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Measurements and calculations of ethylene line-broadening by argon in the ν_7 band at room temperature

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Abstract

Argon broadening coefficients are measured for 32 vibrotational lines in the ν_7 band of ethylene at room temperature using a tunable diode-laser spectrometer. These lines with $3 \leq J \leq 19$, $0 \leq K_a \leq 4$, $2 \leq K_c \leq 19$ in the P , Q and R branches are located in the spectral range 919-1023 cm^{-1} . The fitting of experimental line shapes with Rautian profile provides the collisional widths slightly larger than those derived from Voigt profile. The independent theoretical estimation of these line widths is performed by a semiclassical approach of Robert-and-Bonamy type with exact isotropic trajectories generalized to asymmetric tops. Even with a rough atom-atom intermolecular potential model the calculated values show a quite good agreement with experimental results.

Keywords: Tunable diode-laser; Ethylene; Argon; Collisional broadening; Semiclassical approach

1. Introduction

Ethylene C_2H_4 is an important tropospheric pollutant produced by automobiles, forest fires and plant life [1] as well as a constituent of Saturn's [2], Jupiter's [3] and Titan's [4] atmospheres. The accurate knowledge of its spectral parameters was therefore recognized indispensable and motivated the activity of various scientific groups during last two decades. While the absorption frequencies of the C_2H_4 vibrotational lines are relatively well known, their collisional self- or foreign-gas broadening coefficients have not been extensively studied. Indeed, due to the high density of absorption lines, the collisional line widths of C_2H_4 are difficult to measure accurately. They require thus a high-resolution spectrometer and rather low perturber pressures to minimize the overlapping between neighbouring lines. Owing a diode-laser spectrometer with resolution of about $5 \times 10^{-4} \text{ cm}^{-1}$, the laboratory of Namur has effectively launched out on this subject of research. A series of measurements on N_2 -, H_2 - and self-broadening coefficients (particularly required by atmospheric studies) in the ν_7 band of C_2H_4 at room and low temperatures have been performed by some of us [5-9]. Even if the role of noble gases such as argon, helium, neon etc. is minor in the terrestrial and planetary atmospheres, the precise knowledge of C_2H_4 line-broadening by these gases is extremely important from the theoretical point of view as allowing a deeper insight into the origins of this process. Except the measurements of Reuter and Sirota [10] for only two transitions near 948 cm^{-1} with Ar, He, N_2 and O_2 used as the broadening gases, no other study has been yet reported. In the present paper we present so a study of C_2H_4 Ar-broadening coefficients of 32 lines located between 919 and 1024 cm^{-1} .

From the one hand, using the same tunable diode-laser spectrometer as in the previous works, we have measured these coefficients for 32 lines in the ν_7 band of C_2H_4 at room temperature (298 K). In order to extract the collisional widths, each recorded lineshape has been fitted with a simple Voigt profile and with a Rautian profile taking into account the collisional narrowing.

From the other hand, we have computed these broadening coefficients with a semiclassical approach proposed originally by Robert and Bonamy [11] (RB) for linear molecules and modified later [12] by introducing exact trajectories [13] for the relative classical motion of colliding molecules. This exact-trajectory modified RB approach is named hereafter RB-E. Further extensions of RB-E method were performed to symmetric tops (NO - N_2 [14], NO - O_2 [15], OH - $N_2(O_2, Ar)$ [16]) and asymmetric tops (C_2H_4 - N_2 [17]). In the last paper C_2H_4 had been treated for the first time as an "exact asymmetric top" in contrast with a simplified "prolate top" consideration of [5-9] and led to a clearly better agreement with

experiment; the next step was thus to test the RB-E approach for C₂H₄-atom collisions. To our knowledge, no line width calculation for such a case is presently available. To describe the intermolecular potential, as a first attempt, we have adopted a simple sum of pair atom-atom interactions approximated by Lennard-Jones dependences.

The remainder of the paper is organized as follows. The next section gives a brief description of the experimental procedure. The data reduction and the experimental results are presented next. The fourth section reminds shortly the key points of the semi-classical linewidth computation. After, experimental and theoretical values of collisional broadening coefficients are put together and their dependence on the rotational quantum numbers is discussed in detail. Some concluding remarks are collected in the final section.

2. Experimental procedure

The experimental line shapes were recorded by an improved Laser Analytic diode-laser spectrometer described in detail in ref. [18]. 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 while the absolute wavenumbers of lines were taken from refs. [19, 20]. Each line shape record consisted of 2048 frequency data points; in order to increase the signal-to-noise ratio it was averaged over 100 scans with a sweep frequency of 13.5 Hz.

The purity of ethylene and argon purchased from L'Air Liquide was 99.50 and 99.99%, respectively. The gas samples were set in the White-type multipass cell with an optical path length of 20.17 m. For each broadened line, the measurements were made for a fixed partial pressure of C₂H₄ (≤ 0.07 mbar) with four different pressures of Ar varying between about 30 and 75 mbar. All pressures were measured with two MKS gauges with full-scale reading of 1.2 and 120 mbar. The cell temperature was kept at 298 $\pm$ 1 K.

The study of an absorption line of C₂H₄ perturbed by Ar required several successive records: the record of the empty cell which represents the laser emission profile (100% transmission level), four records of broadened line with a constant C₂H₄ pressure diluted in different Ar pressures, the étalon fringes with the cell evacuated, the pure C₂H₄ line at very low pressure (≤ 0.01 mbar) providing an effective Doppler profile used to determine the apparatus function, and a saturated spectrum of this line giving the 0% transmission level. Figure 1 shows an example of the spectra (except for the saturated line, for clarity) obtained for the 7_{3,5}←6_{2,5} line.

After being recorded, to correct the slightly nonlinear tuning of the diode-laser radiation, the spectra were linearized in frequency with a constant step of about $1 \times 10^{-4} \text{ cm}^{-1}$ by means of a cubic spline technique.

In this work, the measurements have been performed on 32 lines distributed in all P , R and Q branches of the ν_7 band of C_2H_4 .

3. Data reduction and experimental results

To obtain the collisional half-widths on the half height, before starting various fittings, we extracted, for each line, the contributions due to a small Doppler effect and to the instrumental distortions. To do so, instead of the true theoretical Doppler half-width γ_D^{th} , we used an effective Doppler half-width γ_D defined as $\gamma_D = \sqrt{\gamma_{D^{th}}^2 + \gamma_{app}^2}$. The apparatus function may be assimilated to a Gaussian function with a half-width γ_{app} which has a typical value of $5 \times 10^{-4} \text{ cm}^{-1}$ in this work. The fitting procedure is similar to that described previously in Ref. [5]. Indeed, we firstly used the usual Voigt profile [21, 22] considering independently Doppler and collisional broadenings. As a consequence, the resulting profile was simply the convolution of the Gaussian-type Doppler profile with the Lorentzian-type collisional one. In order to include the collisional narrowing of the Doppler profile (Dicke effect), the well-known Rautian profile [23] was considered too. It seems necessary to mention that the Galatry model was not used in the present analysis since many studies had shown that when the mass ratio between two partners is close to 1 the Galatry (soft collisions) and Rautian (hard collisions) profile models lead to the same qualitative results.

Thus, we fitted consecutively the Voigt and the Rautian profiles to the measured absorbance $\alpha(\nu)$ which is defined by the Beer-Lambert law as

$$\alpha(\nu) = -\ln\left(\frac{I_t(\nu)}{I_0(\nu)}\right), \quad (1)$$

where $I_0(\nu)$ and $I_t(\nu)$ are the transmitted intensities obtained, respectively, with the cell under vacuum and the cell filled with the gas sample. For the Voigt profile model three parameters were adjustable: the line center position, the collisional half-width and an intensity factor, whereas for the Rautian model the collisional narrowing was included too. Figure 2 gives an example of the theoretical Voigt profile fitted to the measured absorbance $\alpha(\nu)$ for the $7_{3,5} \leftarrow 6_{2,5}$ line of C_2H_4 (at 0.02 mbar) perturbed by 47.59 mbar of Ar. At the bottom of the figure, the residuals (observed minus calculated) multiplied by 10 are shown for Voigt and

Rautian profiles. It is not difficult to realize that the actual experimental lineshape is higher and narrower than a Voigt profile whereas, incorporating the Dicke effect, the Rautian profile leads to a nearly perfect fit.

Among retrieved parameters (line center position, collisional half-width, intensity factor and, additionally, collisional narrowing for Rautian profiles) only the collisional half-widths were considered in the framework of our study. Consecutive fits at four different pressures of Ar furnished the pressure dependence of the collisional half-widths for each line. As an example, figure 3 displays this dependence for $7_{3,5} \leftarrow 6_{2,5}$ line and for Voigt and Rautian profiles. The point close to the origin represents the self-broadening contribution determined from the self-broadening coefficients of ref. [7]. These collisional linewidths extracted by two profile models exhibit naturally a linear behaviour in function of the perturber pressure. The slope of the associated straight lines issued from a linear regression gives us the corresponding Ar-broadening coefficients. The collisional half-widths obtained with the Rautian model are systematically slightly larger than those derived from Voigt profile.

Given the fact that the main sources of uncertainties arise from the baseline location, the perturbations due to neighbouring lines, the slight nonlinear tuning of the laser and also from the lineshape model used, the absolute errors are estimated to be twice the standard deviation given by the linear least-squares procedure plus 2% of γ_0 .

The comparison with previous measurements of Reuter and Sirota [10] is difficult because the studied transitions are different. It seems that the two values determined in [10] using direct measurement of half-width at half-height of the lines or Voigt profile fit are lower than the average value obtained in the present studied.

4. Collisional line width computation

Theoretical interpretation of the broadening coefficients studied experimentally was performed on the basis of a semiclassical approach. Despite the fact that the most precise treatment of molecular collisions is provided by quantum-mechanical methods, a huge CPU time required for such computations make them sometimes unfeasible for polyatomic systems (even at not very high temperature). It is the reason why semiclassical approaches are always current. Among them the semi-classical formalism of Robert and Bonamy [11] appears to be the most advanced due to a development of the scattering matrix via an exponential representation, the introducing of parabolic trajectory curved by the isotropic part of the intermolecular potential and the incorporation of the short-range interactions which play a

crucial role for non-polar colliders (C_2H_4 -Ar system, for example). Always remaining in the frame of isotropic trajectories, the parabolic trajectory model employed in the RB formalism can be replaced by another one corresponding to the exact solution of the classical equations of motion in the field of an isotropic potential [13]. The using of exact trajectories made computations more complicated (numerical integration) but its clear advantage in comparison with traditional parabolic trajectories is that the isotropic part of the interaction potential can be kept its initial form (no fitting by a Lennard-Jones function is needed). Moreover, this RB-E approach deals naturally with the laboratory-fixed frame [12], so that the anisotropic potential for two colliding molecules is developed, in the general case, in series of three spherical harmonics tied to the corresponding orientations of the molecular axes and the intermolecular distance vector $\vec{r}$ [24].

In the framework of the RB formalism, for the case considered here, the collisional line width (in cm^{-1}) for the radiative transition $f \leftarrow i$ is given by

$$\gamma_c = \frac{n_b}{2\pi c} \int_0^\infty v f(v) dv \int_0^\infty 2\pi b db \left\{ 1 - \exp \left[- (S_{2,f2} + S_{2,i2} + S_{2,f2i2}^{(C)}) \right] \right\}. \quad (2)$$

In this equation, n_b is the number density of perturbing particles and the S_2 terms are different second-order contributions. Since the speed dependence phenomena were not considered experimentally in this work (only Voigt and Rautian profiles were used), the mean thermal velocity $\bar{v} = \sqrt{8kT/\pi m^*}$ (where k is the Boltzmann constant, T is the temperature and m^* is the reduced mass of the molecular-atomic pair) is employed instead of the integration over relative velocity v with Maxwell-Boltzmann distribution. The integration over the impact parameter b is replaced by the integration over the distance of the closest approach r_c which are related with each other via the energy and momentum conservation condition, i.e.: $b/r_c = \sqrt{1 - V_{iso}^*(r_c)}$, where $V_{iso}^*(r_c)$ denotes the reduced value of the isotropic potential defined by $V_{iso}^* = 2V_{iso}/(m^* v^2)$.

As mentioned just above, for the exact trajectory model we do not need to adapt the isotropic part of potential with a Lennard-Jones model, thus neither ε nor σ (intermolecular parameters) of C_2H_4 -Ar system has been extracted. The analytical relation between $b db$ and $r_c dr_c$ in the original RB formalism may be replaced by a numerical form as [25]

$$b db = r_c dr_c \left[1 - V_{iso}^*(r_c) - \frac{r_c}{2} V_{iso}^{*'}(r_c) \right], \quad (3)$$

where the accurate numerical derivation of $V_{iso}^{*}(r_c)$ with respect to the intermolecular distance is necessary.

The detailed general expressions of the S_2 contributions for asymmetric top colliders are given in ref. [17] but must be specified for our particular case of the perturbation by an atom. To do so, it is necessary to precise the interaction potential used. For the C_2H_4 -Ar system, the refined *ab initio*-computed potential by Cappelletti et al. [26] is recently available in the literature. However, we preferred for the present work an analytical potential derived from the well-known atom-atom model for which the semiclassical calculations work better (see ref. [27]). Approximated by Lennard-Jones functions between atoms of the (first) active C_2H_4 molecule and the (second) perturbing Ar atom, the pair atom-atom interactions are given by:

$$V = V_{at-at} = \sum_i \left(\frac{d_{i2}}{r_{i2}^{12}} - \frac{e_{i2}}{r_{i2}^6} \right), \quad (4)$$

where the summation is taken over the i -th atoms of C_2H_4 . The geometric parameters of C_2H_4 analogous to ref. [17] (figure 4) as well as the atom-atom parameters d_{i2} and e_{i2} are given in table 1. As mentioned above, for further application, the potential of Eq. (4) should be rewritten in terms of the spherical harmonics expansion:

$$V(\vec{r}) = \sum_{l,n} V_{l,n}(r) \sum_m D_{mn}^l(\omega_1)^* C_{lm}(\omega)^*, \quad (5)$$

where $\omega_1 \equiv \phi_1, \theta_1, \chi_1$ (Euler angles) and $\omega \equiv \theta, \phi$ (polar angles) represent respectively the orientations of C_2H_4 molecule principle axis and of the intermolecular distance vector $\vec{r}$ in the laboratory fixed frame, $D_{mn}^l(\omega)$ are the generalized spherical harmonics, $C_{lm}(\omega)$ are the Racah spherical harmonics defined by $C_{lm}(\omega) = \left(\frac{2l+1}{4\pi} \right)^{-1/2} Y_{lm}(\omega)$ and the asterisk stands for the complex conjugation.

The isotropic part of the interaction potential given by Eq. (5) governs the trajectories of the relative molecular motion which are defined by two quantities: the intermolecular distance r and the phase Ψ (the collision is supposed to take place in the plane XOY of the laboratory fixed frame so that the polar angles of $\vec{r}$ are written as $\omega \equiv \pi/2, \Psi$), for which the exact solutions of the classical equation of motion can be used [12].

Apart from the trajectory model, the computation of S_2 terms in Eq. (2) needs the energy levels of C_2H_4 as well as the rotational wave functions before and after collision. While the latter are involved in the computation of the matrix elements of anisotropic potential, the former are required for the determination of the resonance parameter k_c defined as $k_c = \omega r_c / v$ [12]. These rotational wave functions and the energy levels numerically computed by a diagonalisation of the rotational Hamiltonian have been kindly provided by Dijon's group [28]. We note that the collisional line width computation has been only made for the radiative transitions studied experimentally. Moreover, to simplify the computation like Refs [5,9,16], the single allowance $\Delta K_{a,i}$ (or $\Delta K_{a,f}$) = 0 has been taken into account for the collision induced transitions.

5. Results and discussion

Concerning the measurements, we recall that, the collisional line widths extracted by the Rautian profile model for any studied line are always slightly larger than those obtained from the Voigt profile; the difference goes to about 2-4%. However, since the experimental errors, estimated as twice the standard deviation plus 2% of γ_0 , are of about 3%, such a difference does not play any important role in the determination of the collisional line broadening coefficients in this work.

All the Ar-broadening coefficients of C_2H_4 lines studied experimentally (using Voigt and Rautian profiles) and theoretically are reported in table 2. We have sorted them in the increasing order of absorption wavenumbers ν_0 corresponding to radiative $f \leftarrow i$ transitions. The quantum numbers J, K_a and K_c associated with the i and f states are also indicated for each line. For the sake of illustrative comparison, all the results are shown on figure 5 in function of the rotational quantum number J . Although it can be seen that, from both experimental and theoretical points of view, an overall decrease of γ_0 with increasing J is retrieved, such J -dependence given from the calculated γ_0 is weaker than the one obtained from measurements. In order to separate the different γ_0 values of different corresponding transitions with the same J , we plotted on figure 6 our results in function of $J + 0.2K_a$ for P , Q and R branches; for clarity, only the experimental broadening coefficients obtained from Rautian profile are displayed. (The coefficient 0.2 is chosen since the K_a values in this work are inferior or equal to 4.) A good agreement between theoretical and experimental results

(within the error bars) is stated for the majority of lines, except the transitions $4_{1,4} \leftarrow 5_{2,4}$, $9_{4,5} \leftarrow 10_{3,7}$, $10_{0,10} \leftarrow 10_{1,10}$, $12_{0,12} \leftarrow 12_{1,12}$ and $20_{1,19} \leftarrow 19_{0,19}$ (overestimation of more than 10%).

According to the studies of Sumpf et al. on collisional line broadening in asymmetric tops (see for example ref. [29]) the variation of γ_0 with K_c may be disregarded, so that only K_a -dependence is worthy to be considered next. This dependence is however quite complicated and not clearly established. For a given J , such a K_a -dependence of coefficients is only studied for the radiative transitions allowed by a particular selection rule: we consider the lines belonging to a given ΔJ branch in a particular ΔK_a sub-branch. In this work there are only two couples of transitions $8_{1,7} \leftarrow 7_{0,7}$ and $8_{2,6} \leftarrow 7_{1,6}$ as well as $11_{2,9} \leftarrow 11_{3,9}$ and $11_{3,8} \leftarrow 11_{4,8}$ with $\Delta J = -1$ and $\Delta J = 0$ respectively, and four transitions $20_{1,19} \leftarrow 19_{0,19}$, $20_{3,18} \leftarrow 19_{2,18}$, $20_{4,17} \leftarrow 19_{3,17}$ and $20_{5,16} \leftarrow 19_{4,16}$ with $\Delta J = 1$ to examine this K_a -dependence. These eight experimental line widths deduced from Voigt or Rautian profile show a tendency to increase with K_a increasing whereas the behaviour of the corresponding theoretical values is not similar: the increasing γ_0 are obtained when K_a increases only for the transitions $8_{1,7} \leftarrow 7_{0,7}$ and $8_{2,6} \leftarrow 7_{1,6}$; $11_{2,9} \leftarrow 11_{3,9}$ and $11_{3,8} \leftarrow 11_{4,8}$, but not for $20_{1,19} \leftarrow 19_{0,19}$, $20_{3,18} \leftarrow 19_{2,18}$, $20_{4,17} \leftarrow 19_{3,17}$ and $20_{5,16} \leftarrow 19_{4,16}$. This discrepancy of the K_a -dependence has been also reported in the literature for the traditional RB computations for $O_3-N_2(O_2)$ system [30] as well as for the RB-E computations for $C_2H_4-N_2$ system [16]. We note also that a few lines experimentally available to study the K_a -dependence do not allow to make a final conclusion. The disagreement observed between some theoretical values and experimental data can be also attributed to the approximate values of atom-atom parameters (whose role is crucial for a polyatomic molecule colliding with an atom) and/or to the lost of semiclassical approaches validity for polyatomic molecules (rototranslational decoupling recently investigated for C_2H_2 -Ar and C_2H_2 -He line-broadening [27, 31]).

6. Conclusion

In the present paper, we have performed for the first time a detailed study of 32 Ar-broadening coefficients of C_2H_4 in the ν_7 band at room temperature from both experimental and theoretical points of view. All the measurements have been made thank to a high resolution diode-laser spectrometer. When the more sophisticate Rautian profile model taking into account the Dicke effect was employed, we have observed nearly zero values for the

residuals with the recorded line shape and the collisional line widths were found to be slightly larger than those derived from the simple Voigt profile. However, the latter remark has not any important signification whereas the experimental uncertainty is considered. From the theoretical point of view, the linewidths computed by a semi-classical approach with exact isotropic trajectories demonstrated a quite agreement with the measurements for the majority of lines. Even though the J -dependence of broadening coefficients is more or less visible and the identical behaviour is reported from calculations and measurements, it is still difficult to obtain a final conclusion on K_a -dependence.

From the experimental point of view, in order to study the temperature dependence of the broadening coefficients, a series of measurements at different temperatures varying from 198.2 to 273.2 K are now worthy to be realized, using a home-made absorption cell cooled by a liquid-N₂ flow. Moreover, it seems to be interesting to perform the semiclassical calculation of collisional linewidths using a refined *ab initio* potential. These points could form the subject of future studies.

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Table 1 Physical parameters characterizing the intermolecular potential of C₂H₄-Ar.

C ₂ H ₄ [32]	e_{i2} (10 ⁻¹⁰ erg Å ⁶) [33]	d_{i2} (10 ⁻⁷ erg Å ¹²) [33]
$ r_{C-H} = 1.071 \text{ Å}$ $ r_{C-C} = 1.353 \text{ Å}$ $\angle HCH = 119^\circ 55'$	$e_{CAr} = 0.9009$ $e_{HAr} = 0.1613$	$d_{CAr} = 1.8540$ $d_{HAr} = 0.1283$

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Table 2 Ar-broadening coefficients γ_0 measured and calculated in the ν_7 band of C_2H_4 at 298 K

ν_0 (cm ⁻¹)	J_f	$K_{a,f}$	$K_{c,f}$	J_i	$K_{a,i}$	$K_{c,i}$	γ_0 (10 ⁻³ cm ⁻¹ atm ⁻¹)		
							Voigt	Rautian	Calc.
919.8311	9	1	8	10	2	8	71.2 ± 1.9	74.2 ± 2.2	76.7
922.6008	11	3	8	11	4	8	71.0 ± 1.7	73.5 ± 1.6	71.0
922.7116	12	3	9	12	4	9	71.2 ± 2.2	73.7 ± 2.5	70.4
923.5326	7	1	6	8	2	6	75.9 ± 2.6	78.5 ± 1.6	79.9
926.6493	7	0	7	8	1	7	76.0 ± 2.4	77.7 ± 3.1	76.0
926.7510	13	2	12	13	3	10	69.5 ± 2.4	72.3 ± 2.2	69.9
927.0739	4	1	4	5	2	4	80.0 ± 1.8	80.9 ± 2.3	88.3
931.3365	2	1	2	3	2	2	84.2 ± 2.1	86.1 ± 3.0	89.9
931.5019	11	2	9	11	3	9	70.6 ± 1.8	72.6 ± 2.2	69.9
931.8834	5	0	5	6	1	5	76.6 ± 1.8	78.5 ± 2.6	78.2
936.1209	4	1	4	4	2	2	81.9 ± 2.3	84.2 ± 2.5	87.8
939.4905	13	3	10	14	2	12	68.8 ± 1.6	71.0 ± 2.1	74.2
943.3529	13	1	12	13	2	12	68.1 ± 2.0	69.9 ± 2.6	70.0
947.0301	8	0	8	8	1	8	70.9 ± 2.3	73.9 ± 2.1	77.1
947.3806	9	0	9	9	1	9	69.8 ± 1.8	72.0 ± 2.1	76.6
947.7002	10	0	10	10	1	10	67.2 ± 1.7	68.7 ± 2.4	76.5
948.2275	12	0	12	12	1	12	64.9 ± 3.0	66.5 ± 1.8	76.9
951.3717	6	1	6	6	0	6	73.8 ± 2.2	75.4 ± 2.2	80.0
951.7394	5	1	5	5	0	5	76.6 ± 2.0	79.4 ± 3.3	81.7
959.3072	11	1	10	10	2	8	70.8 ± 1.8	72.5 ± 2.0	76.0
960.0769	9	4	5	10	3	7	65.3 ± 2.6	68.9 ± 1.8	77.7
962.9599	20	3	17	19	4	15	66.6 ± 1.7	68.7 ± 2.1	72.0
963.1025	16	2	14	15	3	12	68.2 ± 1.9	69.9 ± 1.9	73.7
966.9867	3	2	2	2	1	2	83.7 ± 2.2	85.5 ± 2.1	89.9
967.2054	11	3	9	11	2	9	71.4 ± 2.3	73.0 ± 2.1	69.9
970.7542	8	1	7	7	0	7	73.5 ± 1.9	74.7 ± 2.5	76.0
970.8737	11	3	8	11	2	10	71.5 ± 1.8	73.4 ± 2.3	72.0
982.7607	7	3	5	6	2	5	78.7 ± 1.9	80.6 ± 3.1	81.8
1011.5135	20	1	19	19	0	19	65.9 ± 3.3	68.4 ± 3.7	76.4
1011.8617	20	3	18	19	2	18	66.3 ± 2.2	69.2 ± 2.8	75.1
1015.3474	20	4	17	19	3	17	66.6 ± 2.0	69.4 ± 2.0	71.5
1023.1019	20	5	16	19	4	16	65.3 ± 2.0	68.6 ± 2.3	70.6

Figure captions

Fig. 1. Example of the spectra recorded for the $7_{3,5} \leftarrow 6_{2,5}$ line of the ν_7 band of C_2H_4 perturbed by Ar: (1) diode-laser emission profile recorded with an empty cell; (2-5) broadened line at 36.08, 47.59, 60.50 and 73.67 mbar of Ar; (6) confocal étalon fringes; (7) low pressure line of pure C_2H_4 ; (8) 0% transmission level.

Fig. 2. Example of Voigt profile fit (●) to the experimental line shape (line) for the $7_{3,5} \leftarrow 6_{2,5}$ line of the ν_7 band of C_2H_4 (at 0.02 mbar) diluted in 47.59 mbar of Ar. For better visibility, one fitted value out of five is represented here. Residuals (observed values minus calculated ones) multiplied by ten are shown for both Voigt and Rautian profiles.

Fig. 3. Pressure dependence of the collisional half-width γ_c for the $7_{3,5} \leftarrow 6_{2,5}$ line of C_2H_4 in the ν_7 band, derived from the fits of Voigt (■) and Rautian (○) profiles. The slopes of the corresponding best-fit lines represent the Ar-broadening coefficients.

Fig. 4. Geometry of C_2H_4 .

Fig. 5. Dependence of the Ar-broadening coefficients γ_0 on the quantum number J in the ν_7 band of C_2H_4 . Experimental values derived from Voigt (■) and Rautian (▲) profiles. Calculations (○) are performed for all the transitions studied experimentally.

Fig. 6. Ar-broadening coefficients γ_0 for C_2H_4 lines in the R , P and Q branches plotted in function of $J + 0.2K_a$. For clarity, only experimental (▲) results obtained with Rautian profile and theoretical values (○) are displayed.

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