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CAVITY RING DOWN MEASUREMENT OF THE (1, 0) B $^2\Sigma_u^+$–X $^2\Sigma_g^+$ ABSORPTION BAND OF THE N_2^+ CATION

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The ultraviolet (1, 0) B $^2\Sigma_u^+$–X $^2\Sigma_g^+$ transition in the N_2^+ cation was measured with the absorption cavity ring down technique. The N_2^+ cations were produced in a stationary DC discharge in nitrogen under reduced ($\approx$ 0.5 Tr) pressure. The weak band due to the (4, 0) A $^2\Pi_u$–X $^2\Sigma_g^+$ transition in the red part of the spectrum was also recorded. Several of the observed transitions correspond to absorptions from the vibrationally excited ($\nu' = 1$) states of N_2^+ and to absorptions from the neutral N_2 molecules in the triplet state.

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1. Introduction

The cavity ring down (CRD) method, based on the measurement of the decay time of a light pulse injected into an optical resonator, has been first proposed by O'Keefe and Deacon [1]. This method allows for measurement of very weak absorptions in gas phase molecular species. The approach originates from the techniques developed previously to determine the reflectance coefficients of dielectric mirrors [2]. In the CRD spectroscopy the decay time of a light pulse, oscillating between the mirrors of a high finesse optical resonator, is measured for each wavelength. It is usually assumed that this decay should have a monoexponential character. The decay time τ depends on the resonator length L, losses on the mirrors $(1 - R)$, and the absorbance (αL) (α — absorption coefficient):

$$\tau = \frac{L}{c(1 - R + \alpha L)}.$$

Hence, upon an increase in the absorbance, the decay time would become shorter, with respect to a decay time measured for an empty cavity. The conditions under which the above expression holds are thoroughly discussed in Ref. [3].

The main advantage of the CRD method is high sensitivity. This depends principally on the reflectance coefficient of applied dielectric mirrors. With this coefficient as high as $R \geq 0.9999$ the cavity ring down measurement is equivalent to the classical absorption spectroscopy in a cell of optical path length through the sample longer than 10 km. Moreover, the decay time may be determined much more accurately than the ratio of light intensities in classical methods. Sensitivity corresponding to absorbance values of 10^{-7} cm^{-1} (or better [4]) per one pass through the optical resonator can be achieved.

In the classical CRD method pulsed laser sources were employed. Recently, however, several examples of successful application of cw laser sources for this techniques were reported [4–6]. With cw lasers the cavity is first pumped by the cw light, and, after sufficient build-up of photons is achieved, the incident light is shut by an acousto-optic modulator and the decay is recorded. The length of the cavity has to be continuously adjusted to the wavelengths of the incident light, so that each time the transverse TEM_{00} mode is excited. These requirements make the cw cavity ring down spectroscopy more complicated.

During the 10 years, which have passed since its advent [1], the CRD method has become a very fruitful tool for spectroscopic investigations of the species in the gas phase. As a method of absorption measurements this technique may be applied for virtually every chemical species. That, obviously, is not the case for other high sensitivity methods based on photoluminescence or photoionization.

Using CRD spectroscopy the absorption bands corresponding to doubly forbidden transitions $^1\Sigma_g$–$^3\Sigma_g$ in molecular oxygen [1], as well as a number of weak bands due to vibrational overtone transitions of HCN [7], N_2O [5], CHF_3 [6], HC_2H [4] were recorded in the visible. In those studies the whole resonator cavity was uniformly filled with the absorbing gaseous sample. Cavity ring down spectroscopy has also been applied for studies of transient radicals [8] and metal clusters [9] in molecular free jet expansions. Much attention has been devoted to the studies of reactive individuals CH_3 [10, 11], HCO [12], OH [13] emerging in low-pressure methane-oxygen flames. CRD spectroscopy has proved to be very powerful technique for these studies.

In very few reported experimental works the cavity ring down spectroscopy has been applied for studies of unstable species generated in discharge tubes. The high sensitivity offered by the CRD method allowed for recording of very weak electronic absorption band (6, 0) A $^2\Pi_u$–X $^2\Sigma_g^+$ of the N_2^+ cation, which was produced in the pulsed discharge in nitrogen–helium mixture [14]. In a discharge of acetylene in helium a radical of astrophysical importance C_6H was created [15] and its gas phase spectra have been recorded. The electronic absorption spectra of this species were previously known only from the matrix isolation studies [16]. The excellent quality dielectric mirrors ($R \geq 0.9999$), available for the wavelength $\lambda > 550$ nm, were applied in both of the above-mentioned studies.

In the present paper the cavity ring down apparatus based on standard quality ($R = 0.995$) mirrors is described and its performance is demonstrated on an example of the measurements of the UV electronic absorption spectrum of N_2^+ produced in a stationary DC discharge in nitrogen.

2. Experimental

The scheme of the apparatus used in the present study is presented in Fig. 1. The system consists of the Lambda Physik FL 3001 dye laser pumped by the Lambda Physik LPX 100 excimer laser, the optical resonator, discharge tube, liquid nitrogen traps, photomultipier light detector, transient recorder, and computer used for data acquisition and signal processing.

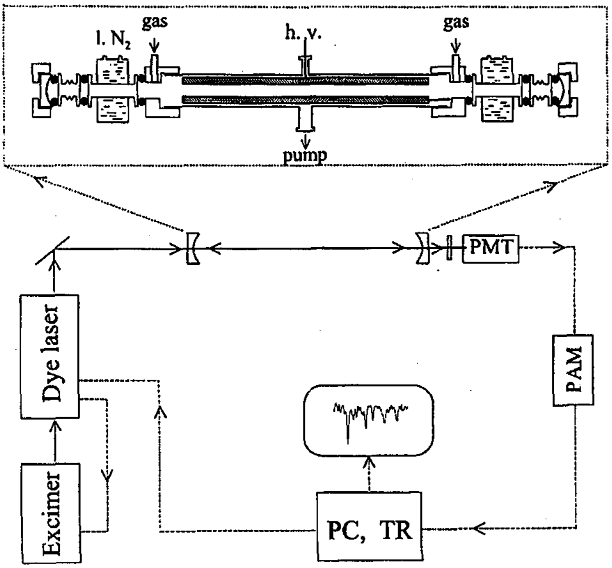

Fig. 1. Schematic diagram of the cavity ring down setup. PMT — photomultiplier tube, PAM — preamplifier, TR — transient recorder card. The upper panel shows an expanded view of the discharge cell and the optical resonator. l. N_2 — liquid nitrogen trap, h.v. — high voltage.

Molecular nitrogen cations were produced in the discharge tube, coaxial with the optical resonator. The pressure of nitrogen flowing through the tube was kept in the range of several hundred mTr, by pumping the tube with a rotary pump and regulating the flow from the nitrogen supply. Liquid nitrogen cooled trap protected the discharge tube from the backstream from the rotary pump. The discharge occurred between two stainless steel bars oriented along the optical axis of the resonator. The bars (8 mm in diameter) were spaced by 25 mm and the light oscillating in the resonator probed the region between them. The DC glow discharge occurred for applied voltage in the range (500–700 V), while the current was kept at 0.2 A.

During the discharge, even in pure argon or nitrogen gases, a gradual decline of the reflectance coefficient of the mirrors was observed — most probably due to deposition on the mirror surfaces of the decomposition products of some trace impurities present in the discharge tube. The placing of liquid nitrogen cooled traps between the mirrors and the discharge tube was found to inhibit mirrors degradation. Mirror holders were connected to the traps by stainless steel bellows to allow for alignment of the resonator.

The optical resonator was built of two dielectric mirrors with moderately high reflection coefficients. Two sets of mirrors were applied in the present study. The mirrors for the measurements in the near ultraviolet had the reflection coefficient 0.995 and the radius of curvature of 3 meters, while for the mirrors used in the red spectral region the corresponding parameters were 0.998 and 2 m. The mirrors were fixed in kinematic mounts spaced by 1.8 m. With such resonator the observed light decay times for evacuated cavity were 2.5 μs (near UV) or 6.0 μs (red).

The light leaving the resonator was detected with a photomultiplier tube. The electrical signal was amplified and the waveform, corresponding to the decay of light in the resonator, was recorded for each laser shot with a 250 MHz, 8 bit transient recorder. For every spectral step, 20 (ultraviolet) or 60 (red region) decay curves (corresponding to single shots) were coadded in order to improve signal-to-noise ratio. The waveforms obtained in such manner presented smooth, monoexponentially decaying curves. The decay time was determined by a least squares fit of the function

$$y = y_0 + I \exp(-t/\tau)$$

to the experimental curve. This procedure is superior to that based on two boxcars, which register signals in the time gates one delayed by several microseconds with respect to the other.

The absorption spectrum was obtained by scanning the dye laser and recording the decay time for each wavelength.

3. Results and discussion

The electronic absorption spectrum due to the (1, 0) B $^2\Sigma_u^+$–X $^2\Sigma_g^+$ transition in N_2^+ ions in the gas phase was collected using the experimental setup described above. The spectrum presented in Fig. 2a,b is to our best knowledge the first direct absorption measurement of the UV (1, 0) band of N_2^+. The rotational components of this band belong to P_1, P_2 branches (which form the head of the band) or to the R_1, R_2 branches. Each of the rotational lines is split in two due to the coupling of the electron spin with the rotational angular momentum of the molecule. The part of the spectrum seen in Fig. 2a,b (rotational lines belonging to P_1 and P_2 branches) was previously observed in emission from the hollow cathode discharge in nitrogen, although the spectrum was not presented [17]. Only the spectral positions of the rotational components of the P_1 and P_2 branches were tabulated, and spectroscopic constants were evaluated therein [17]. The positions of the rotational lines of P_1 and P_2 branches are identical with the wavelengths at which the absorption lines were observed in the present measurement. Several lines, visible in Fig. 2a on the long wavelength side of the band heads, belong to the same system as the lines which form the heads. These lines result from the perturbation of the rotational sublevels $N' = 12 \div 15$ in the B $^2\Sigma_u^+$ state by the closely lying sublevels of the ($\nu' = 11$) A $^2\Pi_u$ state. The effects of perturbation caused by this state are also clearly seen in R_1 and R_2 branches (Fig. 2b) as irregularities in the positions of the rotational lines for $N' = 12 \div 15$.

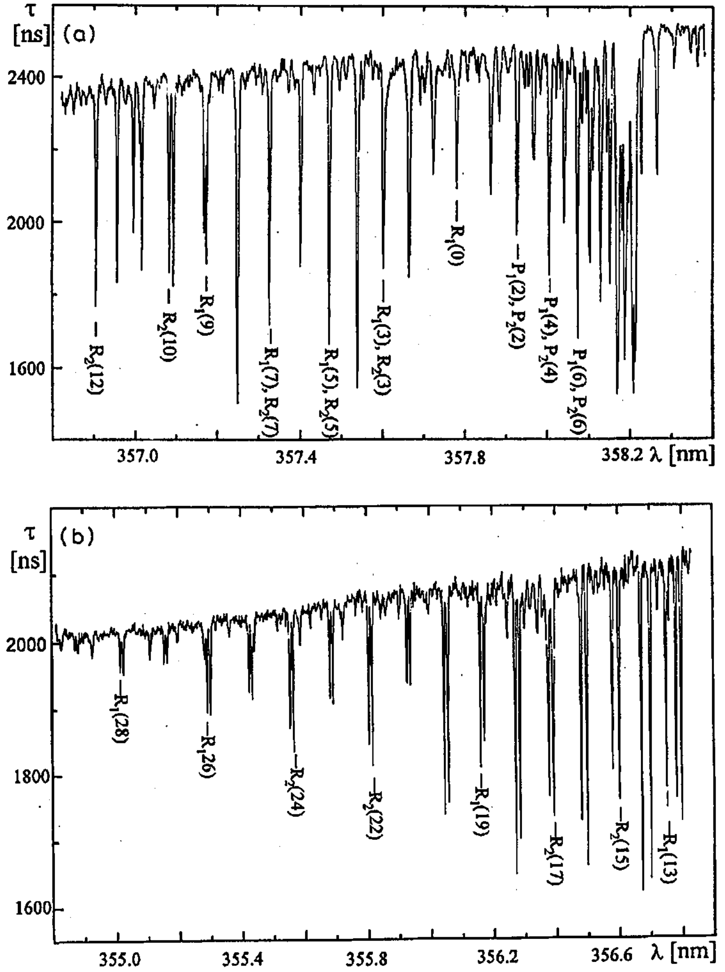

Fig. 2. (a), (b) Cavity ring down absorption spectra of the N_2^+ B $^2\Sigma_u^+$–X $^2\Sigma_g^+$ (1 –0) band.

Cavity ring down absorption measurements, in contrary to emission and other techniques give true values of the line intensities from which concentration of molecules in a specific rotational level can be evaluated. The simulations of the electronic band of N_2^+ based on classical Boltzmann statistics give the population distribution over the rotational levels of N_2^+ closest to that observed experimentally, for temperature in the range 450–500 K.

The weak lines visible in Fig. 2b between the strong components of R_1 and R_2 branches ($N'' = 17 \div 28$) are not due to the (1, 0) B $^2\Sigma_u^+$–X $^2\Sigma_g^+$ transition. In this spectral range the band belonging to the (2, 1) B $^2\Sigma_u^+$–X $^2\Sigma_g^+$ transition in N_2^+ should be expected. The spectral pattern of these weak lines, which is similar to that in P branches (with heads of the band) and to R branches in the

(1, 0) B $^2\Sigma_u^+$–X $^2\Sigma_g^+$ band, seems to indicate the presence of vibrationally excited ($\nu' = 1$) N_2^+ cations in the discharge.

An effort has been made to collect the absorption spectrum of N_2^+ in the red region (at 610 nm) corresponding to the (4, 0) A $^2\Pi_u$–X $^2\Sigma_g^+$ transition. This transition is more than three orders of magnitude weaker than that observed in near UV. Dielectric mirrors with slightly better reflectance coefficient (with respect to those used for near UV measurements) were available for this red spectral region. A fragment of the recorded spectrum is presented in Fig. 3. The spectrum consists of large number of weak, but reproducible (from run to run) rotational lines due to the (4, 0) A $^2\Pi_u$–X $^2\Sigma_g^+$ transition. This structure is much richer than that of the near UV transition in N_2^+. This is well visible in the synthetic spectrum of N_2^+ presented at the bottom of Fig. 3. The presence of two *Q* branches and of the satellite branches increases the total number of branches to 12. In the region presented in Fig. 3, the lines due to five branches are present [18]. In addition, rotational lines belonging to the B $^3\Pi_g$–A $^3\Sigma_u^+$ band in neutral molecular nitrogen are also expected in this region. This band has a very rich rotational structure, consisting of 27 branches of the absorption lines. The origin of the vibronic $\nu' = 4$, $\nu'' = 0$ transition in neutral nitrogen is placed at 16200 cm^{-1}, and for the $\nu' = 5$, $\nu'' = 1$ transition the origin is at 16350 cm^{-1} [19, 20]. Both the vibronic bands are located in the vicinity of the (4, 0) A $^2\Pi_u$–X $^2\Sigma_g^+$ electronic transition in molecular nitrogen cation. On taking into account the complexity of the rotational structure of the band due to absorptions from the triplet state of nitrogen and the possible overlapping of the lines belonging to the absorptions of N_2^+, the assignment of the lines presented in Fig. 3, to a specific species becomes rather problematic.

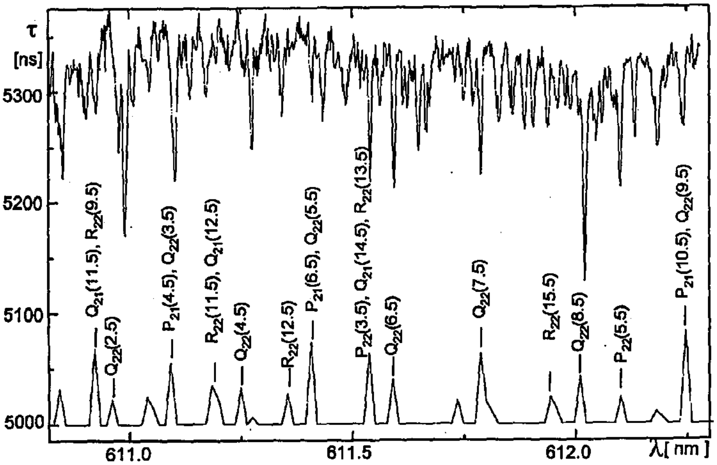

Fig. 3. Part of the N_2^+ (A $^2\Pi_u$–X $^2\Sigma_g^+$ (4 –0)) absorption spectrum measured with the CRD method. The lines from the B $^3\Pi_g$–A $^3\Sigma_u^+$ transition of molecular nitrogen obscure the N_2^+ spectrum. The bottom trace shows a synthetic spectrum of N_2^+.

4. Summary

The results of measurements carried within this work demonstrate the very high sensitivity of the cavity ring down method, even in the case when the dielectric mirrors, in the resonator, are not of an extremely high reflection coefficient. A setup built with these mirrors allowed for detection of the reactive transients (N_2^+ cations) produced in a DC discharge. Application of pulsed, instead of stationary discharge, should increase the concentration of transients at the time when the discharge is probed with light.

The sensitivity of the CRD method can be further considerably improved using high reflectance dielectric mirrors instead of standard ones.

Cavity ring down as an absorption method can be used for all chemical species and gives true values of the line intensities from which the molecular concentration can be evaluated.

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