# New vibrational assignments for the nu1 to nu17 vibrational modes of aziridine and first analysis of the high resolution infrared spectrum of aziridine between $720 \mathrm{~cm}-1$ and $1050 \mathrm{~cm}-1$ 

Malick Ngom, Fridolin Kwabia-Tchana, Agnes Perrin, Jean-Claude Guillemin, Jean Marie Flaud, Jean Demaison, Abib Ngom

## - To cite this version:

Malick Ngom, Fridolin Kwabia-Tchana, Agnes Perrin, Jean-Claude Guillemin, Jean Marie Flaud, et al.. New vibrational assignments for the nu1 to nu17 vibrational modes of aziridine and first analysis of the high resolution infrared spectrum of aziridine between $720 \mathrm{~cm}-1$ and $1050 \mathrm{~cm}-1$. Molecular Physics, 2011, pp.1. 10.1080/00268976.2011.605774 . hal-00723312

HAL Id: hal-00723312
https://hal.science/hal-00723312
Submitted on 9 Aug 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.


## New vibrational assignments for the nu1 to nu17 vibrational modes of aziridine and first analysis of the high resolution infrared spectrum of aziridine between $\mathbf{7 2 0} \mathbf{~ c m - 1}$ and 1050 cm-1

| Journal: | Molecular Physics |
| ---: | :--- |
| Manuscript ID: | TMPH-2011-0132.R1 |
| Manuscript Type: | Special Issue Paper - Dijon HRMS |
| Author: | 20-Jun-2011 |
| Complete List of Authors: | Ngom, Malick; Univ Paris Est Ceteil <br> Kwabia-Tchana, Fridolin; LISA <br> Perrin, Agnes; Univsersite Paris EST Creteil, CNRS UMR 7583; LISA <br> Guillemin, Jean-Claude; École Nationale Supérieure de Chimie de <br> Rennes, UMR 6226 <br> FLAUD, Jean Marie; LISA <br> Demaison, Jean; Université de Lille I, PhLAM <br> Ngom, Abib; Université Cheikh Anta Diop |
| Keywords: aziridine, (C2H4NH), ab initio, ethylenimine, vibrational <br> assignments |  |
| Note: The following files were submitted by the author for peer review, but cannot be converted <br> to PDF. You must view these files (e.g. movies) online. |  |
| figures.zip |  |

## SCHOLARONE ${ }^{\text {m }}$ Manuscripts

New vibrational assignments for the $v_{1}$ to $v_{17}$ vibrational modes of aziridine and first analysis of the high resolution infrared spectrum of aziridine between $720 \mathrm{~cm}^{-1}$ and $1050 \mathrm{~cm}^{-1}$<br>M. Ngom ${ }^{1,2}$, F. Kwabia Tchana ${ }^{1^{*}}$, A. Perrin ${ }^{1 *}$, J.-C. Guillemin ${ }^{3}$, J.-M. Flaud ${ }^{1}$, J. Demaison ${ }^{4}$, El. A. Ngom ${ }^{2}$<br>${ }^{1}$ Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583,<br>Université Paris Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, 61 Avenue de Général de Gaulle, 94010 Créteil Cedex, France.<br>${ }^{2}$ Université Cheikh Anta Diop, Ecole Supérieure Polytechnique, BP 5085, Dakar, Sénégal.<br>${ }^{3}$ École Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France.<br>${ }^{4}$ Laboratoire de Physique des Lasers, Atomes et Molécules, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France.<br>\section*{Paper submitted to Molecular Physics in the honor of Pr Gianfranco Dilonardo, for his many contributions for Science}<br>*Corresponding Authors:<br>Fridolin KWABIA TCHANA<br>Email: fridolin.kwabia@lisa.u-pec.fr<br>Tel. +33 (0)1 451715 29, Fax. +33 (0)1 45171564<br>and<br>Agnès PERRIN<br>Email: agnes.perrin@lisa.u-pec.fr

$$
\text { Tel. +33 (0)1 } 451765 \text { 57, Fax. +33 (0)1 } 45171564
$$


#### Abstract

$\underline{\text { Abstract }}$

Fourier transform spectra of aziridine $\left(\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{NH}\right)$ were recorded at high resolution ( 0.002 or $0.003 \mathrm{~cm}^{-1}$ ) in the $600-1750$ and $1750-4000 \mathrm{~cm}^{-1}$ regions, using a Bruker IFS 125 HR (an upgraded version of the IFS120HR) spectrometer, located at the LISA facility in Creteil. In parallel, the harmonic force field of aziridine was evaluated analytically at the optimized geometry with second-order Møller-Plesset perturbation theory (MP2) together with the correlation-consistent polarized valence triple zeta basis sets cc-pVTZ. These ab initio predictions were used to perform consistent vibrational assignments for the $v_{1}$ to $v_{17}$ fundamental bands of aziridine observed in the infrared spectra recorded during this study. Finally, a first detailed rotational assignment was performed for two B-type bands located at $772.3571 \mathrm{~cm}^{-1}\left(v_{10}, \mathrm{CH}_{2}\right.$ rock) and $997.1592 \mathrm{~cm}^{-1}$ ( $v_{8}$, NH bend) and for an A-type band located at $904.0429 \mathrm{~cm}^{-1}$ ( $v_{17}$, ring deform). We noticed that the $v_{10}$ band is weakly perturbed, presumably because the $\mathrm{v}_{10}=1$ rotational levels are coupled with those of the $\mathrm{v}_{18}=1$ dark band located around $817 \mathrm{~cm}^{-1}$ through B-type and C-type Coriolis resonances.


## 1. Introduction

Aziridine, $c-\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{NH}$, also called ethylenimine, is a three-membered heterocycle with an amine group. Its rotational spectrum has already been studied in details (see Refs. [1-3] and references herein). It is an oblate top (Ray's asymmetry parameter, $\kappa=+0.670$ ) which makes its centrifugal distortion analysis more difficult [3]. It is a molecule worth to be studied because of its potential astrophysical interest [1-3]. Aziridine is indeed a possible interstellar molecule candidate since many small nitrogen derivatives and epoxide [4] have already been observed in the Interstellar Medium. It could also be detected in the atmosphere of Titan [5]. Despite its interest, there is not much information on its infrared spectrum. As far as we know, the most recent papers are by Potts [6] Mitchell et al. [7] and by Gunasekaran and Uthra [8]. These authors proposed assignments for all fundamentals bands, based on low resolution Raman $[6,8]$ and infrared spectra $[6-8]$ recorded for vapour phase and liquid phase for the main isotopic species of aziridine. In addition Mitchell et al. [7] used for its analysis infrared spectra recorded for imine-deuterated and ${ }^{15} \mathrm{~N}$ isotopologues [7].
First let us mention that, according to [6, 7], no fundamental bands exist below $600 \mathrm{~cm}^{-1}$ and this is confirmed by the present study (See below). Therefore the analysis performed by Gunasekaran and Uthra [8] who assigned the first three fundamental vibrational bands of ethyleneimine at 526,563 , and $654 \mathrm{~cm}^{-1}$ respectively, is clearly incorrect and will not be considered further in the text. When comparing the experimental study performed by Mitchell et al. [7] and Potts [6] few of their vibrational assignments differ. On the otherhand some of their results are not compatible with the results of high-level ab initio calculations as shown below. For this reason, we have recorded at high resolution the infrared spectra of aziridine and reassigned all fundamental bands using all available experimental informations as well as results of ab initio calculations.

Finally, the rotational analysis of the $v_{8}, v_{10}$ and $v_{17}$ bands was also undertaken and allowed us to determine both rotational and vibration rotation interaction constants which were compared to the ab initio predictions.

The present paper is organized as follows. Section 2 summarizes the experimental details. Section 3 describes the ab initio computational details. Using the ab initio predictions, the vibrational assignments for the $v_{1}$ to $v_{17}$ bands were performed as described in Section 4. For the $v_{8,} v_{10}$ and $v_{17}$ bands, a detailed rotational assignment could be performed (section 5).

## 2. Experimental details:

$\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{NH}$ was prepared starting from 2-chloroethylamine hydrochloride (99 \% stated purity, Sigma Aldrich) and sodium hydroxide ( $\geq 98 \%$ stated purity, Sigma Aldrich). In a flask equipped with a reflux condenser, 2-Chloroethylamine hydrochloride ( $58 \mathrm{~g}, 0.5 \mathrm{~mol}$ ), 90 ml of water and sodium hydroxide ( $60 \mathrm{~g}, 1.5 \mathrm{~mol}$ ) were heated at $50^{\circ} \mathrm{C}$ for 2 hours. The solution was then distilled at reduced pressure until 70 mL of distillate had been collected. The cooled distillate was mixed with 35 g of sodium hydroxide, and the amine was distilled at atmospheric pressure through a one-foot column packed with glass helices. A $50 \%$ sodium hydroxide solution was run in slowly at the top of the column during the distillation. The pot temperature did not exceed $70^{\circ} \mathrm{C}$ during the distillation. The aziridine was stored over a few pellets of sodium hydroxide. The yield ranges between 20 and $39 \%$ in function of the efficiency of the stripping operation and the condensation of the low-boiling distillate but the yield of the Ref. [9] (73 \%), has never been obtained.

The White-type multipass absorption cell, made of pyrex glass and equipped with CsBr windows, was connected to the Fourier transform spectrometer with a dedicated optical interface (six mirrors) inside the back sample compartment of the Bruker spectrometer. Its base length is 0.80 m , and, for the experiment described here, an optical path of 19.249 m was used. This value takes into account the distance between the surface of the field mirror and the windows of the cell $(2 \times 2.45 \mathrm{~cm})$. The following procedure was used for measurements: first a background spectrum was collected while the cell was being continuously evacuated; next the infrared gas cell was treated with $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{NH}$ vapour several times, until no proton exchange with the surface could be detected and, for the final measurements sample pressures of 0.0341 (1) and 0.1188 (5) hPa were used. Sample pressure in the cell was measured using a calibrated MKS Baratron capacitance manometer ( 2 hPa full scale) which has a stated uncertainty of $0.12 \%$ of full scale, according to the manufacturer. The absolute uncertainty given for the sample pressure is the sum of $0.12 \%$ and $0.3 \%$ for the variation of the pressure during the recording of the spectra. This gives an estimation of $0.42 \%$ on the pressure.

The infrared spectra of $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{NH}$ used in this study were recorded at high resolution in the $600-1750$ and $1750-4000 \mathrm{~cm}^{-1}$ regions, using the Bruker IFS125HR Fourier transform spectrometer of the "Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA)" in Créteil, Paris. A KBr beamsplitter, Globar source (Silicon Carbide, SiC) and either a liquid nitrogen-cooled MCT photovoltaic detector or a liquid nitrogen-cooled InSb detector were employed for these experiments. The optical path of the spectrometer was continuously evacuated to below 0.05 hPa for the duration of all spectral measurements. Spectra were
recorded with an aperture diameter of $1.15 \mathrm{~mm}, 40 \mathrm{kHz}$ scanner frequency, and a maximum optical path difference ( $d_{\text {MOPD }}$ ) of 450 or 300 cm . According to the Bruker definition (Resolution $=0.9 / d_{\text {MOPD }}$ ) this corresponds to a resolution of $0.002 \mathrm{~cm}^{-1}$ or $0.003 \mathrm{~cm}^{-1}$. The spectra were recorded at a stabilized room temperature of $22^{\circ} \mathrm{C}$. Both spectra were ratioed against the empty cell, single-channel background spectrum which was taken at a resolution of $0.512 \mathrm{~cm}^{-1}$, in order to ensure the best possible signal-to-noise in the ratioed spectra. The spectra were the result of the co-addition of 570 interferograms. For the Fourier transform a Mertz-phase correction, $0.5 \mathrm{~cm}^{-1}$ phase resolution and boxcar apodization function were applied to the averaged interferograms. The spectra were calibrated using residual $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ lines observed in the spectra, with their wavenumbers taken respectively from HITRAN08 [10] resulting in an accuracy of $0.0002 \mathrm{~cm}^{-1}$ (RMS) for well isolated lines.

## 3. Ab initio computational details

The harmonic force field of aziridine was evaluated analytically at the optimized geometry with second-order Møller-Plesset perturbation theory (MP2) [11] together with the correlation-consistent polarized valence triple zeta basis sets cc-pVTZ [12]. The coupled cluster method with single and double excitations [13] and a perturbative treatment of connected triples [14] [CCSD(T)] with the cc-pVTZ basis set was also used. The Kohn-Sham density functional theory [15] using Becke's three-parameter hybrid exchange functional [16] and the Lee-Yang-Parr correlation functional [17], together denoted as B3LYP was also used with the split-valence basis set 6-311G, as implemented in Gaussian03 (G03) [18], including appropriate polarization functions. It is indeed well established that multiplying the B3LYP harmonic frequencies by a scaling factor close to one ( $0.96-0.98$ ) permits to obtain a rather accurate estimate of the fundamental frequencies [19].

In order to estimate the vibrational anharmonicity constants, the rotation-vibration interaction constants, and the Fermi interaction constants, the cubic ( $\phi_{i j k}$ ) and semi-diagonal quartic ( $\phi_{i j k k}$ ) normal coordinate force constants were determined at the same reference structure with the use of a finite difference procedure involving displacements along reduced normal coordinates (with step size $\Delta q=0.03$ ) and the calculation of analytic Cartesian second derivatives at these displaced geometries [20, 21] using the MP2/cc-pVTZ method. The evaluation of anharmonic spectroscopic constants was based on second-order rovibrational perturbation theory [22].

The $\operatorname{CCSD}(\mathrm{T})$ computations were performed with the CFOUR [23] electronic structure program package, while the lower-level B3LYP and MP2 computations utilized the G03 program [18].

## 4 Vibrational assignments of the first seventeen ( $v_{1}$ to $v_{17}$ ) fundamental bands of aziridine and rotational analysis of the $v_{\underline{10}}, v_{\underline{17}}$ and $v_{\underline{8}} \underline{\text { bands : }}$

The aziridine structure [24,25] is illustrated on Fig. 1. This non-planar $\mathrm{C}_{\mathrm{s}}$-type molecule possesses eighteen non-degenerate modes of vibration which are listed in Table 1. Of these, ten modes ( $v_{1}$ to $v_{10}$ ) are of A' symmetry, while $v_{11}$ to $v_{18}$ are of A" symmetry. According to the selection rules for an electric dipole moment transition, infrared fundamental bands corresponding to an A" (respectively A') vibrational upper state are A-type bands (respectively hybrid-type bands, with both B- and C-type transitions). The A-type, B-type and C-type transitions correspond to ( $\Delta \mathrm{K}_{\mathrm{a}}=$ even, $\Delta \mathrm{K}_{\mathrm{c}}=$ odd $)$, $\left(\Delta \mathrm{K}_{\mathrm{a}}=\right.$ odd, $\Delta \mathrm{K}_{\mathrm{c}}=$ odd $)$ and ( $\Delta \mathrm{K}_{\mathrm{a}}$ $=$ odd, $\Delta \mathrm{K}_{\mathrm{c}}=$ even ) rotational selection rules, respectively. Finally, transitions with ( $\Delta \mathrm{K}_{\mathrm{a}}=$ even, $\Delta \mathrm{K}_{\mathrm{c}}=$ even) are forbidden in the infrared. In addition to these symmetry considerations, the observed line intensity pattern for each fundamental band is determined by the values of the components of the corresponding transition moment operators on the a-axis (for $A^{\prime} \leftrightarrow A$ " vibrational transitions), or on the b- and c- inertia axes (for $A^{\prime} \leftrightarrow A^{\prime}$ or $A^{\prime \prime} \leftrightarrow A$ " vibrational transitions).

The ab initio calculations described in paragraph 3 were able to predict the band positions and intensities for aziridine fundamental bands. From these predictions, which are quoted in Table 1, it was easy to assign unambiguously the strong and well isolated fundamental bands in the observed experimental spectrum. Accordingly the positions measured in this work for the $v_{2}, v_{8}, v_{9}, v_{11}$ and $v_{17}$ bands differ only marginally from those given previously in the literature [6, 7].

On the other hand, for medium intensity bands, such analysis is more difficult. In this case reliable and unambiguous vibrational assignments could be achieved only by performing detailed comparisons between theoretically-modeled and observed spectra.

To model the absorption for a given $v_{i}$ fundamental band (with $\mathrm{i}=1$ to 18 ), an approximate list of line positions and intensities was generated using the theoretical methods which are described in the next paragraph. The parameters necessary for these computations,
namely, the $\alpha_{i}^{X}(X=A, B$ and $C)$ vibration rotation interaction constants, and the first order derivatives, $\left(\frac{\partial \mu_{\beta}}{\partial q_{i}}\right)_{0}$ of the dipole moment operator (with $\beta=\mathrm{a}, \mathrm{b}$ or c and $\mathrm{q}_{\mathrm{i}}$ is the vibrational quantum coordinate associated to $\mathrm{v}_{\mathrm{i}}$ ) collected in Table 2 are those deduced from the ab initio calculations. More explicitly, for the computation of the $v_{i}=1$ upper state energy levels, we used the vibrational energy $E_{i}$ which was adjusted slightly starting from its ab initio value (Table 1), and the $\alpha_{i}^{\mathrm{X}}$ in order to get the variation of the upper rotational state constants relative to their ground state values [3]. To perform the intensity calculations the $\left(\frac{\partial \mu_{\beta}}{\partial q_{i}}\right)_{0}$ dipole moment derivatives, were adjusted to within $10 \%$ of the values quoted in Table 2 in order to better reproduce the experimental spectra. Let us stress indeed that for hybrid bands,
it is important to have a good value of the ratio $\left\lvert\,\left(\frac{\partial \mu_{b}}{\partial q_{i}}\right)_{0} /\left(\frac{\partial \mu_{c}}{\partial q_{i}}\right)_{0}^{2}\right.$.
Fig. 2 gives an overview of the aziridine spectrum in the 720 to $1050 \mathrm{~cm}^{-1}$ spectral range. As expected from symmetry consideration, the $\nu_{17}$ band at $904 \mathrm{~cm}^{-1}$ exhibits a narrow A-type Q structure. On the other hand, the $v_{10}, v_{9}$ and $v_{8}$ bands, which should be hybrid, are in fact pure B- type bands, and this is what is indeed predicted by the ab initio calculations.
The vibrational assignments deduced in this way differ from the ones obtained from previous studies $[6,7]$ for several bands. For example, as can be seen on Fig. 3, the band located at $1266.67 \mathrm{~cm}^{-1}$ is the hybrid B- and C-type $v_{5}$ band, with a strong C-type character, while in Refs. [6, 7] the Q structure near $1268 \mathrm{~cm}^{-1}$ was erroneously identified as the A-type $v_{14}$ band. On the other hand the $v_{14}$ band is presently located at $1237 \mathrm{~cm}^{-1}$.
Fig. 4 shows a detailed view of the $3070-3090 \mathrm{~cm}^{-1}$ spectral region. It is clear that the $v_{2}$ band at $3079.6 \mathrm{~cm}^{-1}$ is a C-type band which is significantly stronger than the A-type $v_{11}$ band at $3083.73 \mathrm{~cm}^{-1}$. In Refs. [6, 7] both bands were assigned at $3079 \mathrm{~cm}^{-1}$.
Finally we were unable to identify the $v_{18}$ band $\left(\mathrm{CH}_{2}\right.$ rock) which is expected to be extremely weak on the basis of the ab initio prediction. This band which is assumed to be observed near $817 \mathrm{~cm}^{-1}$ is in fact completely blended (see Fig. 2) under the stronger $v_{10}$ and $v_{9}$ bands.

During this work it was also possible to perform a detailed rotational analysis of the $v_{10}, v_{17}$ and $v_{8}$ bands located at $773 \mathrm{~cm}^{-1}, 904 \mathrm{~cm}^{-1}$ and $998 \mathrm{~cm}^{-1}$.

The first assignments were performed using calculated predictions both for line positions and relative intensities.
The upper and lower state energy levels were computed using, as it is usual in infrared, a Watson Hamiltonian written in the $I^{\mathrm{r}}$ representation with an A-type reduction. This choice of Hamiltonian reduction and axes representation need to be justified. Indeed, a recent detailed microwave study [3] performed for rotational transitions measured within the ground vibrational state of aziridine demonstrated that the combination of a S- reduction and a $\mathrm{III}^{\mathrm{r}}$ representation lead to a better convergence of the ground state rotational Hamiltonian than when using the combination of a A-type reduction and $I^{r}$ representation. However the improvements achieved in this way for the ground state energy levels concern $\Phi$ and L centrifugal distortion terms, which are Hamiltonian terms in $\mathrm{J}^{6}$ and $\mathrm{J}^{8}$, respectively. The present study concern the first vibrational states, for which the energy levels are affected by significant vibrational rotational resonances, as it will be demonstrated in the text. Since these perturbations could not be accounted for during the present study, the centrifugal distortion terms are clearly affected starting from terms in $\mathrm{J}^{4}$ ( $\Delta$ terms), and the preference for a $\left(\mathrm{S}, \mathrm{III}^{\mathrm{r}}\right)$ combination rather than $\left(\mathrm{A}, \mathrm{I}^{\mathrm{r}}\right)$ is not relevant for this infrared study.
Table 3 gives the $\left(A, I^{\mathrm{r}}\right.$ ) rotational Hamiltonian used during the present study. The rotational and centrifugal distortion constants quoted in the last column of Table 2 of Ref. [3] and gathered in Table 4 of this work were used for the computation of the ground state levels during all this study. For the upper vibrational states, the preliminary values of the rotational constants were computed from the $\alpha_{i}^{X}$ vibration rotation interaction constants predicted by the ab initio calculations, and using the approximation:

$$
\mathrm{X}_{\mathrm{i}}=\mathrm{X}_{0}-\alpha_{\mathrm{i}}^{\mathrm{X}} \quad(\text { with } \mathrm{X}=\mathrm{A}, \mathrm{~B} \text { and } \mathrm{C}) \quad \text { Eq. (1) }
$$

In this expression, the $\mathrm{X}_{0}$ are the ground state rotational constants of Ref. [3], while the centrifugal distortion constants were maintained at their ground state values during the first calculations.

The line intensities calculations were performed using the method described elsewhere [26], and the first order derivatives, of the dipole moment operator deduced from ab initio calculations.

Using these predictions, some low and medium $J$ and $K_{a}$ transitions in the $v_{10}, v_{8}$ and $v_{17}$ bands were assigned. Then, using the ground state parameters of Ref. [3], the lower state
energy levels were calculated and added to the newly observed line positions to get a list of experimental upper state energy levels. These upper state levels were inserted in a least squares fit to get an improved set of upper states parameters allowing better predictions and hence more assignments to be made. Gradually the vibrational energies and the rotational and centrifugal distortion constants were refined for the $10^{1}, 8^{1}$ and $17^{1}$ vibrational states during the assignment process. This iterative process was carried out until the $v_{10}, v_{8}$ and $v_{17}$ bands were completely assigned.

No noticeable perturbations were noticed during the analysis of the $v_{8}$ and $v_{17}$ bands. However, at a given level, it appeared that transitions of the $\nu_{10}$ band involving $\mathrm{K}^{\prime}{ }_{\mathrm{c}} \approx 20$ and $\mathrm{K}_{\mathrm{c}}{ }_{\mathrm{c}} \approx 8$ rotational quantum numbers in the upper levels are perturbed. It is presumed that the $18^{1}$ dark state, located near $817 \mathrm{~cm}^{-1}$ is involved in the perturbations observed for the $v_{10}$ band, since the ab initio calculations predict rather significant C-type Coriolis resonances coupling the $10^{1} \Leftrightarrow 18^{1}$ energy levels (with $\varsigma_{10,18}^{\mathrm{B}}=-0.025$ and $\varsigma_{10,18}^{\mathrm{C}}=-0.490$ for the B- and C- type Coriolis parameters, respectively).

The results of the final assignments, in term of ranges of the upper state rotational quantum numbers, are given in the upper part of Table 5. Examples of assignments for the $v_{10}, v_{17}$, and $v_{8}$ bands are given in Figs. 5, 6 and 7, respectively.

The same procedure was tentatively applied for the B-type $v_{9}$ band at $855.94 \mathrm{~cm}^{-1}$. However at a given level, it appeared that this band is extremely perturbed: we think that strong B- and C-type resonances are coupling the $9^{1}$ upper state energy levels with those of the $18^{1}$ dark state. This is indeed expected from the results of the ab initio calculations which predict $\varsigma_{9,18}^{\mathrm{B}}=-0.113$ and $\varsigma_{9,18}^{\mathrm{C}}=-0.800$ for the B - and C - type Coriolis parameters, respectively. Unfortunately it was not possible to go in more detail in the analysis of the resonance since no experimental data exist, up to now, for the $\mathrm{v}_{18}=1$ dark state.

Table 4 lists the Hamiltonian constants (vibrational energies, rotational and centrifugal distortion constants) resulting from the final fits of the $10^{1}, 8^{1}$ and $17^{1}$ upper state energy levels, together with their associated statistical uncertainties. For this calculation, the set of $10^{1}$ energy levels was restricted to the set of unperturbed energy levels. As usual the parameters derived for the higher order centrifugal distortion constants are effective with poor physical meaning. This is mainly true for the $10^{1}$ vibrational state, for which clear resonances
are observed. This is also the case for the $17^{1}$ state. Although no noticeable perturbation could be observed during the assignment of the $v_{17}$ band, the ab initio calculations predict that $B$ and C-type Coriolis resonances are coupling together the $17^{1} \Leftrightarrow 8^{1}$ energy levels (with $\varsigma_{17,8}^{B}=-0.1131$ and $\varsigma_{17,18}^{C}=-0.7997$ for the B- and C- type Coriolis parameters, respectively).

The results of the energy levels calculations proved to be rather satisfactory, as can be seen from the standard deviation and statistical analysis given in the lower part of Table 5. It is interesting to compare the observed and calculated spectra.
Figure 2 shows the overview of the observed and calculated spectra in the $720 \mathrm{~cm}^{-1}$ to $1050 \mathrm{~cm}^{-1}$ region. The perturbed $v_{9}$ band, whose analysis is in progress, is not plotted on the calculated spectrum.
Figures 5 and 6 show portions of the Q branch of the $v_{10}$ and $v_{17}$ bands, respectively. Fig. 7 gives a portion of the R branch of the $\nu_{8}$ band. In each case the agreement between the observed and calculated spectra is excellent.

Finally the values of the experimental $\alpha_{i}^{X}$ vibration rotation interaction constants are compared in Table 6 to these ab initio values, showing a reasonable agreement for the three bands under study.

## 8. Conclusion

A new vibrational assignment was performed for the fundamental bands of aziridine, based on ab initio calculations and on Fourier transform spectra recorded at high resolution. In addition the first analysis of the $v_{10}, v_{8}$ and $v_{17}$ fundamental bands of aziridine was performed. No noticeable perturbations were observed during the analyses of $v_{8}$ and $v_{17}$ bands, while the $v_{10}$ band appears to be weakly perturbed. The energy levels resulting from the analyses were used to derive accurate vibrational energies, and rotational and centrifugal distortion constants for the $8^{1}, 10^{1}$ and $17^{1}$ vibrational states.

## Acknowledgments

M. NGOM gratefully acknowledges financial support from the Ministère des Affaires Etrangères (Ambassade de France à Dakar, Sénégal). L. MARGULES is thanked for his help during the calculations with CFOUR. J.-C. GUILLEMIN thanks the Program Physique et Chimie du Milieu Interstellaire (INSU-CNRS) for financial support.

## References

[1] S. Thorwirth, H. S. P. Müller and G. Winnewisser, J. Mol. Spectrosc. 199, 116 (2000).
[2] S. Thorwirth, R. Gendriesch, H. S. P. Müller, F. Lewen and G. Winnewisser, J. Mol. Spectrosc. 201, 323 (2000).
[3] R. A. Motiyenko, L. Margulès, E. A. Alekseev , J.-C. Guillemin and J. Demaison, J. Mol. Spectrosc. 264, 94 (2010).
[4] J.E. Dickens, W.M. Irvine, M. Ohishi, M. Ikeda, S. Ishikawa, A. Nummelin and A. Hjalmarson, Bulletin of the American Astronomical Society 29, 1245 (1997).
[5] P. P. Lavas, A. Coustenis and I.M. Vardavas, Planetary and Space Science 56, 67 (2008).
[6] W. J. Potts, Spectrochimica Act. 21, 511 (1965).
[7] R.W. Mitchell, J.C. Burr and J.A. Merrit, Spectrochim. Acta A 23, 195 (1967).
[8]. S. Gunasekaran and D. Uthra, Indian J. Pure \& Appl. Phys. 46, 100 (2008).
[9] V. P Wystrach ; D. W. Kaiser; F. C. J. Schaefer, Am. Chem. Soc. 77, 5915 (1955).
[10] L.S. Rothman, I.E. Gordon, A. Barbe, D. Chris Benner, P.F. Bernath, M. Birk, V. Boudon, L.R. Brown, A. Campargue, J.-P. Champion, K. Chance, L.H. Coudert, V. Dana, V.M. Devi, S. Fally, J.-M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, et al., The HITRAN 2008 molecular spectroscopic database, Journal of Quantitative Spectroscopy and Radiative Transfer 110, 533 (2009).
[11] C. Møller and M.S. Plesset, Phys. Rev. 46, 618 (1934).
[12] T.H. Dunning, Jr., J. Chem. Phys. 90 , 1007 (1989).
[13] G.D. Purvis III and R.J. Bartlett, J. Chem. Phys. 76,1910 (1982).
[14] K. Raghavachari, G.W. Trucks, J.A. Pople and M. Head-Gordon, Chem. Phys. Lett. 157, 479 (1989).
[15] W. Kohn and L.J. Sham, Phys. Rev. A 140, 1133 (1965).
[16] A.D. Becke, J. Chem. Phys. 98 , 5648 (1993).
[17] C.T. Lee, W.T. Yang and R.G. Parr, Phys. Rev. B 37, 785 (1988).
[18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, Revision D. 01, (2004).
[19] K.K. Irikura, R.D. Johnson III and R.N. Kacker, J. Phys. Chem. A 109, 8430 (2005).
[20] W. Schneider and W. Thiel, Chem. Phys. Lett. 157, 367 (1989).
[21] J.F. Stanton, C. Lopreore and J. Gauss, J. Chem. Phys. 108, 1998, 7190-@ (1998).
[22] I.M. Mills, In Molecular Spectroscopy: Modern Research; Mathews, C.W., Ed., Vol. 1, Academic Press, New York, 115 (1972).
[23]. CFOUR, a quantum chemical program package written by J.F. Stanton, J. Gauss, M.E. Harding, P.G. Szalay with contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W.J. Lauderdale, D.A. Matthews, T. Metzroth, D.P. O'Neill, D.R. Price, E. Prochnow, K. Ruud, F. Schiffmann, S. Stopkowicz, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jörgensen, and J. Olsen),
and ECP routines by A. V. Mitin and C. van Wüllen. 2010. For the current version, see http://www.cfour.de.
[24] B. Bak and S. Skaarup, J. Mol. Structure 10, 385 (1971).
[25] K. Kalcher, W. Kosmus and K. Faegri, Spectrochica Acta 34A, 889 (1981).
[26] J.M. Flaud, C. Camy-Peyret, and R. Toth, "Water vapour line parameters from microwave to medium infrared", Pergamon Press, Oxford, (1981).

## Captions of the figures:

Fig. 1. Structure of the aziridine molecule [24, 25].
The $\mathrm{a}, \mathrm{b}$ and c are the inertial axes and (bc) is the symmetry plane for this non planar $\mathrm{C}_{\mathrm{s}}$-type molecule. The $\mathrm{I}^{\mathrm{r}}$ representation $(\mathrm{x}=\mathrm{b}, \mathrm{y}=\mathrm{c}$ and $\mathrm{z}=\mathrm{a}$ ) was adopted for all calculations.

Fig. 2. Overview of the aziridine spectrum in the $720-1050 \mathrm{~cm}^{-1}$ region $\left(v_{10}, v_{9}, v_{17}\right.$ and $v_{8}$ bands).
The narrow $Q$ branch structure at $904 \mathrm{~cm}^{-1}$ indicates an A-type structure for the $v_{17}$ band. The $v_{10}, v_{9}$ and $v_{8}$ hybrid bands which do not exhibit any sharp Q structure are mainly B-type bands.
Lower trace: observed spectrum recorded with a resolution of $0.002 \mathrm{~cm}^{-1}$ and an optical path length of 19.249 m , at a $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{NH}$ pressure of 0.0341 hPa and a stabilized room temperature of 295.2 K. Upper trace: the synthetic spectrum, calculated for the $v_{10}, v_{17}$ and $v_{8}$ bands is shifted vertically for a clear comparison. The $v_{9}$ perturbed band is not considered in the present analysis (see text).

Fig. 3. Overview of the $v_{5}$ band of aziridine in the $1267 \mathrm{~cm}^{-1}$ spectral region.
Medium trace: observed spectrum (see the caption of Fig. 2). Upper trace: low resolution model for the $v_{5}$ hybrid (both B- and C-type) band (see text). The model assuming an A-type character for this band is clearly incorrect.

Fig.4. Overview of aziridine infrared spectrum in the $3080 \mathrm{~cm}^{-1}$ spectral region.
Lower trace: observed spectrum recorded with a resolution of $0.003 \mathrm{~cm}^{-1}$ and an optical path length of 19.249 m , at a $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{NH}$ pressure of 0.1188 hPa and a stabilized room temperature of 295.2 K. Upper trace: calculated $v_{2}$ C-type band and $v_{11}$ A-type band at 3079.6 and 3083.73 $\mathrm{cm}^{-1}$, respectively.

Fig. 5. Portion of the $Q$ branch of the $v_{10}$ band of aziridine in the $763 \mathrm{~cm}^{-1}$ spectral region. The ${ }^{\mathrm{P}, \mathrm{R}} \mathrm{Q}_{\mathrm{Kc}}$ structure for $\mathrm{K}^{\prime \prime}{ }_{\mathrm{c}}=13$ (solid triangles) is presented together with some additional assignments. The d letters stand for degenerate transitions with $K_{a}=J-K_{c}$ and $K_{a}=J-$ $\mathrm{K}_{\mathrm{c}}+1$ ). Excellent agreement is obtained between the observed (lower) and the calculated (upper) spectrum.

Fig. 6. Portion of the Q branch of the $v_{17}$ band of aziridine in the $903.5 \mathrm{~cm}^{-1}$ spectral region. Together with additional assignments, series of ${ }^{Q} \mathrm{Q}_{\mathrm{K}_{\mathrm{a}}}(\mathrm{J})$ are presented for the $\mathrm{K}_{\mathrm{a}}=\mathrm{J}$ and $\mathrm{K}_{\mathrm{a}}=\mathrm{J}-1$ series by solid and open triangles, respectively. For both series, the d letter stands for $\mathrm{K}_{\mathrm{c}}=\mathrm{J}-\mathrm{K}_{\mathrm{a}}$ and $\mathrm{J}-\mathrm{K}_{\mathrm{a}}+1$ values.

Excellent agreement is obtained between the observed (lower) and the calculated (upper) spectrum.

Fig. 7. Portion of the R branch of the $v_{8}$ band of aziridine in the $1013 \mathrm{~cm}^{-1}$ spectral region. For this oblate molecule, the $\left[J^{\prime}, \mathrm{K}_{\mathrm{a}}^{\prime}=\mathrm{d}, \mathrm{K}_{\mathrm{c}}^{\prime}\right] \leftarrow\left[\mathrm{J}^{\prime}=\mathrm{J}^{\prime}-1, \mathrm{~K}_{\mathrm{a}}^{\prime \prime}=\mathrm{d}, \mathrm{K}_{\mathrm{c}}^{\prime \prime}\right]$ series of R transitions are grouped in stacks corresponding to equal values of $\mathrm{s}^{\prime}=\left(2 \mathrm{~J}^{\prime}-\mathrm{K}^{\prime}{ }_{\mathrm{c}}\right)$. Examples of such stacks are given for $\mathrm{s}=18,19$ and 20 , and the assignments are for the upper level J ' values (d stands for degenerate transitions with $K_{a}=J-K_{c}$ and $K_{a}=J-K_{c}+1$ ).
Excellent agreement is obtained between the observed (lower) and the calculated (upper) spectrum.

## Captions of the tables:

## Table 1:

Vibrational modes for aziridine.

## Caption:

a: Harmonic frequencies calculated at the B3LYP/6-311+G(3df,2pd) level of theory, see text.
b: $\operatorname{CCSD}(\mathrm{T}) / \mathrm{cc}-\mathrm{pVTZ}$ for the harmonic part and MP2/cc-pVTZ for the anharmonic correction.
c: Band intensity in $\mathrm{km} / \mathrm{mol}$, calculated with the double harmonic approximation at the $\operatorname{CCSD}(\mathrm{T}) / \mathrm{cc}-\mathrm{pVTZ}$ level of theory.
d: Ref. [6].
e: Ref. [7].
f: High resolution study (this work).
g: For these bands, only the band center could be determined (this work).
h : This band is a dark band.

## Table 2:

Vibration rotation interaction constants $\alpha_{\mathrm{i}}^{\mathrm{X}}(\mathrm{X}=\mathrm{A}, \mathrm{B}$ and C$)$. Components on the $(\beta=\mathrm{a}, \mathrm{b}$ or c) molecular axes of the first order derivatives, $\left(\frac{\partial \mu_{\beta}}{\partial q_{i}}\right)_{0}$ of the dipole moment operator.

## Caption:

$\mathrm{i}(\mathrm{i}=1,18)$ are the eighteen molecular vibrational modes (see Table 1). $\alpha_{\mathrm{i}}^{\mathrm{X}}$ and $\left(\frac{\partial \mu_{\beta}}{\partial q_{i}}\right)_{0}$ are expressed in MHz and in atomics units $\left(\mathrm{au} /\left(\mathrm{u}^{1 / 2} . \AA\right)\right)$, respectively. One has, $1 \mathrm{au}=2.54174691$ Debye $=8.47835281 .10^{-30} \mathrm{C} . \mathrm{m}, 1 \mathrm{u}=1.660538782(83) \times 10^{-27} \mathrm{~kg}$, and $1 \AA=10^{-10} \mathrm{~m}$.

## Table 3:

Watson's type Hamiltonian (I $\mathrm{I}^{\mathrm{r}}$ representation)

## Table 4:

Vibrational energies, and rotational and centrifugal distortion constants for the ground state and the $8^{1}, 10^{1}$ and $17^{1}$ vibrational states of aziridine.

## Caption:

The vibrational energies are in $\mathrm{cm}^{-1}$, and all other parameters are in $\mathrm{MHz}, \mathrm{KHz}, \mathrm{Hz}$ or mHz . The quoted errors are one standard deviation.
(a) Ref. [3];
(b) fixed at the ground state value [3].

## Table 5:

Results of the analyses of the $v_{10}, v_{17}$ and $v_{8}$ bands.
Statistical analysis of the energy levels calculation.

## Table 6:

Experimental and ab initio values for the $\alpha_{i}^{X}(X=A, B$ or $C)$ vibration rotation interaction constants (in MHz)

## Table 1

| Band centers of aziridine (in $\mathrm{cm}^{-1}$ ) |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Ab initio |  |  | Experimental |  |  |
|  |  | Sym. | B3LYP ${ }^{\text {a }}$ | $\begin{aligned} & \text { CCSD(T)/ } \\ & \text { cc-pVTZ } \end{aligned}$ | Intensity ${ }^{\text {c }}$ | d | e | This work |
| 1 | NH stretch | $A^{\prime}$ | 3514.1 | 3527.4 | 0.67 | 3338 | 3346 | $3337.4{ }^{\text {f }}$ |
| 2 | $\mathrm{CH}_{2}$ a-stretch | $\mathrm{A}^{\prime}$ | 3194.2 | 3231.2 | 25.48 | 3079 | 3079 | $3079.6{ }^{\text {f }}$ |
| 3 | $\mathrm{CH}_{2}$ s-stretch | $\mathrm{A}^{\prime}$ | 3108.1 | 3157.2 | 13.53 | 3015 | 3015 | $3002.8{ }^{\text {f }}$ |
| 4 | $\mathrm{CH}_{2}$ scissor | $A^{\prime}$ | 1526.7 | 1543.9 | 0.83 | 1481 | 1483 | $1482.9{ }^{\text {f }}$ |
| 5 | ring stretch | $\mathrm{A}^{\prime}$ | 1294.4 | 1315.0 | 7.53 | 1210 | 1210 | $1266.67{ }^{\text {f }}$ |
| 6 | $\mathrm{CH}_{2}$ twist | $\mathrm{A}^{\prime}$ | 1239.1 | 1253.3 | 13.96 | 1131 | 1096 | $1210.2{ }^{\text {f }}$ |
| 7 | $\mathrm{CH}_{2}$ wagging | $\mathrm{A}^{\prime}$ | 1116.6 | 1125.9 | 6.63 | 1089.5 | 1090 | $1089.4{ }^{\text {f }}$ |
| 8 | NH bending ring | $A^{\prime}$ | 1006.0 | 1018.6 | 8.58 | 997.5 | 998 | $997.1592{ }^{\text {g }}$ |
| 9 | deformation | $\mathrm{A}^{\prime}$ | 870.3 | 889.8 | 50.20 | 856 | 856 | $855.94{ }^{\text {f }}$ |
| 10 | $\mathrm{CH}_{2}$ rocking | $\mathrm{A}^{\prime}$ | 778.7 | 784.3 | 19.64 | 772.5 | 772 | $772.3571{ }^{\text {g }}$ |
| 11 | $\mathrm{CH}_{2}$ a-stretch | A" | 3180.9 | 3217.4 | 0.54 | 3079 | 3079 | $3083.73{ }^{\text {f }}$ |
| 12 | $\mathrm{CH}_{2}$ s-stretch | A" | 3103.1 | 3148.8 | 25.89 | 3015 | 3003 | $3015.6{ }^{\text {f }}$ |
| 13 | $\mathrm{CH}_{2}$ scissor | A" | 1499.8 | 1511.9 | 0.04 | 1462.5 | 1462 | $1462.2{ }^{\text {f }}$ |
| 14 | $\mathrm{CH}_{2}$ twist | A" | 1237.4 | 1276.8 | 8.37 | 1268 | 1268 | $1237{ }^{\text {f }}$ |
| 15 | NH bending $\mathrm{CH}_{2}$ | A" | 1154.8 | 1165.0 | 2.08 | 1237 | 1237 | $1130.4{ }^{\text {f }}$ |
| 16 | wagging ring | $A^{\prime \prime}$ | 1124.7 | 1123.4 | 2.49 | 1095 | 1131 | $1096.2{ }^{\text {f }}$ |
| 17 | deformation | $A^{\prime \prime}$ | 919.4 | 920.5 | 12.51 | 903.5 | 904 | $904.0429^{\text {g }}$ |
| 18 | $\mathrm{CH}_{2}$ rocking | $A^{\prime \prime}$ | 857.3 | 865.8 | 0.00 | 817 | (820) | Dark ${ }^{\text {h }}$ |

## Table 2

Vibration rotation interaction constants $\alpha_{\mathrm{i}}^{\mathrm{X}}(\mathrm{X}=\mathrm{A}, \mathrm{B}$ or C$)$., Components on the ( $\beta=\mathrm{a}, \mathrm{b}$ or c) molecular axes of the first order derivatives, $\left(\frac{\partial \mu_{\beta}}{\partial q_{i}}\right)_{0}$ of the dipole moment operator.

|  |  | $\alpha_{i}^{\mathrm{X}}$ |  |  | $\left(\frac{\partial \mu_{\beta}}{\partial q_{i}}\right)_{0}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Position ( $\mathrm{cm}^{-1}$ ) | $\mathrm{X}=\mathrm{A}$ | $\mathrm{X}=\mathrm{B}$ | $\mathrm{X}=\mathrm{C}$ | $\beta=\mathrm{a}$ | $\beta=\mathrm{b}$ | $\beta=\mathrm{c}$ |
| $\mathrm{i}=1$ | 3337.4 | 82.95 | 25.34 | 17.50 | 0 | -0.0261 | 0.0032 |
| 2 | 3079.6 | 12.41 | 37.00 | 12.98 | 0 | -0.0129 | 0.1612 |
| 3 | 3002.8 | 23.81 | 41.91 | 8.74 | 0 | -0.1142 | -0.0287 |
| 4 | 1482.9 | -7.16 | 45.88 | -28.71 | 0 | -0.0210 | 0.0201 |
| 5 | 1266.67 | -25.70 | -134.91 | -106.15 | 0 | 0.0777 | 0.0412 |
| 6 | 1210.2 | 37.62 | 195.78 | 444.15 | 0 | -0.1190 | -0.0124 |
| 7 | 1089.4 | 17.97 | -4.13 | 107.82 | 0 | 0.0824 | -0.0035 |
| 8 | 997.1592 | 58.06 | 13.57 | 94.92 | 0 | -0.0938 | -0.0035 |
| 9 | 855.94 | 18.44 | 47.29 | -554.17 | 0 | -0.2266 | -0.0116 |
| 10 | 772.3571 | -13.26 | 54.88 | 166.43 | 0 | -0.1419 | 0.0052 |
| 11 | 3083.73 | 16.69 | 30.24 | 12.33 | 0.0235 | 0 | 0 |
| 12 | 3015.6 | 23.63 | 39.41 | 7.87 | 0.1630 | 0 | 0 |
| 13 | 1462.2 | -22.80 | 25.98 | -41.72 | -0.0064 | 0 | 0 |
| 14 | 1237 | -19.73 | -62.60 | -297.39 | -0.0926 | 0 | 0 |
| 15 | 1130.4 | -50.98 | 69.80 | -127.77 | -0.0462 | 0 | 0 |
| 16 | 1096.2 | 48.33 | 17.46 | 37.30 | 0.0506 | 0 | 0 |
| 17 | 904.0429 | 98.38 | -15.44 | -177.68 | -0.1133 | 0 | 0 |
| 18 | dark | 214.10 | 10.17 | 756.74 | -0.0014 | 0 | 0 |

with: $\{\mathrm{A}, \mathrm{B}\}=\mathrm{AB}+\mathrm{BA}$ and $\mathrm{J}_{\mathrm{xy}}^{2}=\mathrm{J}_{\mathrm{x}}^{2}-\mathrm{J}_{\mathrm{y}}^{2}$

## Table 4

Vibrational energies, and rotational and centrifugal distortion constants for the ground state and the $10^{1}, 17^{1}$ and $8^{1}$ vibrational states of aziridine.

|  | Ground ${ }^{(a)}$ | $10^{1}$ | $17^{1}$ | $8^{1}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{E}_{\mathrm{V}}$ |  | 772.35710 (95) | 904.042857 (76) | 997.159192 (21) |
| A/MHz | 22736.172428 | 22745.759(319) | 22634.3242(431) | 22666.6856(119) |
| B/MHz | 21192.486318 | 21133.107(232) | 21202.3339(324) | 21177.41211(916) |
| C/MHz | 13383.159073 | 13187.563(204) | 13488.6240(149) | 13275.75195(454) |
| $\Delta_{\mathrm{J}} / \mathrm{KHz}$ | 18.9965530 | 16.336(269) | 23.6076(354) | 16.98074(955) |
| $\Delta_{\text {JK }} / \mathbf{K H z}$ | 9.25169 | 26.198(874) | -3.020(129) | 12.2790(305) |
| $\Delta_{\mathrm{K}} / \mathrm{KHz}$ | 20.05041 | 6.046(782) | 27.601(145) | 18.4084(406) |
| $\delta_{J} / \mathrm{KHz}$ | 5.880024 | 7.1253(739) | 3.8068(178) | 6.76170(429) |
| $\delta_{\mathrm{K}} / \mathrm{KHz}$ | 12.70180 | b | 16.8013(172) | 10.32504(773) |
| $\mathrm{H}_{\mathrm{J}} / \mathrm{Hz}$ | -0.007240 | -0.501(103) | 0.2294(183) | -0.07287(259) |
| $\mathrm{H}_{\text {JK }} / \mathrm{Hz}$ | 0.49776 | b | -1.2833(929) | b |
| $\mathrm{H}_{\mathrm{KJ}} / \mathrm{Hz}$ | -1.91427 | -7.49(120) | 1.803(164) | b |
| $\mathrm{H}_{\mathrm{K}} / \mathrm{Hz}$ | 1.51860 | 7.31(108) | -0.377(159) | 1.5646(241) |
| $\mathrm{h}_{\mathrm{J}} / \mathrm{Hz}$ | -0.003784 | b | -0.11888(921) | b |
| $\mathrm{h}_{\mathrm{JK}} / \mathrm{Hz}$ | 0.21084 | b | b | b |
| $\mathbf{h}_{\mathbf{K}} / \mathbf{H z}$ | -0.28571 | b | b | b |
| $\mathrm{L}_{\mathrm{JJK}} / \mathrm{mHz}$ | -0.002039 | b | b | b |
| $\mathrm{L}_{\mathrm{JK}} / \mathrm{mHz}$ | 0.00619 | b | b | b |
| $\mathbf{L}_{\text {KKJ }} / \mathrm{mHz}$ | -0.00837 | b | b | b |
| $\mathrm{L}_{\mathrm{K}} / \mathrm{mHz}$ | 0.00323 | b | b | b |
| $\mathrm{l}_{\mathrm{J}} / \mathrm{mHz}$ | -0.0000531 | b | b | b |
| $\mathrm{l}_{\mathrm{JK}} / \mathrm{mHz}$ | -0.001007 | b | b | b |
| $\mathbf{l}_{\mathbf{K J}} / \mathbf{m H z}$ | 0.004547 | b | b | b |
| $\mathbf{l}_{\mathbf{K}} / \mathbf{m H z}$ | -0.006888 | b | b | b |

## Table 5

Some details about the observed energy levels

| Band | $\mathbf{v}_{\mathbf{1 0}}$ | $\mathbf{v}_{\mathbf{1 7}}$ | $\mathbf{v}_{\mathbf{8}}$ |
| :---: | :---: | :---: | :---: |
| Number of lines | 2497 | 2875 | 1959 |
| Vibrational state : | $18^{1}$ | $7^{1}$ | $16^{1}$ |
| $\mathrm{~J}_{\mathrm{Max}}=$ | 47 | 47 | 45 |
| $\mathrm{~K}_{\mathrm{a}}$ | $\mathrm{K}_{\mathrm{a}} \leq 40$ | $\mathrm{~K}_{\mathrm{a}} \leq 30$ | $\mathrm{~K}_{\mathrm{a}} \leq 34$ |
| Number of levels | 753 | 1290 | 811 |

Statistical analysis of the energy levels calculation:

| Vibrational states | $\mathbf{1 0}^{\mathbf{1}}$ | $\mathbf{1 7}^{\mathbf{1}}$ | $\mathbf{8}^{\mathbf{1}}$ |
| :---: | :---: | :---: | :---: |
| Number of levels: | 753 | 1290 | 811 |
| Number of levels considered in the least squares fit: | 731 | 1290 | 811 |
| $0 \leq \delta<0.5 \times 10^{-3} \mathrm{~cm}^{-1}$ | $52.94 \%$ | $90.39 \%$ | $96.42 \%$ |
| $0.5 \times 10^{-3} \leq \delta<1 \times 10^{-3} \mathrm{~cm}^{-1}$ | $18.06 \%$ | $6.20 \%$ | $3.08 \%$ |
| $1 \times 10^{-3} \leq \delta<2 \times 10^{-3} \mathrm{~cm}^{-1}$ | $17.51 \%$ | $2.95 \%$ | $0.49 \%$ |
| Standard deviation $\left(10^{-3} \mathrm{~cm}^{-1}\right):$ | 41.47 | 4.15 | 1.29 |

$$
\delta=\left|\mathrm{E}_{\mathrm{obs}}-\mathrm{E}_{\text {calc }}\right| \text { in } 10^{-3} \mathrm{~cm}^{-1}
$$

## Table 6

Experimental and ab initio values for the $\alpha_{i}^{X}(X=A, B$ or $C)$ vibration rotation interaction constants (in MHz)

|  | $\mathbf{1 0}^{\mathbf{1}}$ |  | $\mathbf{1 7}^{\mathbf{1}}$ |  | $\mathbf{8}^{\mathbf{1}}$ |  |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: |
| $\alpha_{i}^{\mathrm{X}}$ | Exp | Ab Initio | Exp | Ab Initio | Exp | Ab Initio |
| $\alpha_{i}^{\mathrm{A}}$ |  |  |  |  |  |  |
| $\alpha_{i}^{\text {B }}$ | -9.59 | -13.26 | 101.85 | 98.38 | 69.49 | 58.06 |
| $\alpha_{i}^{\text {C }}$ | 59.38 | 54.88 | -9.85 | -15.44 | 15.07 | 13.57 |
|  | 195.60 | 166.43 | -105.46 | -177.68 | 107.41 | 94.92 |

Fig. 1




Fig. 5




