15, 208.15, and 243.65 K). The collisional halfwidths are obtained by fitting the spectral lines with a Voigt and a Rautian profile. For these lines, the *n* parameter of the temperature dependence has been determined giving a mean value of 0.700.

1. Introduction

Allene (CH_2CCH_2), an isomer of methylacetylene (CH_3CCH), is an asymmetric-top molecule possessing D_{2d} symmetry. Although allene was not observed with certainty, photochemical models predict its presence in the atmosphere of Titan [1] and the fundamental bands ν_{10} located near 10 μm and ν_{11} located near 28 μm are candidate for its detection [2]. Allene may exist also in the atmosphere of giants planets Jupiter [3] and Saturn [4].

While many works have been published to allene transitions frequencies and their analyses (see for instance Refs. [5,6]), only few papers have been devoted to absolute line intensities and to line broadenings. For absolute line intensities, Sirota et al. [7] have reported high resolution measurements by diode-laser spectroscopy for eight lines in the ν_{11} band at 160 and 190 K; Wang et al. [8] have presented an extensive FTIR study in the ν_9 and ν_{10} bands at 200 K. For N_2-broadening coefficients, Wang et al. [9] have reported values determined at 201 K and more recently, diode-laser measurements have presented by our group at room temperature [10] and low temperatures [11]. However for self-broadening, there is only one measurement by Sirota et al. [7] for the $^{R}R4(8,4)$ line (359.2260 cm^{-1}) at 189 K: 0.0856 cm^{-1} atm^{-1}.

Using a tunable diode-laser (TDL) spectrometer, we present here results on the self-broadening coefficients obtained for four lines in the ν_{10} band of allene at three temperatures: 178.15 K, 208.15 K and 243.65 K. These ^{P}P lines are located in the spectral range 797–825 cm^{-1}. These lines were relatively sufficiently isolated to be individually fitted by Voigt and Rautian lineshape models. From these measurements, we have determined the temperature dependence *n* parameter. The experimental and data reduction procedures are similar to those described previously [12,13] and will be briefly presented in the following sections.

2. Experimental procedure

The absorption measurements of allene gas have been performed with a tunable diode-laser spectrometer. More details on the apparatus and recording procedures are given in Ref. [10]. To increase the signal to noise ratio, each record was the result of an average over 100 scans with a sweep frequency of 13.5 Hz. The relative wavelength calibration was obtained by introducing in the laser beam a confocal étalon with a free spectral range of 0.008323 cm^{-1}. The allene sample was provided by Sigma–Aldrich company with a stated purity of 97%. Fig. 1 presents a comparison of allene spectra recorded near 824.4 cm^{-1} at same pressure (1 mbar) and at two different temperatures (room temperature and 178.15 K). For clarity, the spectrum at low temperature is arbitrary shifted down. The spectrum at room temperature shows the great number of lines belonging to hot bands and thus the necessity to work at low temperatures to decrease their perturbing effect on the profile of the studied line.

For measurements, we used a low temperature cell with a variable optical pathlength ranging from 0.3 to 4.5 cm and similar to that described previously [14]. According to the line studied, the low temperature cell was used with two absorption pathlengths 1.80 and 4.31 cm and was cooled down to three temperatures 178.15, 208.15 and 243.65 ± 0.5 K. We also used a multipass White-type cell with 1 m between mirrors and very low C_3H_4 pressure ($\leqslant$0.05 mbar) in order to provide “Doppler” spectra of C_3H_4 lines. For each broadened line, we used five different pressures of C_3H_4, ranging from 7 to 22 mbar. These pressures were measured

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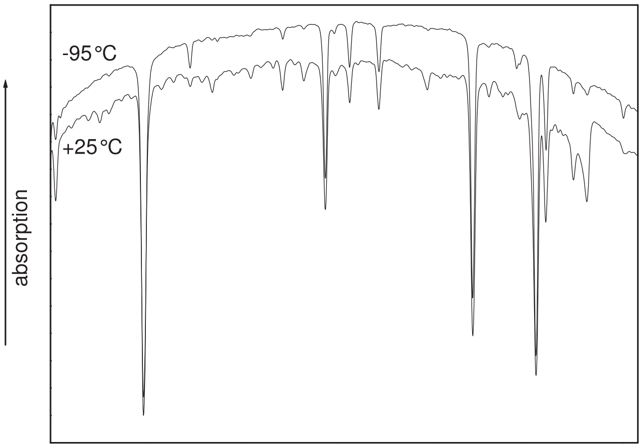

Fig. 1. Comparison between allene spectra near 825.4 cm^{-1} recorded at room temperature and at 178.15 K. For clarity, the spectrum at 178 K has been shifted down.

by two MKS baratron gauges with a full scale reading of 12 and 120 mbar.

The study of a broadened line of C_3H_4 requires eight consecutive spectra: records of the broadened lines at five pressure of allene, the empty cell giving the laser emission profile, the étalon fringes pattern with the absorption cell evacuated, as well the record of the pure C_3H_4 line at very low pressure ($\leqslant$0.05 mbar) which provides an observed Doppler profile. Before recording spectra, the purity of the mode was checked by the smoothness of the étalon fringe pattern, the laser emission regularity and the level of the saturated line.

After being recorded the spectra were linearized, to correct the weak nonlinear tuning of the diode laser, with a constant step of about 7×10^{-5} cm^{-1}. An example of the spectra obtained for the self-broadened ${}^{P}P(12,4)$ line of the ν_{10} band at 801.2217 cm^{-1} and to a temperature of 178 K is shown in Fig. 2. The assignments and wavenumbers of the measured lines of allene are taken from Refs. [15,16].

3. Data reduction and results

The observed absorbance $\alpha(\nu)$ at wavenumber ν (cm^{-1}) is obtained through the Beer–Lambert's law as

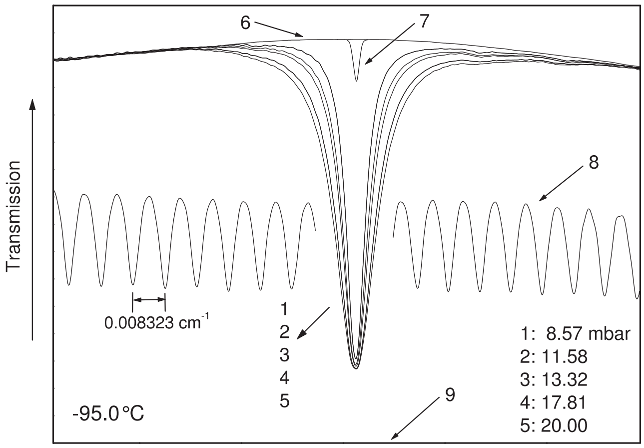

Fig. 2. Example of the spectra obtained at 178.15 K for the self-broadened ${}^{P}P(12,4)$ line at 801.2217 cm^{-1} in the ν_{10} band of allene: (1–5) broadened line at 8.57, 11.58, 13.32, 17.81 and 20.00 mbar of C_3H_4; (6) diode-laser emission profile recorded with an empty cell; (7) low pressure C_3H_4 line (Doppler regime); (8) confocal étalon fringes; (9) 0% transmission level.

$$\alpha(\nu) \;=\; \ln\left[I_0(\nu)/I_t(\nu)\right] \tag{1}$$

,where $I_0(\nu)$ and $I_t(\nu)$ are transmitted intensities measured with the cell under vacuum and filled with the gas sample, respectively.

To determine the self-broadening coefficient of a line, the collisional half-width at half-maximum (HWHM) γ_c of each of the five broadened experimental profiles was measured. Since most of the lines studied are more or less perturbed in the wings by neighboring lines, this was obtained by fitting only in the (apparently) unperturbed part of $\alpha(\nu)$ two theoretical line-shapes: the Voigt and Rautian profiles. The latter model incorporates the Dicke narrowing due to the averaging effect of velocity-changing collisions.

The Voigt profile is usually described by [17,18].

$$\alpha_v(x,y) = A\frac{y}{\pi}\int_{-\infty}^{+\infty}\frac{\exp(-t^2)}{y^2+(x-t)^2}dt \tag{2}$$

with

$$Y = \sqrt{\ln 2}\,\frac{\gamma_c}{\gamma_D}, \quad x = \sqrt{\ln 2}\,\frac{\nu-\nu_0}{\gamma_D}. \tag{3}$$

Here A is an intensity factor, ν_0 is the line center wavenumber and γ_D is the Doppler half-width. This profile may be also expressed as the real part of the complex error function $W(x,y)$ defined by

$$W(x,y) = \frac{i}{\pi}\int_{-\infty}^{+\infty}\frac{\exp(-t^2)}{(x+iy-t)}dt. \tag{4}$$

The hard collision model of Rautian and Sobel'man [19] may be described as

$$\alpha_R(x,y,z) = A\ \mathrm{Re}\left[\frac{W(x,y+z)}{1-\sqrt{\pi}zW(x,y+z)}\right] \tag{5}$$

where A, x and y are the same as above, $z = \sqrt{\ln 2}\,\beta_c/\gamma_D$, and β_c (cm^{-1}) is the narrowing parameter

To take into account the small instrumental distortions, we have used an apparent Doppler half-width γ_{DA} instead of the true Doppler half-width γ_D in the lineshape expressions [20] such that

$$\gamma_{DA} = \sqrt{\gamma_D^2 + \gamma_{TDL}^2} \tag{6}$$

where γ_{TDL} is the apparatus half-width determined by fitting to the low pressure C_3H_4 line a convolution of the true Doppler profile with a Gaussian function representing the instrumental profile. Typical values of the apparatus function γ_{TDL} are in the order of 0.5×10^{-3} cm^{-1}.In the fitting procedure, fixed values are used for γ_{DA} and three parameters are calculated by a nonlinear IMSL least-squares subroutine: the line center position, the collisional halfwidth γ_c, an intensity factor. For the Rautian profile, as the additional parameter the collisional narrowing 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, $\beta_c = P \times \beta_0^{\mathrm{diff}}$ where P is the gas pressure and β_0^{diff} is the dynamical friction parameter deduced from $\beta_0^{\mathrm{diff}} = \frac{k_B T}{2\pi c m D_{12}}$. Here, k_B is the Boltzmann constant (0.6950 cm^{-1}/K), m is the molecular mass of C_3H_4 and D_{12} is the self-diffusion coefficient. The values used for β_0^{diff} are 93.1; 106.1 and 123.8×10^{-3} cm^{-1} atm^{-1} respectively at 178.15, 208.15 and 243.65 K.

Fig. 3 gives the comparison of the fits of Voigt and Rautian profiles to the measured absorbance $\alpha(\nu)$ of the ${}^{P}P(19,4)$ line in the ν_{10} band at 797.0669 cm^{-1} and for a temperature of 243.65 K. The observed-minus-calculated residuals (multiplied by 10) are better for the Rautian lineshape leading to slightly larger intensities and collisional halfwidths $\gamma_{c.}$

A typical plot of the collisional hafwidth γ_c derived from the Rautian lineshape model versus P is shown in Fig. 4 for the ${}^{P}P(20,1)$ line in the ν_{10} band at 208.15 K. The slope of the straight