Precision measurements of sodium - sodium and sodium - noble gas molecular absorption

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Precision measurements of molecular absorption

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Abstract.

Experimental apparatus and measurement technique are described for precision absorption measurements in sodium - noble gas mixtures. The absolute absorption coefficient is measured in the wavelength range from 425 nm to 760 nm with ±2% uncertainty and spectral resolution of 0.02 nm. The precision is achieved by using a specially designed absorption cell with an accurately defined absorption path length, low noise CCD detector and double-beam absorption measurement scheme. The experimental set-up and the cell design details are given. Measurements of sodium atomic number density with ±5% uncertainty complement absorption coefficient measurements and allow derivation of the reduced absorption coefficients for certain spectral features. The sodium atomic number density is measured using the anomalous dispersion method. The accuracy of this method is improved by employing a least-squares fit to the interference image recorded with CCD detector and the details of this technique are given. The measurements are
aimed at stringent testing of theoretical calculations and improving the values of molecular parameters used in calculations.

**Keywords:** absorption cell, molecular absorption, anomalous dispersion method

1. Introduction

Atomic collision processes significantly influence the absorption and emission of light by atomic vapors at high pressures. As a result the absorption and emission spectra reveal not only atomic line broadening but also very broad, essentially molecular features with rich rotational-vibrational structure and satellite peaks due to formation of molecules and quasi-molecules. Since pioneering work by Hedges *et al.* [1], such spectra have been a subject of extensive studies, both theoretical and experimental, and proved to be a rich source of information about the interaction potentials, collision dynamics and transition dipole moments [2-12]. The experimental approaches employed include absorption measurements [4,5,8,9,12], laser-induced fluorescence [3,6,9] and thermal emission spectra [7]. While laser-induced fluorescence and emission spectra provide the shapes and positions of many molecular bands, the measurements of absorption coefficient spectra also give absorption coefficients over a large spectral range. Absolute measurements of the absorption spectra may allow more comprehensive tests of theoretical calculations. As a result, better differentiation between different theoretical approaches and improved values for various molecular parameters and potentials can be obtained. However, in many cases absorption spectra are obtained on a relative scale or only the absorption coefficient or optical depth is measured accurately. Extraction of absolute cross-sections (or reduced absorption coefficients) from traditional measurements of the optical depth as well as any quantitative comparisons of absorption spectra with theoretical calculations require accurate knowledge of the absorption path length and the absorbing species concentrations.

Most of absorption spectroscopy experiments with hot and corrosive vapors such as sodium have been performed using heat pipes [8,9,13]. In a heat pipe the alkali vapor is contained in the hot middle of the furnace between cold zones where windows are located. Buffer noble gas facilitates the alkali containment and protects cold windows from alkali deposits. In this
type of absorption cell the vapor density is not uniform at the ends of the absorption path and the path length is not accurately defined. In addition, the temperature of the vapor-gas mixture is not uniform and at higher alkali vapor densities formation of fog at the alkali-buffer gas interface seriously affects the optical absorption coefficient measurements [13,14]. Absorption cells have been designed, where heated windows, placed in the cell hot zone, define the absorption length with good precision [14-16]. The absorption cell described in [15] is suitable for hot sodium vapors up to 1000K but it is difficult to make it with a long absorption path. The cell described in [16] is not suitable for corrosive vapors and may still have problems with window transmission due to metal deposits [16]. Schlejen et. al. [14] designed a cell specifically for spectroscopy of sodium dimers at high temperatures. Their cell allowed uniform concentration of absorbers and uniform temperature up to 1450K with an absorption length defined accurately by hot sapphire windows. However, the cell design is not suitable for spectroscopy of gas-vapor mixtures because it was completely sealed and did not easily enable changing the mixtures.

As well as defining the absorption length accurately, an equally important aspect is measuring the alkali vapor density. While the noble gas density can be calculated reasonably well from the measurements of pressure and temperature using the ideal gas law, it is difficult to establish the density of alkali atoms. In the majority of reported experiments alkali concentration was determined from the temperature and published saturated vapor pressure curves but this approach can introduce significant uncertainties. For example, in measurements of oscillator strengths or $f$-values significant discrepancies were often obtained between oscillator strengths measured by methods involving knowledge of the number density and by methods not requiring it [17]. Even if the vapor pressure curve is well known for pure saturated vapor, introducing buffer gas or using unsaturated vapors prohibit accurate knowledge of the vapor density along the absorption path. To achieve a higher precision in determination of absolute cross-sections or reduced absorption coefficients it is necessary to measure the alkali vapor density directly.

In this paper we describe experimental apparatus and technique used for precision measurements on an absolute scale of molecular absorption coefficients in sodium vapor + noble gas mixtures. To overcome the above-mentioned difficulties with definition of absorption length we have designed a special absorption cell. In our cell, heated sapphire windows, resistant to
hot sodium vapor, are used to define the absorption path. A high temperature valve, kept at the same temperature as the cell itself, is utilized to introduce different noble gases. A separate sodium reservoir, maintained at a lower temperature, is used to control the sodium vapor pressure independently of the cell temperature. The cell can be operated at temperatures up to 900K. During the spectral measurements we measure and monitor the sodium number density at different temperatures and pressures using the anomalous dispersion or 'hook' method [8,9,18,19]. The 'hook' method allows accurate measurement of $nfl$ value where $n$ is the atomic number density, $f$ is the atomic line oscillator strength and $l$ is the absorption length. If the absorption length and $f$-value for sodium D lines are known, the sodium number density is accurately obtained. The next section concentrates on the details of the experiment and the absorption cell design.

2. Experiment

2.1 Experimental set-up

Fig. 1 shows schematically the experimental set-up that is used for our absorption measurements. The light source is a 100W halogen lamp powered by a voltage-stabilized DC power supply. A well-collimated beam of white light is produced with the help of a condenser lens, an achromat lens, a pinhole aperture 0.4 mm diameter and another achromat lens of shorter focal length. The light beam is sent through a Mach-Zender interferometer and focused on the entrance slit of 3m Czerny-Turner spectrograph (McPherson model 2163) with a combination of spherical and cylindrical lenses. An absorption cell is placed in the test-beam arm of the Mach-Zender interferometer. Beam blocks are used in both arms to switch the beams or block them altogether. The light beam through the reference arm of the Mach-Zender interferometer is used as a reference for the absorption in the usual manner of double-beam absorption spectroscopy [9].

The spectra are recorded with a two-dimensional CCD detector (Andor Technology model V420-0E) placed in the focal plane of the spectrograph. This detector has 1024 pixels horizontally and 256 pixels vertically with pixel size of 26x26 m. For spectral measurements the detector is used in the vertical bin mode, that is, as a one-dimensional array detector. The stigmatic spectrograph has a plane diffraction grating with 2400 grooves/mm and theoretical resolution of $\sim 0.005$ nm at 500 nm wavelength. We used 150 m
entrance slit width which gives actual resolution of 0.02 nm. At least 5 pixels of the array detector are used over 0.02 nm wavelength interval and as a result smoother spectral data are obtained from the array detector.

The overall spectral range determined by the diffraction grating and the detector sensitivity is 425 nm to 760 nm. To record spectra through this spectral range the diffraction grating is rotated through 160 different positions by a stepper motor. Backlash is avoided by rotating the grating in one direction from its calibration position at 425 nm, which in turn is set by rotating the grating beyond the calibration point. The calibration point is located by a rotation photosensor placed on the worm screw of the spectrograph sine-bar mechanism. The photosensor signal is sent to a programmable stepper motor controller (New England Affiliated Technology NEAT-310) which drives the stepper motor and allows the grating to be set at the calibration position automatically.

Each position of the grating permits recording consecutively spectral intervals ranging from about 3 nm at 430 nm to 1.1 nm at 760 nm, which are determined by the linear reciprocal dispersion of the spectrograph at a given wavelength and the overall length of the array detector. All grating positions are wavelength-calibrated using a large number of different atomic lines obtained from a number of different hollow cathode spectral lamps. The wavelength calibration enables identifying the wavelength of any pixel of the CCD detector within ± 0.05 nm in the range 425 to 760 nm.

To measure the sodium atomic density using the anomalous dispersion or 'hook' method, both beams through the Mach-Zender interferometer are unblocked and interfere to produce a spectrally dispersed two-dimensional interference pattern in the focal plane of the spectrograph. The Mach-Zender interferometer is adjusted to localize the interference fringes at infinity. This insures that the integral sodium number density along the absorption path is measured. The CCD detector is used in its normal two-dimensional array mode to record the interference pattern. From the analysis of the interference pattern recorded in the vicinity of sodium D lines, sodium number density is derived. The general description of the 'hook' method is given in [17,18,19] and the details of analyzing the interference pattern recorded with CCD detector are given in the next section. A glass plate and a stack of windows, identical to those used in the absorption cell, are placed in the reference arm of the Mach-Zender interferometer [17]. These compensating optics remain in the reference beam during spectral absorption measurements as well and
have no effect on the spectral measurements due to the nature of the dual-beam absorption technique.

A simple vacuum system consisting of a turbomolecular pump (Sargent Welch model 3106S) backed by a rotary vane pump (Sargent Welch model 1402) is used to evacuate the absorption cell. The turbomolecular pump can handle short bursts of increased pressure and gas flow load and therefore it is utilized also to pump gases from the cell. A liquid nitrogen trap is placed in between the cell and the pump to trap sodium vapor. A precision pressure gauge (Omega Engineering model PGT-45) is used to measure accurately the pressure of noble gases when filling the cell.

An experiment control and data acquisition computer (Pentium PC) controls the CCD detector, spectral data acquisition and the spectrograph diffraction grating via the stepper motor controller connected to the serial port. The absorption cell temperature is monitored constantly through a number of thermocouples connected via commercial plug-in data acquisition board (American Data Acquisition Corporation) and the cell heaters are controlled via output channels of the data acquisition board and solid state relays. Andor Technology CCD software and custom ‘in-house’ written software are used to perform all these tasks.

2.2 Absorption cell

Fig. 2 shows the schematic diagram of the absorption cell. The cell body is made of stainless steel (SS) 316 and is approximately 470 mm in length and 8 mm internal diameter. A vertical extension is welded to the middle of the cell body, 70 mm in length and 11 mm internal diameter. A sodium reservoir is located at the end of this extension. It is made of SS 316 with internal diameter 5.5 mm and 70 mm length and it is connected using a Swagelok fitting which enables disconnection for loading sodium. The sodium reservoir is heated with a separate heater to introduce sodium vapor into the cell or it can be cooled with a circulating water cooler to reduce the alkali number density. Both the heater and cooler are made to slide on and off the sodium reservoir. A valve is connected to the vertical extension through which the cell is evacuated and noble gases can be admitted. This valve is a special bellows-sealed high-temperature valve (Nupro Company) rated to work at temperatures up to 920K. The valve is heated to the same temperature or 5 to 10 K higher than the cell itself to prevent sodium from condensing in the
valve.

The major problem one faces when designing an absorption cell with heated windows is making good vacuum seals for the windows. In case of sodium, sapphire proved to be material of choice for the windows because of its excellent resistance to hot sodium [14]. However, it is difficult to make a reliable sapphire to metal seal that withstands repeated heating cycles up to 900K. In our design (Fig. 2) the sapphire windows are sealed into polycrystalline alumina (PCA) tubes with special sealing ceramics (frit) used in the construction of commercial high-pressure sodium (HPS) lamps. The sealing technique used was similar to the one described by Schlejen et. al. [14]. The PCA tubes have 10.2 mm outside diameter and 110 mm length. They are made from commercial OSRAM SYLVANIA standard HPS lamps ULX880 by cutting off slightly larger diameter portions. Since PCA and sapphire have similar thermal expansion coefficients, such window-tube assembly retains its integrity over a wide range of temperatures. The tubes are inserted into the heated cell body so that the windows are located in the hot zone while the tube ends extend to cooler cell ends where Viton O-rings are used for vacuum seals. Additional external windows made of fused silica are used with O-ring seals to create an evacuated transition zone from the heated middle of the cell to the cooler ends. These silica windows are not heated.

Our cell design allows sodium to condense along the PCA tube towards the colder zone where O-ring seals are located. To reduce the amount of sodium condensed there the PCA tubes were carefully selected in outside diameter tolerance and straightness to match closely the internal diameter of the SS cell body at room temperature. When the cell is heated the SS expands more than PCA thus creating some space for sodium to condense. Once the sodium build-up reaches the hot zone, no more sodium is lost into the void along the PCA tubes.

The windowed ends of the PCA tubes rest against the stepped profiles inside the SS cell body as shown in Fig. 2. These stepped profiles determine the positions of the heated windows and thus the absorption length. To ensure that the PCA tubes are always firmly pressed against these stepped profiles regardless of the thermal expansion differences between PCA and SS, compression springs are used to push the PCA tubes via stacks of spacers, made of SS 316, and the external windows. Cap nuts complete the assembly of the windows, PCA tubes, O-ring seals and spacers as Fig. 2 illustrates. These caps allow easy removal of all windows for cleaning if needed as well as
adjustment of the spring compression. The compression springs are chosen to produce about 12 N force, equivalent to about 1.5 atm on the surface area of the heated windows.

The absorption length at room temperature is measured using a special tool made of two rods about 4 mm in diameter inserted into a tube of 6 mm outside diameter. One rod is permanently fixed while the other can slide in and out with friction, thus allowing change in the overall length of the tool. The ends of the tool are rounded and polished. With one sapphire window completely in place at one end of the cell, the tool is inserted into the cell and the second PCA tube with sapphire window is put in place. The tool adjusts its length precisely to the distance between two sapphire windows. Then the PCA tube and the tool are carefully taken out and the length of the tool is measured with a micrometer. In our cell the absorption length at room temperature was measured 190.03 ± 0.025 mm. The absorption length at operating temperature is calculated from the temperature of the cell and the thermal expansion coefficient for SS of 18 ± 2.2 x 10^-6 K^-1 [20]. Since the change in the absorption path length due to thermal expansion is a small percentage of the overall length, large uncertainties in the thermal expansion calculation do not lead to a large uncertainty in the resulting absorption length at a given temperature.

The whole absorption cell including the valve is heated by sets of heaters made of Nickel-Chromium wire. Separate sets of heaters are used to heat the cell and the valve. Each heater set consists of two separate heaters. One is switched on constantly while the other one is used in on-off mode, controlled from the experiment control computer, to maintain average cell and valve temperatures constant. Six type K thermocouples are used to measure the temperatures at different points. Three thermocouples are placed in contact with the main cell body, one of them in the middle and the other two at the locations of heated windows. Another thermocouple measures the valve temperature. Two thermocouples are used to measure the temperatures at the bottom and at the top of the sodium reservoir. The heaters are isolated from each other and the SS parts of the cell by embedding them into insulation made of moldable Alumina-Silica blankets (Zircar Products). All heated parts are wrapped into thermal insulation made of Alumina blankets (Zircar Products). The positions of the heaters are chosen as shown schematically in Fig. 2. The middle part of the cell of ~60 mm length does not have heaters but is nevertheless heated sufficiently by thermal conductance. Also
the thermal insulation is adjusted in such a way that the temperature, measured with thermocouple in the middle of the cell, is 5 to 10 K lower than the temperature at the points where the heated windows are located. Heating sapphire windows to a slightly higher temperature ensures they remain free from any deposits during the operation of the cell.

The cell body thermocouple and the valve thermocouple readings give an average temperature of the cell body. The gas mixture temperature is assumed to be equal to the average temperature of the cell body. Since the thermocouples are located between the SS cell body and the heaters, they may give readings of slightly higher temperature than the actual temperature of the cell and the gas inside it. Given this fact and the temperature reading differences between the thermocouples, the uncertainty in the gas mixture temperature is estimated to be + 10 K - 50 K.

2.3 Measurement technique

Absorption spectroscopy is based on Beer’s law describing absorption of light in homogeneous absorbing media

$$I_1(\lambda) = I_0(\lambda) \exp(-k(\lambda)l)$$  \hspace{1cm} (1)

where $I_1$ is the transmitted intensity of light, $I_0$ is the incident intensity of light, $k$ is absorption coefficient and $l$ is the absorption length. In real experimental measurements the transmission through optics, absorption cell windows and spectrograph, detector sensitivity and light source spectral characteristics all have to be taken into account. In the dual beam arrangement for absorption spectroscopy the test $S_t(\lambda)$ and reference $S_r(\lambda)$ beam spectra, obtained from the detector, are

$$S_t(\lambda) = k^0_t(\lambda)I_0(\lambda) \exp(-\tau_t(\lambda) - k(\lambda)l)$$  \hspace{1cm} (2)

$$S_r(\lambda) = k^0_r(\lambda)I_0(\lambda) \exp(-\tau_r(\lambda))$$  \hspace{1cm} (3)

where $I_0$ is the intensity of the light source, $k(\lambda)$ is the absorption coefficient to be measured, $l$ is the absorption length and $k^0_t$, $\tau_t$ and $k^0_r$, $\tau_r$ are the coefficients that take into account the detector efficiency, absorption of all optics elements such as windows and lenses and spectrograph transmission. To eliminate all unknown parameters represented in (2) and (3) by $k^0_t$, $\tau_t$, $k^0_r$, and $\tau_r$. 

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and $\tau_r$, we measure first the reference spectra (the spectra obtained without sodium in the absorption path and thus without atomic and molecular absorption we are interested in). Sodium concentration in the absorption path is reduced to less than $10^{14}$ cm$^{-3}$ by cooling the sodium reservoir down to between $+5$ to $+10$ C using the circulating water cooler around it. At densities below $10^{14}$ cm$^{-3}$ the molecular absorption of both sodium-sodium and sodium-noble gas is negligible and $k(\lambda) = 0$. Both test and reference beam spectra are taken at each grating position and their ratio

$$\frac{S_{t}^0(\lambda)}{S_{r}^0(\lambda)} = k_{t}^0 k_{r}^{-1} e^{\exp(\tau_r(\lambda) - \tau_t(\lambda))}$$ (4)

is calculated. Thus obtained reference spectra contain information about all unknown parameters. To reduce statistical error a number of measurements are performed and the average is calculated.

To measure the absorption spectra of sodium-sodium and sodium-noble gas molecules, the sodium vapor is introduced in the absorption path by heating the sodium reservoir. Both test and reference beam spectra are taken at each diffraction grating position and their ratio is calculated:

$$\frac{S_{t}^{Na}(\lambda)}{S_{r}^{Na}(\lambda)} = \frac{k_{t}^0}{k_{r}^0} e^{\exp(\tau_r(\lambda) - \tau_t(\lambda) - k(\lambda) l)}$$ (5)

Once again to reduce statistical error a number of measurements are performed and averaged. From (4) and (5) it follows that the absorption coefficient $k(\lambda)$ is obtained from measurements of absorption and reference spectra with all unknown parameters eliminated:

$$k(\lambda) = -\frac{1}{l} \ln \left( \frac{S_{t}^{Na}}{S_{r}^{Na}} \right)$$ (6)

Using the procedure described above we are able to measure the absolute absorption coefficient with as small as $\pm 1\%$ statistical error in the range 425 - 760 nm with spectral resolution $\sim 0.02$ nm.

Derivation of the reduced absorption coefficient for sodium-sodium and sodium-noble gas quasi-molecules requires accurate knowledge of atomic number densities. The atomic density for noble gas is calculated from pressure and temperature using the ideal gas relationship and the sodium density is measured by the 'hook' method [17-19]. Fig. 3 shows the 'hook' interference
pattern recorded with CCD detector in the focal plane of the spectrograph. The analysis of this pattern and extraction of the sodium atomic number density is performed by a least-squares fit of the interference fringe model to the recorded pattern using software specifically written for this purpose. The following equation can be used to describe the positions $y_k$ of interference fringes of maximum intensity in the focal plane of the spectrograph [19]:

$$y_k = a \left( k\lambda - \left( \frac{A_1}{\lambda_1 - \lambda} - \frac{A_2}{\lambda_2 - \lambda} \right) N + \Delta nl \right),$$

where $r_0$ is the classical electron radius, $g_1, f_1, \lambda_1$ are respectively the $g$-factor, the oscillator strength and the wavelength of sodium D1 line, $g_2, f_2, \lambda_2$ are respectively the $g$-factor, the oscillator strength and the wavelength of sodium D2 line, $l$ is the absorption path length, $\Delta n$ is the coefficient accounting for optical path length difference between test and reference beams of the Mach-Zender interferometer, $a$ is the scaling factor accounting for imaging properties of the optical set-up, $k$ is the fringe order and $N$ is the sodium number density. The above equation is valid at wavelengths separated from the atomic line core by more than the FWHM of the broadened line, $\lambda - \lambda_i >>> \Delta \lambda$ [17].

Our model calculations of the 'hook' interference pattern, which included the atomic line broadening, showed that the error introduced by neglecting the atomic line broadening in the above equation, is negligible when atomic number density of sodium is above $5 \times 10^{14}$ cm$^{-3}$ and noble gas pressure is below 500 Torr. These conditions are always met in our measurements. After some algebraic manipulations the following fringe model equation is obtained which gives positions $y_i$ of a number of fringes in terms of 2D CCD detector coordinates and fit parameters:

$$y_i = a_3 + a_2 \lambda + a_1 i \lambda + a_4 \left( \frac{A_1}{\lambda_1 - \lambda} + \frac{A_2}{\lambda_2 - \lambda} \right)$$

where $y_i$ is the vertical fringe coordinate at a given wavelength $\lambda$, $i = 0, 1, 2, 3, 4, 5$ denotes adjacent fringes seen by the detector and $a_1, a_2, a_3$ and $a_4$ are the fit parameters. The sodium number density is calculated from fit parameters $a_1$ and $a_4$:

$$N = \frac{a_4}{a_1}$$

From the recorded interference pattern three to five interference fringes, defined at maximum intensity, are extracted at each side of the sodium dou-
blet and the \((y, \lambda)\) coordinates for each fringe are calculated from the CCD pixel coordinates and wavelength calibration to provide the data set for the least-squares fit. Fig. 4a shows the interference fringes obtained from the image presented in Fig. 3 and Fig 4b shows the fitted model curves. Since a large number of points are used to locate the fringe positions, higher accuracy can be achieved in comparison with traditional methods of extracting atomic number density from measuring the location of the ‘hook’ maxima of a single fringe [17]. The main limitation on the accuracy of this new technique is imposed by wavelength calibration, especially at lower atomic densities. Using the system described above, the sodium density is routinely measured with \( \pm 2\% \) uncertainty, given the wavelength uncertainty \( \pm 0.03 \) nm in the vicinity of the sodium D-lines and the uncertainty in the interference fringe position of \( \pm 5 \) pixels. During consecutive spectral measurements used in calculating the resultant average spectra, the sodium number density was measured at the beginning of each measurement and was found to remain constant within \( \pm 4\% \) to \( \pm 5\% \).

3. Measurement results

Fig. 5 presents a spectrum of the absolute absorption coefficient of a sodium - xenon mixture measured at 900\( K^{+10K}_{-50K} \) cell temperature. The Xe pressure is 400 \( \pm 0.5 \) Torr, which gives xenon density \( 4.29 \times 10^{18} \) cm\(^{-3}\) at 900 K temperature. Sodium density is measured as \( 2.05 \pm 0.06 \times 10^{16} \) cm\(^{-3}\). The absorption coefficient in the 425 nm to 760 nm range consists of contributions from the broadened sodium atomic lines around 589 nm, the sodium - noble gas and the sodium - sodium molecular spectra. From 460 nm to about 550 nm a blue wing of the sodium dimer absorption is apparent [5]. At 560 nm there appears a sodium-xenon blue wing satellite feature [6] and towards the longer wavelength of the significantly broadened sodium D-lines there are red wings of the sodium dimer [5] and the sodium-xenon molecules [6]. Fig 6 shows a spectrum of the absolute absorption coefficient of a sodium - argon mixture measured at 900\( K^{+10K}_{-50K} \) cell temperature. The Ar pressure is 401 \( \pm 0.5 \) Torr, which gives argon density \( 4.3 \times 10^{18} \) cm\(^{-3}\) at 900 K temperature. Sodium density is measured as \( 1.00 \pm 0.04 \times 10^{16} \) cm\(^{-3}\). This spectrum is similar to the sodium - xenon spectrum shown in Fig. 5 except that the sodium - argon blue wing satellite is located at a slightly shorter wavelength of 554.5 nm and the sodium - argon red wing extends further from the sodium.
atomic line core. The magnitude of the absorption coefficient is lower in proportion to the lower sodium density.

Fig. 7 illustrates rotational-vibrational features of sodium dimer absorption at a 0.02 nm resolution in the vicinity of the 520 nm band. The features are a complicated superposition of many rotational-vibrational bands of the sodium dimer and identification of these bands has not yet been attempted. The statistical uncertainty in the absorption coefficient magnitude is indicated. This uncertainty includes both detector statistical errors and the uncertainty in the absorption path length. At any wavelength in the 425 nm to 760 nm range the uncertainty in the absorption coefficient does not exceed $\pm2\%$ where absorption coefficient values are larger than 0.008 cm$^{-1}$.

The measured spectra can serve for stringent quantitative tests of theoretical calculations [21]. Preliminary comparisons showed good overall agreement between the measurements and theoretical calculations at a temperature of 870 K, which is within our experimental temperature uncertainty [22]. Full details of the calculations and comparisons with experiment will be presented in the forthcoming publication [23].

A reduced absorption coefficient is calculated for the blue wing of sodium dimer absorption, which is well separated from the rest of the spectrum, using the measured absorption coefficient and sodium atomic number density and it is presented in Fig. 8. Apart from the broad and strong molecular absorption arising mostly from transitions from bound to bound states between $\text{X}^1\Sigma_g^+$ and $\text{B}^1\Pi_u$ molecular singlet states of the sodium dimer, there are also features from the triplet transitions $2^3\Pi_g \leftarrow a^3\Sigma_u^+$ and $c^3\Pi_g \leftarrow a^3\Sigma_u^+$ [5,24].

Since the sodium-xenon molecular absorption bands are very close to the sodium D-lines, it is difficult to separate them completely from atomic lines and to derive the reduced absorption coefficient. Fig.9 presents the absolute absorption coefficient in the vicinity of sodium-xenon blue satellite features at different xenon densities and sodium density of $7.7\times10^{15}$ cm$^{-3}$ and at 900 K temperature. There are two satellite features present at 560 nm and 564 nm. The positions and relative magnitude of these features can provide some insights into potentials of the sodium-xenon molecule as well as transition dipole moments [21,23].

4. Conclusion
Details of precision absorption measurements in sodium - noble gas mixtures at high spectral resolution have been presented. To perform more stringent tests of theoretical calculations and molecular parameters used in the calculations the goal was to obtain the absorption coefficient spectra on an absolute scale with better than ± 2% uncertainty at near UV and visible wavelengths. To achieve such precision an absorption cell for containment of sodium vapor with accurately defined absorption path was constructed. The measurements were performed using double-beam absorption measurement scheme eliminating all unknown parameters such as detector sensitivity and optics transmission. A low noise CCD detector was used to record the spectra and a number of separate measurements were averaged to reduce statistical error. To measure accurately the alkali number density the anomalous dispersion or 'hook' method was employed. The accuracy of the 'hook' method was improved by means of least-squares fit to the interference fringes image recorded using 2D CCD detector in the focal plane of the spectrograph. The measurements obtained with the apparatus and technique described extend the available data on the sodium - sodium and sodium - rare gas absorption to different temperatures and higher precision and spectral resolution.

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**Figure 1.** Schematic diagram of the experimental set-up.

**Figure 2.** Schematic diagram of the absorption cell.

**Figure 3.** Image of a 'hook' pattern obtained with a two-dimensional CCD detector.
Figure 4. Interference fringes extracted from 'hook' pattern image (a) and fitted model curves (b).

Figure 5. Absorption coefficient of sodium - xenon mixture at 900 K.

Figure 6. Absorption coefficient of sodium - argon mixture at 900 K.

Figure 7. Rotational-vibrational features of sodium dimer absorption spectra at 0.02 nm resolution.

Figure 8. Reduced absorption coefficient for the blue wing of sodium dimer molecular absorption.

Figure 9. Blue wing of sodium-xenon molecular absorption.
Cylindrical lens

Absorption cell

3m Czerny-Turner spectrograph

Stepper motor controller

CCD detector 256x1024

Mach-Zender interferometer

Pressure

Beam bl

Pinho

Compensation plate

Cell window compensation

Experiment control and data acquisition computer

Beam (optical)
uncertainty
$k/n^2 \times 10^{-18} \text{ (cm}^2\text{)}$

- $2^3\Pi_g \leftarrow a^3\Sigma^+$
- $B^1\Pi_u \leftarrow X^1\Sigma^+$
- $c^3\Pi_g \leftarrow a^3\Sigma^+$

wavelength, nm
Xe: 10 Torr

Xe: 100 Torr

Xe: 200 Torr

Xe: 400 Torr