CAVITY RING-DOWN SPECTROSCOPY OF THE $^{14}NH_2$ ISOTOPOMER RADICAL

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Abstract. We report the absorption spectroscopy of the $^{14}NH_2$ radical in its $\tilde{A}\ ^2A_1(0,9,0) \leftarrow \tilde{X}\ ^2B_1(0,0,0)$ vibronic band located around 16700 cm^{-1} by Cavity Ring-Down Spectroscopy technique. For $^{14}NH_2$ radical production, a discharge in a mixture of $^{14}NH_3$ in Argon has been provided. We have also been able to extract precise accurate positions and intensities of the most intense lines of the $^{14}NH_2$ radical.

Keywords: *Absorption spectroscopy, $^{14}NH_2$ radical, Cavity Ring-Down technique*.

I. INTRODUCTION

Cometary spectra are known to exhibit intense emission in all the visible range. Part of this intense emission is due to the $\tilde{A}\ ^2A_1(0,v_2,0) \leftarrow \tilde{X}\ ^2B_1(0,0,0)$ vibronic bands of the NH_2 radical which can be easily detected in comet. This radical containing an amine (-NH) functional group is produced in comets after photo dissociation by solar radiation of NH_3 molecules, contained in huge amounts in this particular objects.

The $^{14}NH_2$ radical is a prototype molecule exhibiting a strong Renner-Teller effect in its electronic ground state [1]. The doubly degenerated $^2\Pi$ split into two components, the strongly bent $\tilde{X}\ ^2B_1$ having a barrier to linearity equal to 11000 cm^{-1} and a slightly bent $\tilde{A}\ ^2A_1$ having a barrier of about 700 cm^{-1}. The transition between these two components gives rise to a long vibrational progression covering the near IR to UV range. All of this work has been initiated by Dressler & Ramsay [2] and Herzberg [3]. The bending mode has a characteristic spacing of about 1500 cm^{-1} in the ground state and about 625 cm^{-1} in the excited state. The HNH angle equals to about 105° in its electronic ground state, while the excited state behaves like a linear molecule. There are a number of studies which have been dedicated to theoretical as well as experimental comprehension of the complex Renner–Teller effect for $^{14}NH_2$ radical. The goal of this work is not to understand completely the very complicated spectroscopy of this molecule. It is just important to understand that these radical exhibits strong coupling between the two already presented electronic states and that is coupling will be different in the $^{15}NH_2$ isotopomer. Thus only a complete experimental measurement of the lines is needed to know their precise positions and intensity ratios, have already investigated, in the visible range, the spectroscopy of the $^{15}NH_2$ less abundant isotopomer but they don't give any table with precise positions of the lines of this radical and show only a non-precise linear correlation between the $^{14}NH_2$-$^{15}NH_2$ isotope shift against the wavenumber of the $^{14}NH_2$ lines. In this paper, we present the results of studying

absorption spectrum of the $^{14}NH_2$ radical, from 16678 to 16748 cm^{-1} corresponding to the region of the $\widetilde{A}\ ^2A_1(0,9,0) \leftarrow \widetilde{X}\ ^2B_1(0,0,0)$ rovibronic transition by Cavity Ring-Down Spectroscopy technique. The best conditions for $^{14}NH_2$ production, positions and intensities of the most intense lines of the $^{14}NH_2$ radical will be presented and discussed.

II. EXPERIMENT

The experimental set-up details are described in Figure 1. We used a pulsed XeCl (308 nm) excimer laser (Coherent, CompexPro, typical pulse energy of 300 mJ, pulse width of 15 ns, repetition rate 10 Hz) to pump a dye laser (Lambda Physik, LPD 3002), the latter operating with the following dyes (Exciton): RH 610C in ethanol for the range around 600 nm region. The dye laser pulse energy at the CRDS cavity entrance was about 1 mJ. One pairs of CRDS mirrors (Layertec GmbH, curvature radius R_C=1 m) were used, covering the region of interest: 585-605 nm, with reflection coefficients R not lower than 99.99 % respectively. The distance between mirrors was fixed at $L = 100$ cm to meet the stability condition for the cavity and the maximum distance between mirrors and plasma of the discharge. The highest ring-down time constant τ_0 reached for the empty cavity was about 34 µs (around 590 nm). In these conditions, the value of α_{min} is about 8.10^{-8} cm^{-1} for a single shot and for an average over 20 laser shots, we reached a value of α_{min} about 2.10^{-8} cm^{-1} and a figure of merit of $M \approx 10^{-7}\ cm^{-1}/\sqrt{Hz}$.
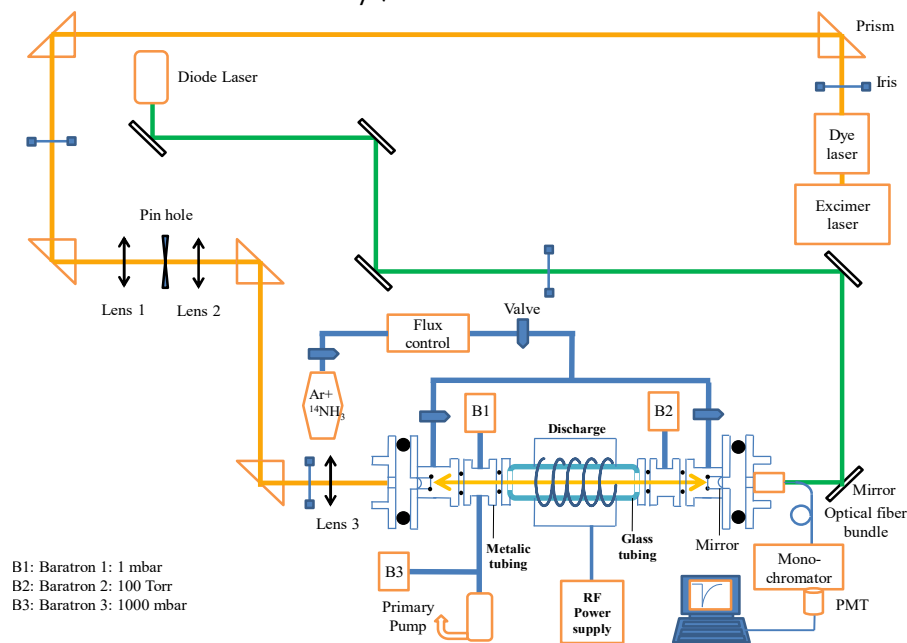

Figure 1. *Experimental set-up of CRDS coupled with Radio frequency discharge to produce $^{14}NH_2$ isotopomer radical*

III. RESULTS AND DISCUSSION

First work was devoted to find the best conditions allowing optimization of the production of $^{14}NH_2$ radical with a Radio Frequency 13.56 MHz discharge in a cell containing ammonia $^{14}NH_3$ as precursor in a rare gas mixture. The parameters we changed were concentration of NH$_3$ in rare gas (He or Ar), flux of the mixture, pressure in the cell

and power of discharge. We have also filled different bottle with several concentrations of NH_3 in Ar or He, ranging from 0.5 % to 5 %.

The best conditions reached for $^{14}NH_2$ production correspond to a concentration of 1% of $^{14}NH_3$ in Ar, a flux of Ar of 1 l/min, a power of discharge in the plasma of 50W and a pressure in the glass tube cell of 0.5 mbar.

Figure displays the spectrum of the $\widetilde{A}\ ^2A_1(0,9,0) \leftarrow \widetilde{X}\ ^2B_1(0,0,0)$ rovibronic transition of the $^{14}NH_2$ radical from 16678 to 16748 cm^{-1} (respectively 599.59 to 597.09 nm), measured with our CRDS technique. The laser step was fixed to 10^{-3} nm, giving a step of about 0.03 cm^{-1} around 16735 cm^{-1}. All the most intense lines appearing in the spectrum have been assigned in the light of the previous work of Ross *et al.*[4] to the $\widetilde{A}\ ^2A_1(0,9,0) \leftarrow \widetilde{X}\ ^2B_1(0,0,0)$ rovibronic transition of the $^{14}NH_2$ radical and has been marked with red bars (without taking account intensity) in the Figure 2. Several relatively intense lines could have been assigned to transitions between excited states in neutral Argon and has been marked by blue arrows. The 6 more intense not assigned lines (beyond $2x10^{-7}$ cm^{-1}) have been marked with a star.
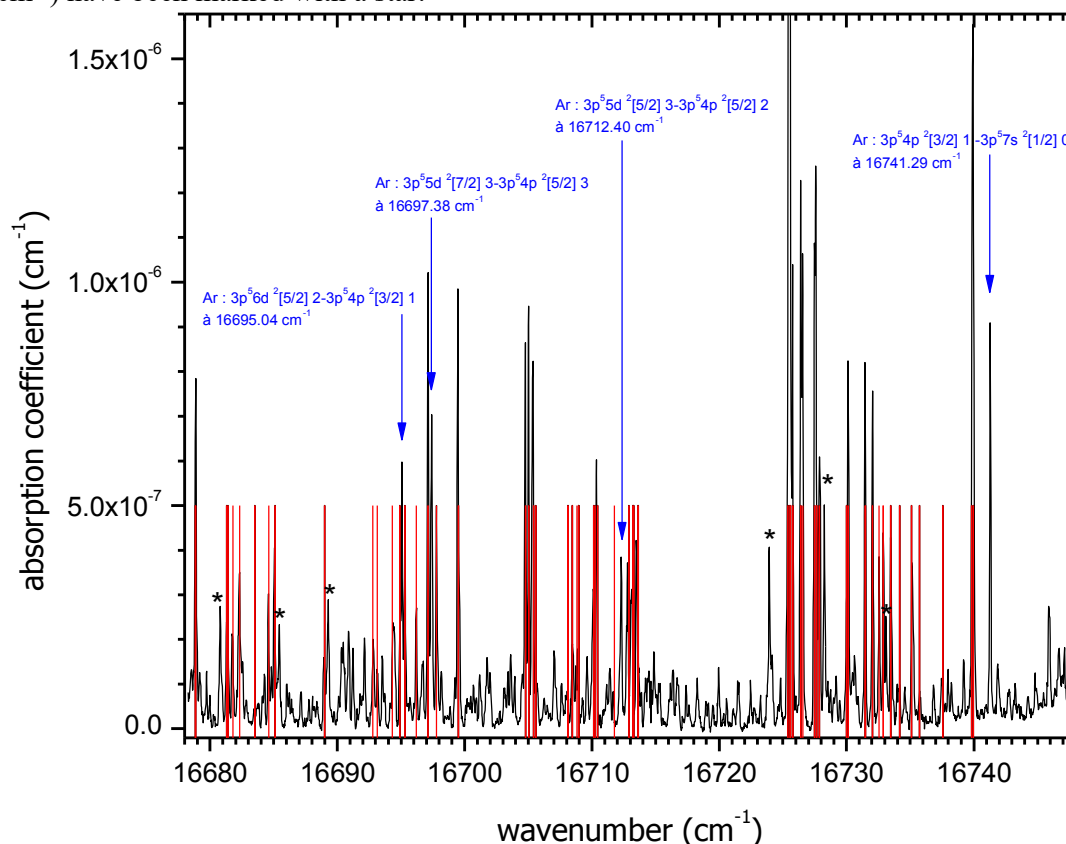

Figure 2. *Absorption spectrum of the $^{14}NH_2$ radical, from 16678 to 16748 cm^{-1}, corresponding to the region of the $\widetilde{A}\ ^2A_1(0,9,0) \leftarrow \widetilde{X}\ ^2B_1(0,0,0)$ rovibronic transition.*

In all these experiments, we have tried to minimize chemical reactions by decreasing the total pressure in the cell and the concentration of NH_3 precursor molecules. Despite all these precautions, we have not been able to suppress completely the production of N_2 molecules in the plasma, during the RF discharge, after complete dissociation of $^{14}NH_3$ and recombination after collisions. Indeed, in this wavelength range, almost all weaker lines

appearing in this spectrum have been assigned to rotational line Q_{ij} (J") and R_{ij} (J") of the $B\ ^3\Pi_g \leftarrow A\ ^3\Sigma_u^+\ (7\text{-}3)$ vibronic band of $^{14}N_2$.

The Figure shows a detail of the rovibronic transition of the $^{14}NH_2$ radical from 16720 to 16750 cm^{-1} (respectively 598.09 and 597.01 nm). The rotational line Q_{ij} (J") and R_{ij} (J") of the $B\ ^3\Pi_g \leftarrow A\ ^3\Sigma_u^+\ (7\text{-}3)$ vibronic band of $^{14}N_2$ have been marked with green bars (without taking account intensity). The lines marked with a star have not yet been assigned.
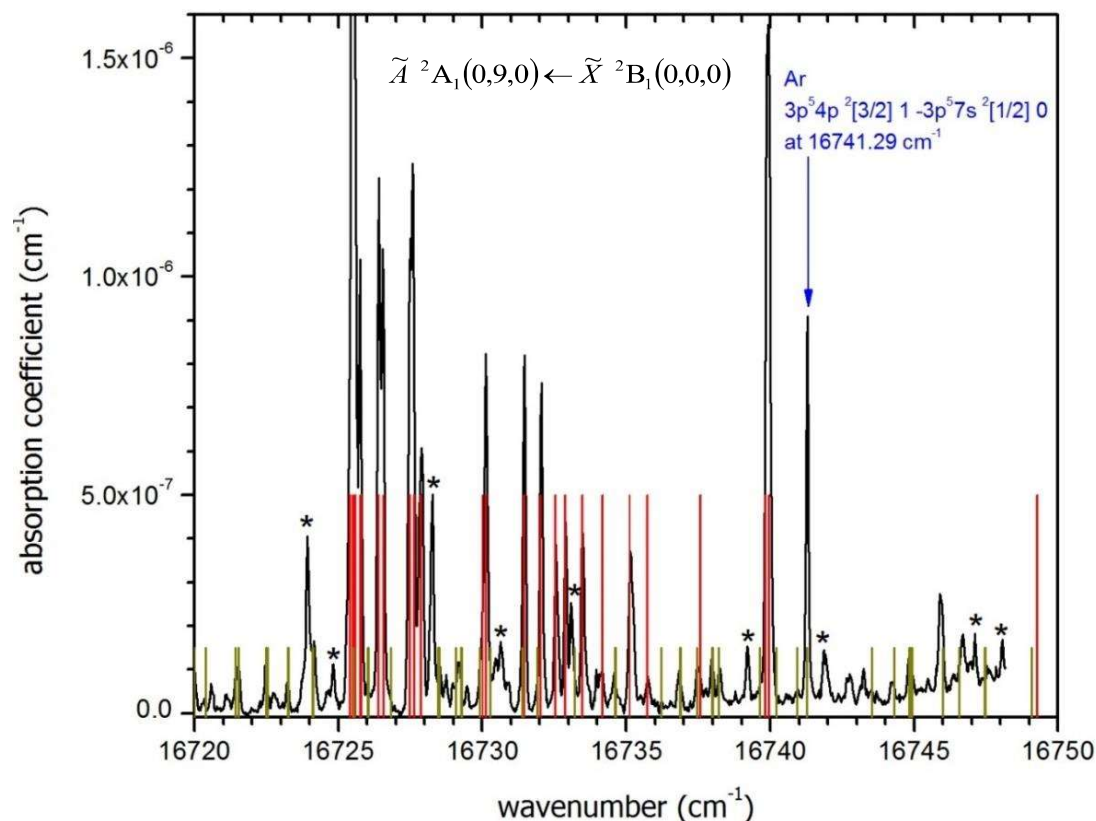

Figure 3. *The* $\widetilde{A}\ ^2A_1(0,9,0) \leftarrow \widetilde{X}\ ^2B_1(0,0,0)$ *rovibronic transition of the* $^{14}NH_2$ *radical from 16720 to 16750 cm^{-1}*

The first column of the Table 1 gives vacuum wavenumbers in cm^{-1} of the most intense absorption lines of the $^{14}NH_2$ isotopomer radicals recorded in this work, in the 16678-16748 cm^{-1} range. The second column gives the corresponding absorption coefficient of the selected lines. We have selected all the lines having, in this range, an absorption coefficient above 2.7 10^{-7} cm^{-1}. The lines with an absorption coefficient beyond 10^{-6} cm^{-1} have been marked in blue. The third column gives vacuum wavenumbers in cm^{-1} of the same lines reported by Ross *et al*.[4].

Table 1. *List of the positions (cm^{-1}) and absorption coefficients (cm^{-1}) of the most intense lines (target lines) in the range of 16678-16748 cm^{-1} corresponding to the region of the $\widetilde{A}\ ^2A_1(0,9,0) \leftarrow \widetilde{X}\ ^2B_1(0,0,0)$ rovibronic transition for the $^{14}NH_2$.*

Vacuum wavenumbers[a] (cm^{-1})	Absorption coefficient[a][b] (cm^{-1})	Wavenumbers (cm^{-1}) Ross *et al.*[4]
16678.9	7.8 10^{-7}	16678.859
16682.3	3.5 10^{-7}	16682.326
16684.6	3.0 10^{-7}	16684.624
16685.1	4.1 10^{-7}	16685.102
16695.3	4.9 10^{-7}	16695.302
16696.2	2.7 10^{-7}	16696.190
16697.1	10.2 10^{-7}	16697.117
16697.8	5.0 10^{-7}	16697.776
16699.5	9.8 10^{-7}	16699.506
16704.8	8.6 10^{-7}	16704.787
16705.0	9.5 10^{-7}	16705.047
16705.4	8.2 10^{-7}	16705.409
16710.1	3.1 10^{-7}	16710.133
16710.3	6.0 10^{-7}	16710.228
16712.8	3.7 10^{-7}	16712.911
16713.1	3.1 10^{-7}	16713.210
16713.5	4.2 10^{-7}	16713.619
16725.5	42.5 10^{-7}	16725.411
16725.8	10.4 10^{-7}	16725.784
16726.4	12.3 10^{-7}	16726.398
16727.6	12.6 10^{-7}	16727.488
16727.9	6.1 10^{-7}	16727.872
16730.1	8.2 10^{-7}	16730.129
16731.5	8.2 10^{-7}	16731.463
16732.1	7.6 10^{-7}	16732.038
16732.6	3.9 10^{-7}	16732.550
16732.9	4.4 10^{-7}	16732.888
16733.5	4.3 10^{-7}	16733.471
16735.1	3.7 10^{-7}	16735.118
16740.0	16.0 10^{-7}	16739.956

a) This work, b) Uncertainty is 2 10^{-8} cm^{-1}.

IV. CONCLUSION

We have succeeded to couple a Radio Frequency discharge to our Cavity Ring Down setup to produce enough amount of the $^{14}NH_2$ from a mixture of $^{14}NH_3$ precursor diluted in Ar to do spectroscopy. The absorption spectroscopy of the $^{14}NH_2$ radical in its vibronic band was measured by Cavity Ring-Down Spectroscopy technique. We have also been measured intensities and precise accurate positions of the most intense lines of the $^{14}NH_2$ radical in the range of 16678-16748 cm^{-1} corresponding to the region of the $\widetilde{A}\ ^2A_1(0,9,0) \leftarrow \widetilde{X}\ ^2B_1(0,0,0)$ rovibronic transition.

V. ACKNOWLEDGMENT

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