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**New vibrational assignments for the  $\nu_1$  to  $\nu_{17}$  vibrational modes of aziridine and first analysis of the high resolution infrared spectrum of aziridine between 720  $\text{cm}^{-1}$  and 1050  $\text{cm}^{-1}$**

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**New vibrational assignments for the  $\nu_1$  to  $\nu_{17}$  vibrational modes of aziridine and first analysis of the high resolution infrared spectrum of aziridine between  $720\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$**

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New vibrational assignments for the  $\nu_1$  to  $\nu_{17}$  vibrational modes of aziridine and first analysis of the high resolution infrared spectrum of aziridine between  $720\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$

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**Paper submitted to Molecular Physics in the honor of Pr Gianfranco Dilonardo, for his many contributions for Science**

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### Abstract

Fourier transform spectra of aziridine ( $C_2H_4NH$ ) were recorded at high resolution ( $0.002$  or  $0.003\text{ cm}^{-1}$ ) in the  $600\text{--}1750$  and  $1750\text{--}4000\text{ cm}^{-1}$  regions, using a Bruker IFS125HR (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  $\nu_1$  to  $\nu_{17}$  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  $772.3571\text{ cm}^{-1}$  ( $\nu_{10}$ ,  $CH_2$  rock) and  $997.1592\text{ cm}^{-1}$  ( $\nu_8$ , NH bend) and for an A-type band located at  $904.0429\text{ cm}^{-1}$  ( $\nu_{17}$ , ring deform). We noticed that the  $\nu_{10}$  band is weakly perturbed, presumably because the  $\nu_{10} = 1$  rotational levels are coupled with those of the  $\nu_{18} = 1$  dark band located around  $817\text{ cm}^{-1}$  through B-type and C-type Coriolis resonances.

## 1. Introduction

Aziridine,  $c\text{-C}_2\text{H}_4\text{NH}$ , 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  $^{15}\text{N}$  isotopologues [7].

First let us mention that, according to [6, 7], no fundamental bands exist below  $600\text{ cm}^{-1}$  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  $654\text{ cm}^{-1}$  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  $\nu_8$ ,  $\nu_{10}$  and  $\nu_{17}$  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  $\nu_1$  to  $\nu_{17}$  bands were performed as described in Section 4. For the  $\nu_8$ ,  $\nu_{10}$  and  $\nu_{17}$  bands, a detailed rotational assignment could be performed (section 5).

## 2. Experimental details:

$C_2H_4NH$  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 g, 0.5 mol), 90 ml of water and sodium hydroxide (60 g, 1.5 mol) were heated at  $50^\circ C$  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  $70^\circ C$  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 ( $2 \times 2.45$  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  $C_2H_4NH$  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  $C_2H_4NH$  used in this study were recorded at high resolution in the 600-1750 and 1750-4000  $cm^{-1}$  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

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3 recorded with an aperture diameter of 1.15mm, 40kHz scanner frequency, and a maximum  
4 optical path difference ( $d_{\text{MOPD}}$ ) of 450 or 300 cm. According to the Bruker definition  
5 (Resolution =  $0.9/d_{\text{MOPD}}$ ) this corresponds to a resolution of  $0.002 \text{ cm}^{-1}$  or  $0.003 \text{ cm}^{-1}$ . The  
6 spectra were recorded at a stabilized room temperature of  $22^\circ\text{C}$ . Both spectra were ratioed  
7 against the empty cell, single-channel background spectrum which was taken at a resolution  
8 of  $0.512 \text{ cm}^{-1}$ , in order to ensure the best possible signal-to-noise in the ratioed spectra. The  
9 spectra were the result of the co-addition of 570 interferograms. For the Fourier transform a  
10 Mertz-phase correction,  $0.5 \text{ cm}^{-1}$  phase resolution and boxcar apodization function were  
11 applied to the averaged interferograms. The spectra were calibrated using residual  $\text{CO}_2$  and  
12  $\text{H}_2\text{O}$  lines observed in the spectra, with their wavenumbers taken respectively from  
13 HITRAN08 [10] resulting in an accuracy of  $0.0002 \text{ cm}^{-1}$  (RMS) for well isolated lines.  
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### 25 **3. Ab initio computational details**

26 The harmonic force field of aziridine was evaluated analytically at the optimized  
27 geometry with second-order Møller–Plesset perturbation theory (MP2) [11] together with the  
28 correlation-consistent polarized valence *triple* zeta basis sets cc-pVTZ [12]. The coupled  
29 cluster method with single and double excitations [13] and a perturbative treatment of  
30 connected triples [14] [CCSD(T)] with the cc-pVTZ basis set was also used. The Kohn–Sham  
31 density functional theory [15] using Becke’s three-parameter hybrid exchange functional [16]  
32 and the Lee–Yang–Parr correlation functional [17], together denoted as B3LYP was also used  
33 with the split-valence basis set 6-311G, as implemented in Gaussian03 (G03) [18], including  
34 appropriate polarization functions. It is indeed well established that multiplying the B3LYP  
35 harmonic frequencies by a scaling factor close to one (0.96-0.98) permits to obtain a rather  
36 accurate estimate of the fundamental frequencies [19].  
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46 In order to estimate the vibrational anharmonicity constants, the rotation-vibration  
47 interaction constants, and the Fermi interaction constants, the cubic ( $\phi_{ijk}$ ) and semi-diagonal  
48 quartic ( $\phi_{ijkk}$ ) normal coordinate force constants were determined at the same reference  
49 structure with the use of a finite difference procedure involving displacements along reduced  
50 normal coordinates (with step size  $\Delta q = 0.03$ ) and the calculation of analytic Cartesian second  
51 derivatives at these displaced geometries [20, 21] using the MP2/cc-pVTZ method. The  
52 evaluation of anharmonic spectroscopic constants was based on second-order rovibrational  
53 perturbation theory [22].  
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3 The CCSD(T) computations were performed with the CFOUR [23] electronic  
4 structure program package, while the lower-level B3LYP and MP2 computations utilized the  
5 G03 program [18].  
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#### 10 **4 Vibrational assignments of the first seventeen ( $\nu_1$ to $\nu_{17}$ ) fundamental bands of** 11 **aziridine and rotational analysis of the $\nu_{10}$ , $\nu_{17}$ and $\nu_8$ bands :** 12 13

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17 The aziridine structure [24, 25] is illustrated on Fig. 1. This non-planar  $C_s$  -type molecule  
18 possesses eighteen non-degenerate modes of vibration which are listed in Table 1. Of these,  
19 ten modes ( $\nu_1$  to  $\nu_{10}$ ) are of  $A'$  symmetry, while  $\nu_{11}$  to  $\nu_{18}$  are of  $A''$  symmetry. According to  
20 the selection rules for an electric dipole moment transition, infrared fundamental bands  
21 corresponding to an  $A''$  (respectively  $A'$ ) vibrational upper state are A-type bands  
22 (respectively hybrid-type bands, with both B- and C-type transitions). The A-type, B-type and  
23 C-type transitions correspond to ( $\Delta K_a = \text{even}, \Delta K_c = \text{odd}$ ), ( $\Delta K_a = \text{odd}, \Delta K_c = \text{odd}$ ) and ( $\Delta K_a =$   
24  $\text{odd}, \Delta K_c = \text{even}$ ) rotational selection rules, respectively. Finally, transitions with ( $\Delta K_a =$   
25  $\text{even}, \Delta K_c = \text{even}$ ) are forbidden in the infrared. In addition to these symmetry considerations,  
26 the observed line intensity pattern for each fundamental band is determined by the values of  
27 the components of the corresponding transition moment operators on the a-axis (for  $A' \leftrightarrow A''$   
28 vibrational transitions), or on the b- and c- inertia axes (for  $A' \leftrightarrow A'$  or  $A'' \leftrightarrow A''$  vibrational  
29 transitions).  
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41 The ab initio calculations described in paragraph 3 were able to predict the band  
42 positions and intensities for aziridine fundamental bands. From these predictions, which are  
43 quoted in Table 1, it was easy to assign unambiguously the strong and well isolated  
44 fundamental bands in the observed experimental spectrum. Accordingly the positions  
45 measured in this work for the  $\nu_2$ ,  $\nu_8$ ,  $\nu_9$ ,  $\nu_{11}$  and  $\nu_{17}$  bands differ only marginally from those  
46 given previously in the literature [6, 7].  
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52 On the other hand, for medium intensity bands, such analysis is more difficult. In this  
53 case reliable and unambiguous vibrational assignments could be achieved only by performing  
54 detailed comparisons between theoretically-modeled and observed spectra.  
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57 To model the absorption for a given  $\nu_i$  fundamental band (with  $i = 1$  to 18), an  
58 approximate list of line positions and intensities was generated using the theoretical methods  
59 which are described in the next paragraph. The parameters necessary for these computations,  
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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  $\beta = a, b$  or  $c$  and  $q_i$  is the vibrational quantum coordinate associated to  $\nu_i$ ) collected in Table 2 are those deduced from the ab initio calculations. More explicitly, for the computation of the  $\nu_i = 1$  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  $\alpha_i^X$  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  $\left|\frac{\left(\frac{\partial\mu_b}{\partial q_i}\right)_0}{\left(\frac{\partial\mu_c}{\partial q_i}\right)_0}\right|^2$ .

Fig. 2 gives an overview of the aziridine spectrum in the  $720$  to  $1050\text{ cm}^{-1}$  spectral range. As expected from symmetry consideration, the  $\nu_{17}$  band at  $904\text{ cm}^{-1}$  exhibits a narrow A-type Q structure. On the other hand, the  $\nu_{10}$ ,  $\nu_9$  and  $\nu_8$  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  $1266.67\text{ cm}^{-1}$  is the hybrid B- and C-type  $\nu_5$  band, with a strong C-type character, while in Refs. [6, 7] the Q structure near  $1268\text{ cm}^{-1}$  was erroneously identified as the A-type  $\nu_{14}$  band. On the other hand the  $\nu_{14}$  band is presently located at  $1237\text{ cm}^{-1}$ .

Fig. 4 shows a detailed view of the  $3070$ - $3090\text{ cm}^{-1}$  spectral region. It is clear that the  $\nu_2$  band at  $3079.6\text{ cm}^{-1}$  is a C-type band which is significantly stronger than the A-type  $\nu_{11}$  band at  $3083.73\text{ cm}^{-1}$ . In Refs. [6, 7] both bands were assigned at  $3079\text{ cm}^{-1}$ .

Finally we were unable to identify the  $\nu_{18}$  band ( $\text{CH}_2$  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  $817\text{ cm}^{-1}$  is in fact completely blended (see Fig. 2) under the stronger  $\nu_{10}$  and  $\nu_9$  bands.

During this work it was also possible to perform a detailed rotational analysis of the  $\nu_{10}$ ,  $\nu_{17}$  and  $\nu_8$  bands located at  $773\text{ cm}^{-1}$ ,  $904\text{ cm}^{-1}$  and  $998\text{ cm}^{-1}$ .

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  $I^r$  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  $III^r$  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  $J^6$  and  $J^8$ , 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  $J^4$  ( $\Delta$  terms), and the preference for a (S,  $III^r$ ) combination rather than (A,  $I^r$ ) is not relevant for this infrared study.

Table 3 gives the (A,  $I^r$ ) 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:

$$X_i = X_0 - \alpha_i^X \quad (\text{with } X = A, B \text{ and } C) \quad \text{Eq. (1)}$$

In this expression, the  $X_0$  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  $\nu_{10}$ ,  $\nu_8$  and  $\nu_{17}$  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  $\nu_{10}$ ,  $\nu_8$  and  $\nu_{17}$  bands were completely assigned.

No noticeable perturbations were noticed during the analysis of the  $\nu_8$  and  $\nu_{17}$  bands. However, at a given level, it appeared that transitions of the  $\nu_{10}$  band involving  $K'_c \approx 20$  and  $K'_c \approx 8$  rotational quantum numbers in the upper levels are perturbed. It is presumed that the  $18^1$  dark state, located near  $817 \text{ cm}^{-1}$  is involved in the perturbations observed for the  $\nu_{10}$  band, since the ab initio calculations predict rather significant C-type Coriolis resonances coupling the  $10^1 \leftrightarrow 18^1$  energy levels (with  $\zeta_{10,18}^B = -0.025$  and  $\zeta_{10,18}^C = -0.490$  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  $\nu_{10}$ ,  $\nu_{17}$ , and  $\nu_8$  bands are given in Figs. 5, 6 and 7, respectively.

The same procedure was tentatively applied for the B-type  $\nu_9$  band at  $855.94 \text{ cm}^{-1}$ . 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  $\zeta_{9,18}^B = -0.113$  and  $\zeta_{9,18}^C = -0.800$  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  $\nu_{18} = 1$  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

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3 are observed. This is also the case for the  $17^1$  state. Although no noticeable perturbation could  
4 be observed during the assignment of the  $\nu_{17}$  band, the ab initio calculations predict that B and  
5 C-type Coriolis resonances are coupling together the  $17^1 \leftrightarrow 8^1$  energy levels (with  
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9  $\zeta_{17,8}^B = -0.1131$  and  $\zeta_{17,18}^C = -0.7997$  for the B- and C- type Coriolis parameters,  
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11 respectively).

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15 The results of the energy levels calculations proved to be rather satisfactory, as can be  
16 seen from the standard deviation and statistical analysis given in the lower part of Table 5.

17 It is interesting to compare the observed and calculated spectra.

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20 Figure 2 shows the overview of the observed and calculated spectra in the  $720\text{ cm}^{-1}$  to  
21  $1050\text{ cm}^{-1}$  region. The perturbed  $\nu_9$  band, whose analysis is in progress, is not plotted on the  
22 calculated spectrum.  
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26 Figures 5 and 6 show portions of the Q branch of the  $\nu_{10}$  and  $\nu_{17}$  bands, respectively. Fig. 7  
27 gives a portion of the R branch of the  $\nu_8$  band. In each case the agreement between the  
28 observed and calculated spectra is excellent.  
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32 Finally the values of the experimental  $\alpha_i^X$  vibration rotation interaction constants are  
33 compared in Table 6 to these ab initio values, showing a reasonable agreement for the three  
34 bands under study.  
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## 50 **8. Conclusion**

51 A new vibrational assignment was performed for the fundamental bands of aziridine, based on  
52 ab initio calculations and on Fourier transform spectra recorded at high resolution. In addition  
53 the first analysis of the  $\nu_{10}$ ,  $\nu_8$  and  $\nu_{17}$  fundamental bands of aziridine was performed. No  
54 noticeable perturbations were observed during the analyses of  $\nu_8$  and  $\nu_{17}$  bands, while the  $\nu_{10}$   
55 band appears to be weakly perturbed. The energy levels resulting from the analyses were used  
56 to derive accurate vibrational energies, and rotational and centrifugal distortion constants for  
57 the  $8^1$ ,  $10^1$  and  $17^1$  vibrational states.  
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**Captions of the figures:**

**Fig. 1.** Structure of the aziridine molecule [24, 25].

The a, b and c are the inertial axes and (bc) is the symmetry plane for this non planar  $C_s$ -type molecule. The  $\Gamma$  representation ( $x = b$ ,  $y = c$  and  $z = a$ ) was adopted for all calculations.

**Fig. 2.** Overview of the aziridine spectrum in the 720-1050  $\text{cm}^{-1}$  region ( $\nu_{10}$ ,  $\nu_9$ ,  $\nu_{17}$  and  $\nu_8$  bands).

The narrow Q branch structure at 904  $\text{cm}^{-1}$  indicates an A-type structure for the  $\nu_{17}$  band. The  $\nu_{10}$ ,  $\nu_9$  and  $\nu_8$  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  $\text{cm}^{-1}$  and an optical path length of 19.249 m, at a  $\text{C}_2\text{H}_4\text{NH}$  pressure of 0.0341 hPa and a stabilized room temperature of 295.2 K. Upper trace: the synthetic spectrum, calculated for the  $\nu_{10}$ ,  $\nu_{17}$  and  $\nu_8$  bands is shifted vertically for a clear comparison. The  $\nu_9$  perturbed band is not considered in the present analysis (see text).

**Fig. 3.** Overview of the  $\nu_5$  band of aziridine in the 1267  $\text{cm}^{-1}$  spectral region.

Medium trace: observed spectrum (see the caption of Fig. 2). Upper trace: low resolution model for the  $\nu_5$  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  $\text{cm}^{-1}$  spectral region.

Lower trace: observed spectrum recorded with a resolution of 0.003  $\text{cm}^{-1}$  and an optical path length of 19.249 m, at a  $\text{C}_2\text{H}_4\text{NH}$  pressure of 0.1188 hPa and a stabilized room temperature of 295.2 K. Upper trace: calculated  $\nu_2$  C-type band and  $\nu_{11}$  A-type band at 3079.6 and 3083.73  $\text{cm}^{-1}$ , respectively.

**Fig. 5.** Portion of the Q branch of the  $\nu_{10}$  band of aziridine in the 763  $\text{cm}^{-1}$  spectral region.

The  $^{P,R}Q_{K_c}$  structure for  $K''_c = 13$  (solid triangles) is presented together with some additional assignments. The d letters stand for degenerate transitions with  $K_a = J - K_c$  and  $K_a = J - K_c + 1$ . Excellent agreement is obtained between the observed (lower) and the calculated (upper) spectrum.

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5 **Fig. 6.** Portion of the Q branch of the  $\nu_{17}$  band of aziridine in the  $903.5 \text{ cm}^{-1}$  spectral region.  
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7 Together with additional assignments, series of  ${}^Q Q_{K_a}(J)$  are presented for the  $K_a = J$  and  
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9  $K_a = J-1$  series by solid and open triangles, respectively. For both series, the d letter stands for  
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11  $K_c = J-K_a$  and  $J-K_a+1$  values.  
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13 Excellent agreement is obtained between the observed (lower) and the calculated (upper)  
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15 spectrum.  
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18 **Fig. 7.** Portion of the R branch of the  $\nu_8$  band of aziridine in the  $1013 \text{ cm}^{-1}$  spectral region.  
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20 For this oblate molecule, the  $[J', K'_a = d, K'_c] \leftarrow [J'' = J'-1, K''_a = d, K''_c]$  series of R  
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22 transitions are grouped in stacks corresponding to equal values of  $s' = (2J' - K'_c)$ . Examples of  
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24 such stacks are given for  $s = 18, 19$  and  $20$ , and the assignments are for the upper level  $J'$   
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26 values (d stands for degenerate transitions with  $K_a = J-K_c$  and  $K_a = J-K_c+1$ ).  
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28 Excellent agreement is obtained between the observed (lower) and the calculated (upper)  
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**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: CCSD(T)/cc-pVTZ for the harmonic part and MP2/cc-pVTZ for the anharmonic correction.  
 c: Band intensity in km/mol, calculated with the double harmonic approximation at the CCSD(T)/cc-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  $\alpha_i^X$  (X = A, B and C). Components on the ( $\beta = a, b$  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:

$i$  ( $i = 1, 18$ ) are the eighteen molecular vibrational modes (see Table 1).  $\alpha_i^X$  and  $\left(\frac{\partial \mu_\beta}{\partial q_i}\right)_0$  are expressed in MHz and in atomic units (au/(u<sup>1/2</sup> · Å)), respectively. One has, 1 au = 2.54174691 Debye = 8.47835281 · 10<sup>-30</sup> C.m, 1u = 1.660538782(83) × 10<sup>-27</sup> kg, and 1Å = 10<sup>-10</sup> m.

**Table 3:**

Watson's type Hamiltonian (I<sup>r</sup> representation)

**Table 4:**

Vibrational energies, and rotational and centrifugal distortion constants for the ground state and the 8<sup>1</sup>, 10<sup>1</sup> and 17<sup>1</sup> vibrational states of aziridine.

Caption :

The vibrational energies are in cm<sup>-1</sup>, and all other parameters are in MHz, KHz, Hz or mHz. The quoted errors are one standard deviation.

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3 (a) Ref. [3];  
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5 (b) fixed at the ground state value [3].  
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10 **Table 5:**

11 Results of the analyses of the  $\nu_{10}$ ,  $\nu_{17}$  and  $\nu_8$  bands.

12 Statistical analysis of the energy levels calculation.  
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17 **Table 6:**

18 Experimental and ab initio values for the  $\alpha_i^X$  ( $X = A, B$  or  $C$ ) vibration rotation interaction  
19 constants (in MHz)  
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**Table 1**Band centers of aziridine (in  $\text{cm}^{-1}$ )

			Ab initio			Experimental		
Sym.			B3LYP <sup>a</sup>	CCSD(T)/ cc-pVTZ <sup>b</sup>	Intensity <sup>c</sup>	d	e	This work
1	NH stretch	A'	3514.1	3527.4	0.67	3338	3346	3337.4 <sup>f</sup>
2	CH <sub>2</sub> a-stretch	A'	3194.2	3231.2	25.48	3079	3079	3079.6 <sup>f</sup>
3	CH <sub>2</sub> s-stretch	A'	3108.1	3157.2	13.53	3015	3015	3002.8 <sup>f</sup>
4	CH <sub>2</sub> scissor	A'	1526.7	1543.9	0.83	1481	1483	1482.9 <sup>f</sup>
5	ring stretch	A'	1294.4	1315.0	7.53	1210	1210	1266.67 <sup>f</sup>
6	CH <sub>2</sub> twist	A'	1239.1	1253.3	13.96	1131	1096	1210.2 <sup>f</sup>
7	CH <sub>2</sub> wagging	A'	1116.6	1125.9	6.63	1089.5	1090	1089.4 <sup>f</sup>
8	NH bending ring	A'	1006.0	1018.6	8.58	997.5	998	997.1592 <sup>g</sup>
9	deformation	A'	870.3	889.8	50.20	856	856	855.94 <sup>f</sup>
10	CH <sub>2</sub> rocking	A'	778.7	784.3	19.64	772.5	772	772.3571 <sup>g</sup>
11	CH <sub>2</sub> a-stretch	A''	3180.9	3217.4	0.54	3079	3079	3083.73 <sup>f</sup>
12	CH <sub>2</sub> s-stretch	A''	3103.1	3148.8	25.89	3015	3003	3015.6 <sup>f</sup>
13	CH <sub>2</sub> scissor	A''	1499.8	1511.9	0.04	1462.5	1462	1462.2 <sup>f</sup>
14	CH <sub>2</sub> twist	A''	1237.4	1276.8	8.37	1268	1268	1237 <sup>f</sup>
15	NH bending CH <sub>2</sub>	A''	1154.8	1165.0	2.08	1237	1237	1130.4 <sup>f</sup>
16	wagging ring	A''	1124.7	1123.4	2.49	1095	1131	1096.2 <sup>f</sup>
17	deformation	A''	919.4	920.5	12.51	903.5	904	904.0429 <sup>g</sup>
18	CH <sub>2</sub> rocking	A''	857.3	865.8	0.00	817	(820)	Dark <sup>h</sup>

**Table 2**

Vibration rotation interaction constants  $\alpha_i^X$  ( $X = A, B$  or  $C$ ). , Components on the ( $\beta = a, b$  or  $c$ ) molecular axes of the first order derivatives,  $\left(\frac{\partial \mu_\beta}{\partial q_i}\right)_0$  of the dipole moment operator.

		$\alpha_i^X$			$\left(\frac{\partial \mu_\beta}{\partial q_i}\right)_0$		
Position ( $\text{cm}^{-1}$ )		X = A	X = B	X = C	$\beta = a$	$\beta = b$	$\beta = c$
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

Table 3

Watson A-type rotational Hamiltonian written in the  $\Gamma^r$  representation.

$$\begin{aligned}
 H_W = & E_v + \left[ A_v - \frac{1}{2}(B_v + C_v) \right] J_z^2 + \frac{1}{2}(B_v + C_v) J^2 + \frac{1}{2}(B_v - C_v) J_{xy}^2 \\
 & - \Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 J^2 - \Delta_J^v (J^2)^2 - \delta_K^v \{J_z^2, J_{xy}^2\} - 2\delta_J^v J_{xy}^2 J^2 \\
 & + H_K^v J_z^6 + H_{KJ}^v J_z^4 J^2 + H_{JK}^v J_z^2 (J^2)^2 + H_J^v (J^2)^3 \\
 & + h_K^v \{J_z^4, J_{xy}^2\} + h_{KJ}^v \{J_z^2, J_{xy}^2\} J^2 + 2h_J^v J_{xy}^2 (J^2)^2 \\
 & + L_K^v J_z^8 + L_{KKJ}^v J_z^6 J^2 + L_{KJ}^v J_z^4 (J^2)^2 + L_{JJK}^v (J^2)^2 + L_J^v (J^2)^4 \\
 & + l_K^v \{J_z^6, J_{xy}^2\} + l_{KJ}^v \{J_z^4, J_{xy}^2\} J^2 + l_{JK}^v \{J_z^2, J_{xy}^2\} (J^2)^2 + 2l_J^v J_{xy}^2 (J^2)^3 \\
 & + P_K^v J_z^{10} + P_{KKKJ}^v J_z^8 J^2 + P_{KKJ}^v J_z^6 J^4 + \dots
 \end{aligned}$$

with:  $\{A, B\} = AB + BA$  and  $J_{xy}^2 = J_x^2 - J_y^2$

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 <sup>(a)</sup>	$10^1$	$17^1$	$8^1$
$E_v$		772.35710 (95)	904.042857 (76)	997.159192 (21)
$A/\text{MHz}$	22736.172428	22745.759(319)	22634.3242(431)	22666.6856(119)
$B/\text{MHz}$	21192.486318	21133.107(232)	21202.3339(324)	21177.41211(916)
$C/\text{MHz}$	13383.159073	13187.563(204)	13488.6240(149)	13275.75195(454)
$\Delta_J/\text{KHz}$	18.9965530	16.336(269)	23.6076(354)	16.98074(955)
$\Delta_{JK}/\text{KHz}$	9.25169	26.198(874)	-3.020(129)	12.2790(305)
$\Delta_K/\text{KHz}$	20.05041	6.046(782)	27.601(145)	18.4084(406)
$\delta_J/\text{KHz}$	5.880024	7.1253(739)	3.8068(178)	6.76170(429)
$\delta_K/\text{KHz}$	12.70180	b	16.8013(172)	10.32504(773)
$H_J/\text{Hz}$	-0.007240	-0.501(103)	0.2294(183)	-0.07287(259)
$H_{JK}/\text{Hz}$	0.49776	b	-1.2833(929)	b
$H_{KJ}/\text{Hz}$	-1.91427	-7.49(120)	1.803(164)	b
$H_K/\text{Hz}$	1.51860	7.31(108)	-0.377(159)	1.5646(241)
$h_J/\text{Hz}$	-0.003784	b	-0.11888(921)	b
$h_{JK}/\text{Hz}$	0.21084	b	b	b
$h_K/\text{Hz}$	-0.28571	b	b	b
$L_{JJK}/\text{mHz}$	-0.002039	b	b	b
$L_{JK}/\text{mHz}$	0.00619	b	b	b
$L_{KKJ}/\text{mHz}$	-0.00837	b	b	b
$L_K/\text{mHz}$	0.00323	b	b	b
$l_J/\text{mHz}$	-0.0000531	b	b	b
$l_{JK}/\text{mHz}$	-0.001007	b	b	b
$l_{KJ}/\text{mHz}$	0.004547	b	b	b
$l_K/\text{mHz}$	-0.006888	b	b	b



**Table 5**

Some details about the observed energy levels

Band	$\nu_{10}$	$\nu_{17}$	$\nu_8$
Number of lines	2497	2875	1959
Vibrational state :	$18^1$	$7^1$	$16^1$
$J_{\text{Max}} =$	47	47	45
$K_a$	$K_a \leq 40$	$K_a \leq 30$	$K_a \leq 34$
Number of levels	753	1290	811

Statistical analysis of the energy levels calculation:

Vibrational states	$10^1$	$17^1$	$8^1$
Number of levels:	753	1290	811
Number of levels considered in the least squares fit:	731	1290	811
$0 \leq \delta < 0.5 \times 10^{-3} \text{ cm}^{-1}$	52.94%	90.39%	96.42%
$0.5 \times 10^{-3} \leq \delta < 1 \times 10^{-3} \text{ cm}^{-1}$	18.06%	6.20%	3.08%
$1 \times 10^{-3} \leq \delta < 2 \times 10^{-3} \text{ cm}^{-1}$	17.51%	2.95%	0.49%
Standard deviation ( $10^{-3} \text{ cm}^{-1}$ ):	41.47	4.15	1.29

$$\delta = |E_{\text{obs}} - E_{\text{calc}}| \text{ in } 10^{-3} \text{ cm}^{-1}$$

Table 6

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

$\alpha_i^X$	$10^1$		$17^1$		$8^1$	
	Exp	Ab Initio	Exp	Ab Initio	Exp	Ab Initio
$\alpha_i^A$	-9.59	-13.26	101.85	98.38	69.49	58.06
$\alpha_i^B$	59.38	54.88	-9.85	-15.44	15.07	13.57
$\alpha_i^C$	195.60	166.43	-105.46	-177.68	107.41	94.92

Fig. 1

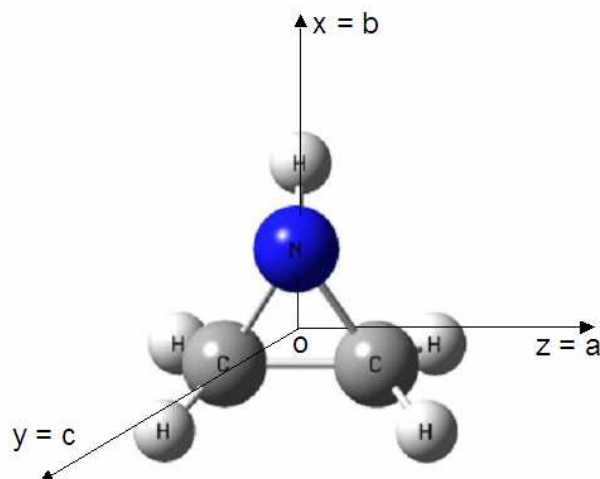
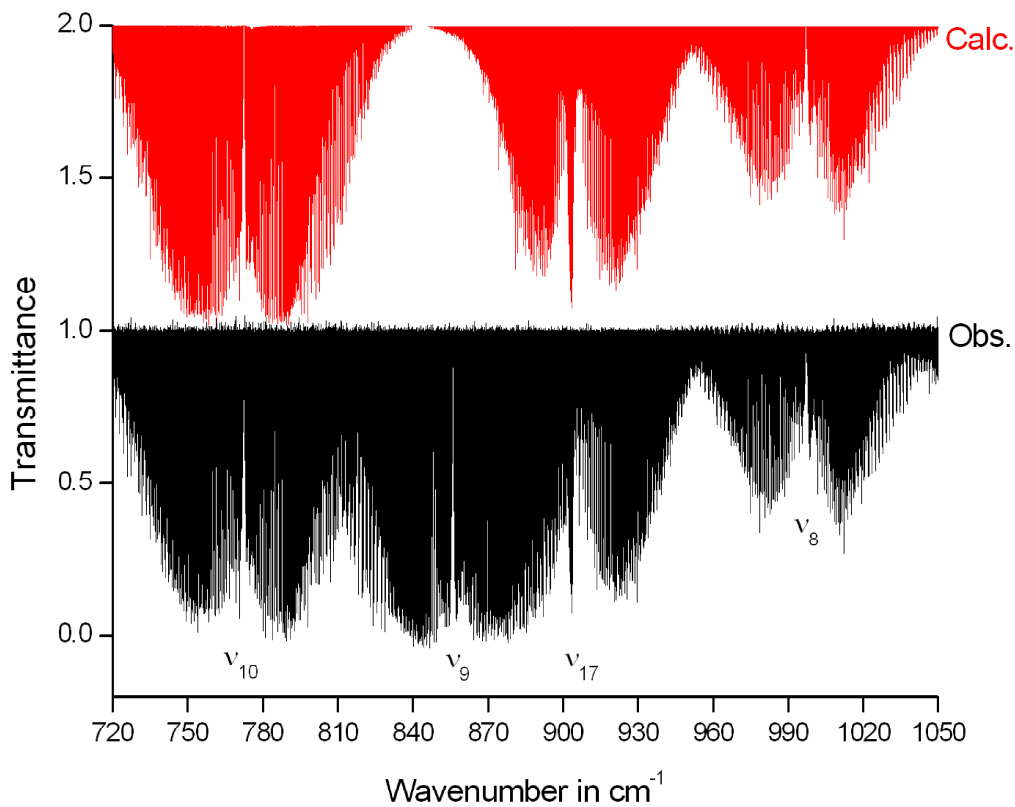


Fig.2



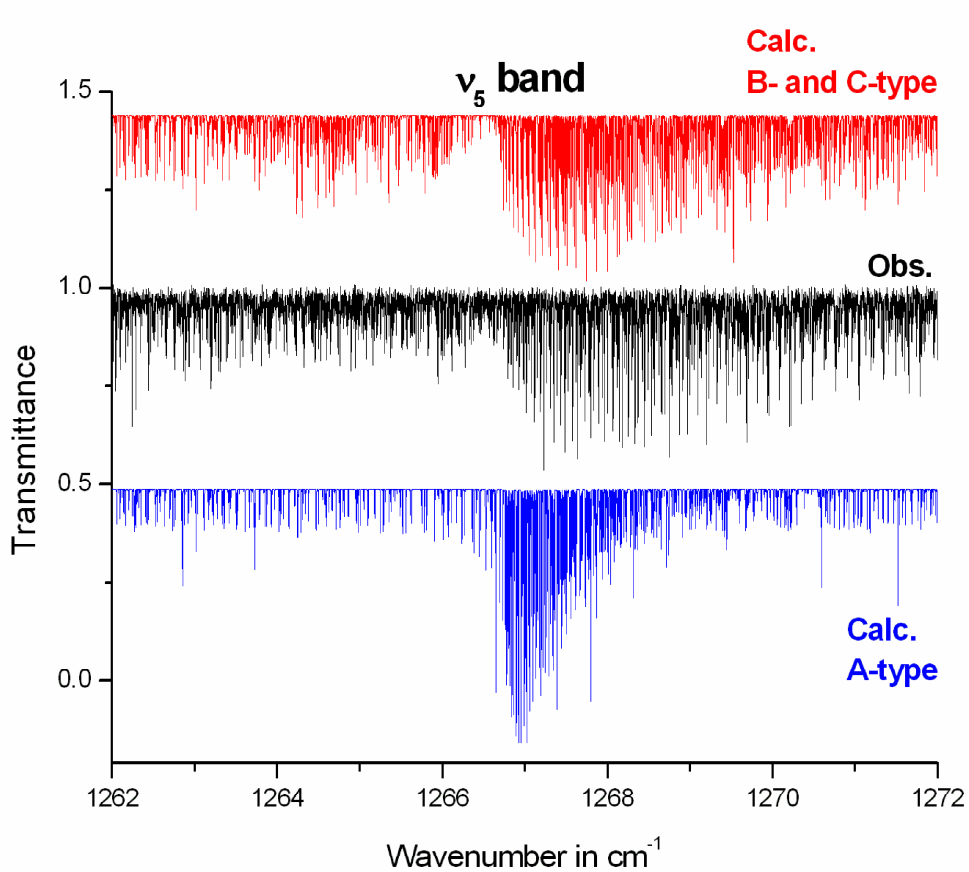
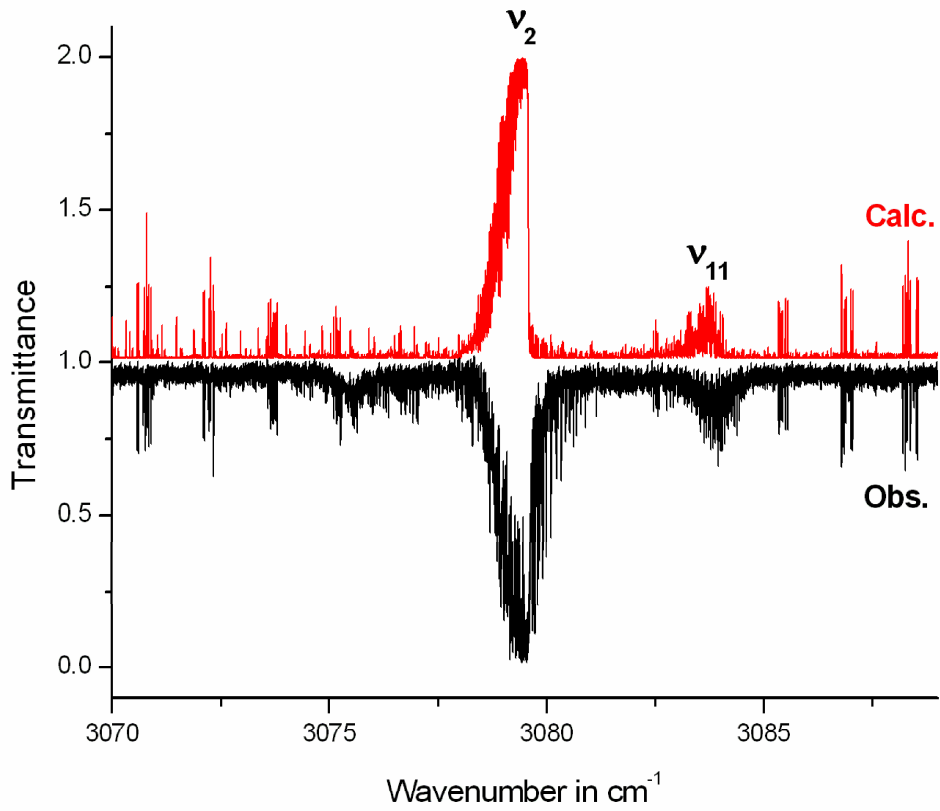
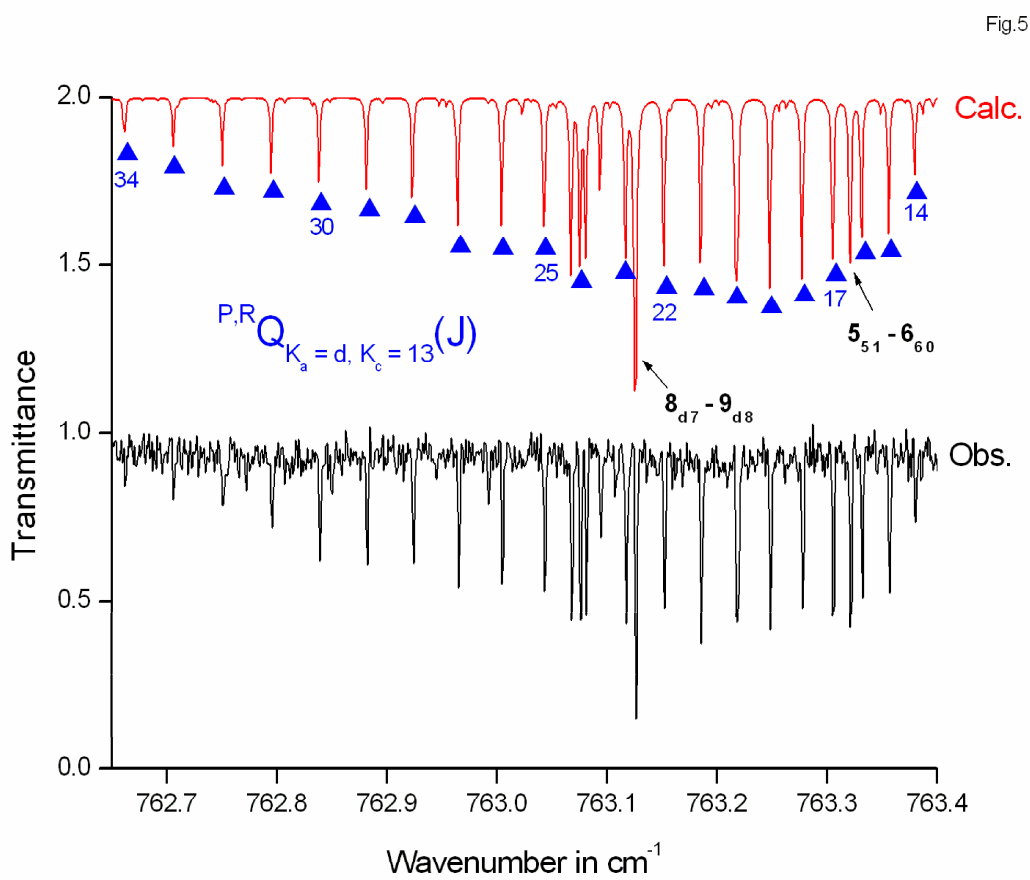


Fig.4



Review Only



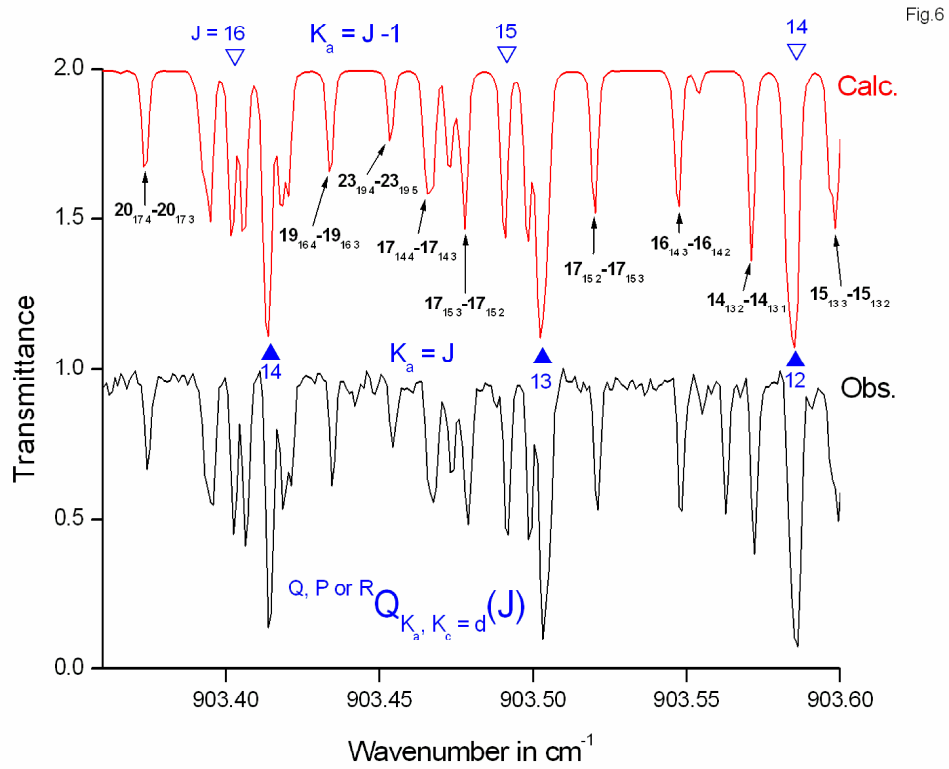


Fig.7

