

## MEASUREMENT SYSTEM FOR STUDY OF ABSORPTION SPECTRA OF GASEOUS MEDIA AT HIGH PRESSURES

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*A system for measuring the absorption spectra of gaseous media at pressures of 0.01–150 atm in the 0.3–25  $\mu\text{m}$  range is considered. Its suitability for studying pressure-induced absorption owing to intermolecular collisions and for measuring spectral absorption coefficients, integrated band intensities, and spectrum line profiles is discussed.*

**Keywords:** *absorption spectrum, spectral absorption coefficient, spectral transmission function, pressure-induced absorption.*

**Introduction.** Many applied problems involving radiative transfer in planetary atmospheres and heat exchange in power engineering installations require information on the spectral transmission functions of gaseous components and their dependences on pressure and temperature. Studies of spectral line shapes in various vibrational-rotational emission bands of molecules as functions of the type of collision partner, as well as studies of pressure-induced absorption owing to the influence of intermolecular interactions on the quadrupole moment, are of great interest. Pressure-induced absorption spectra obey different selection rules and can have a significant influence on radiative heat transfer in planetary atmospheres and in high-pressure engineering equipment [1–3].

In this paper we examine a spectral measurement system for studying the molecular absorption spectra of gases over a wide range of pressures (from low pressures up to 150 atm). The system has path lengths  $L_1 = 8$  cm,  $L_2 = 72$  cm, and  $L_3 = 2\text{--}40$  m employing a multipass gas cell. This measurement system adds significantly to the capabilities of the spectral measurement systems discussed in [3–6].

**The apparatus for measuring the absorption spectra of gases at high pressures** is intended for studying the role of intermolecular collisions in forming the absorption spectra of gases and includes a set of gas cells that operate at pressures of 0.01–150 atm, together with a unit for monitoring the test medium and recording the molecular absorption spectra. The set of gas cells is made up of three sequentially positioned cells with optical path lengths  $L_1 = 8$  cm,  $L_2 = 72$  cm, and  $L_3 = 2\text{--}40$  m. The third gas cell uses a White configuration multipass scheme for the light beam. The optical configuration of the cell system is shown in Fig. 1. Light from the radiation source, which is a globar or incandescent ribbon lamp, passes through the input window 1' via mirrors 3' and 4' to form an image with a magnification of  $1.3\times$  in the plane of the input stop of the White optical system. The mirrors 5', 6', and 7' have the same radius of curvature. Two of them (5' and 7') are objectives and form intermediate images of the input stop on the third mirror 6', which serves as a collector, in two horizontal series of intermediate images. After repeated passes between the mirrors of the White "bench" with a base length of 0.5 m, the beam of light is focussed onto the output stop. An image of the output stop is focussed through the intermediate window 8' and the mirrors 9' and 10' onto the input slit of the spectrometer.

The number of passes (the optical path length) is varied in the multipass gas cell by turning the two rear mirrors 5' and 7' by means of a wedge with an external drive. The number of passes between the mirrors is determined by the ratio of the dimensions of the front mirror and the output stop. When a laser is used as the light source, visual monitoring can be used to detect at least 40 images of the source, which correspond to a path length  $L = 40$  m in the cell.

The cells form three sequentially positioned isolated volumes 1, 2, and 3 and are arranged on a common optical table 4 (Fig. 1). The radiation source lies outside the cells and is installed in a water-cooled housing. An electromechanical

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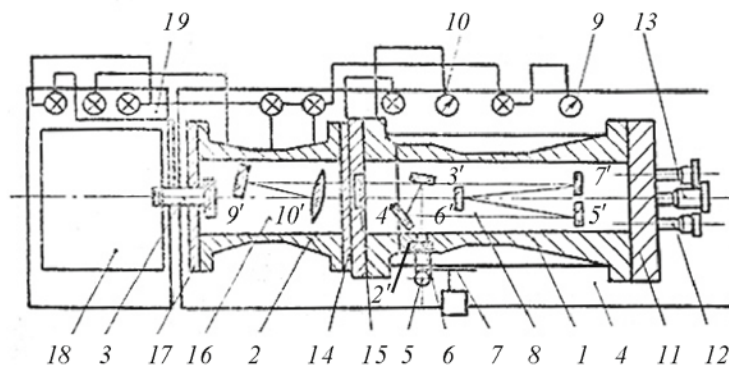


Fig. 1. Functional diagram of the apparatus for measuring the absorption spectra of gases at high pressures.

modulator 7 is mounted between the globar 5 and the protective input window 6 for the purpose of modulating the light beam at frequencies of 9 and 360 Hz. The first frequency can be used to record absorption spectra of gases during operation with standard type IKS-21 and IKS-31 spectrometers 18. The second modulation frequency provides for operation of the detection and recording system with cooled detectors, in particular a germanium bolometer that is cooled by liquid helium, and a photomultiplier. Modulation of the light flux through the input window of the cell makes it possible to eliminate the parasitic signal caused by the radiation of the optical system and the cell walls.

The mirrors in the White configuration are mounted on an optical bench 8 and have adjustable positioners. The rear mirrors are suspended on slabs and can be turned relative to one another by a certain angle that is fixed according to a graduated circle. In order to avoid misalignment during temperature variations in the cell, all the mechanical components of the optical system are made of invar, which has a small coefficient of thermal expansion.

The ends of the high pressure housing are closed by the cover 11 and 14. The following are mounted on cover 11: an ocular for visual monitoring of the number of passes of the light beam, valves 12 for input of the test gas, a wedge mechanism 13 for turning the rear mirrors in the multipass cell, safety valves (working at 150 atm, regulator for 225 atm, and a valve for purging gases from the cell), and a pumpdown valve. The housing of the middle cell is attached to the cover 14 of the multipass cell, and the small gas cell 3, to the cover 17 of the middle cell. The flanges on the cell housing and the covers have grooves for seals. Fiber gaskets are used to seal the volumes. All three cells have independent pumpdown, inlet, and monitoring of the test gas by means of a manometer 9 and a model 1227 vacuum gauge 10; these can be used to model gaseous media that are nonuniform in pressure and temperature.

In order to ensure a good seal at high pressures, a self-sealing conical window design is used which ensures reliable leak tightness of the cell at high pressures, as well as under vacuum. Replaceable windows made of quartz, barium fluoride, KRS-5, and IKS infrared glass cover the spectral range from 0.3–30  $\mu\text{m}$ . The windows 6 and 15 of the multipass gas cell are in the shape of a truncated cone and are installed in conical supports which are screwed into the housing of the cell and the cover 14.

The windows self-seal because the gas pressure at the end contact surfaces is higher than the air pressure outside the cell. Essentially ideal polishing of the crystalline cone with the conical support reduces the tendency of the crystals to fracture. Calculations and testing for hardness showed that the self-sealing design for the windows has considerable advantage over a flat window configuration. U-2-28 high temperature sealant is applied to the contact surface to ensure smooth movement of the crystal with changing pressure and temperature of the test gas and to prevent shear in the crystal layers.

A heater is installed in the inner cavity of the multipass gas cell to heat the gas in the working volume up to 600 K. A coil is welded to the cell housing for cooling with a liquid. The gas temperature in the center cavity of the multipass cell and cell housing is monitored with thermocouples. Power is supplied to the electric furnace and the thermocouples are connected through hermetic seals with glass-textolite insulators and these are sealed with epoxy.

Because of the high mass of the cell assembly and for convenience in replacing the window 15 separating the middle cell and the multipass gas cell, the entire system is mounted on rails and can be moved along the optical table. The set of cells was checked by hydraulic tests at a pressure of 230 atm and under vacuum.

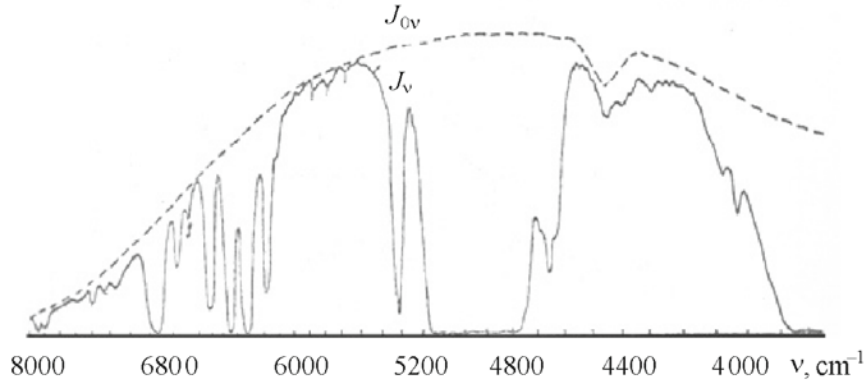


Fig. 2. A trace of the absorption spectrum  $J_v$  of carbon dioxide  $\text{CO}_2$  in the 1.2–2.4  $\mu\text{m}$  range for a pressure  $P_{\text{CO}_2} = 40$  atm and path length  $L = 16$  m;  $J_{0v}$  is the baseline.

For studies in the IR, visible, and UV regions of the spectrum, the system is equipped with a modernized IKS-21 spectrograph and a spectrometer based on an MDR-2 monochromator. To eliminate atmospheric absorption, the spectrometer and source unit are flushed with nitrogen and helium to remove contaminants.

Given the comparatively small cell dimensions and the possibility of modelling high gas pressures, this spectral system can be used to study absorption spectra for high contents of the absorbing gas. Thus, it is possible to investigate weak vibrational-rotational absorption bands of the atmospheric gases, pressure-induced absorption, and continuum absorption of (vibrational-rotational) bands by the wings of spectrum lines for different pressures and temperatures of the test gas.

Figure 2 shows a spectral trace of absorption by commercial carbon dioxide recorded using the IKS-21 spectrometer with an LiF prism and a diffraction grating used as the dispersing element.

**Experimental Results and Discussion.** The major results obtained with this measurement system reduce to obtaining the spectral transmission functions for different temperatures and pressures of the components of the atmospheres of planets in the solar system, in order to parametrize then and carry out radiative transfer calculations in planetary atmospheres [1, 2] taking continuum absorption by the wings of spectrum lines and pressure-induced absorption into account. The measured spectral transmission functions  $\tau_v$  ( $\nu$  is the wave number) are defined by

$$\tau_v = J_v/J_{0v}, \quad (1)$$

where  $J_v$  is the spectral intensity of the radiation after passage through the medium in the cells and  $J_{0v}$  is the intensity distribution of the radiation when the cells are evacuated. Figure 3 shows a measured spectra  $\tau_v$  of carbon dioxide at different pressures  $P_{\text{CO}_2}$  and abundances  $\omega_{\text{CO}_2}$  in the multipass cell together with the spectral transmission function of  $\text{CO}_2$  calculated by direct integration. The measurements with high amounts of  $\text{CO}_2$  have revealed new absorption bands of different isotopes of  $\text{CO}_2$ , which did not show up for small amounts of  $\text{CO}_2$  and made it possible to determine the continuum absorption coefficients owing to absorption lines of strong vibrational-rotational bands. The experimental data on continuum absorption by  $\text{CO}_2$  were processed using all the data on the experimental parameters of the absorption lines [7] for an analytic dependence

$$b'(\nu - \nu_i) = (\nu - \nu_i)^{-\alpha} \exp[-a((\nu - \nu_i) - d)^c] \quad (2)$$

of the factor characterizing the difference between the true line profile  $b = b_L b'(\nu - \nu_i)$  and a Lorentz profile  $b_L$  when  $(\nu - \nu_i) \geq d$  for vibrational-rotational bands near 1.4, 1.6, 2.0, 2.7, 4.3, and 15.0  $\mu\text{m}$ , and  $\text{CO}_2\text{-CO}_2$  and  $\text{CO}_2\text{-N}_2$  collisions.

The parameters  $a$ ,  $b$ ,  $c$ , and  $\alpha$  were determined by a least squares method. As opposed to theoretical formulas [11] indicating a strong asymmetry in the  $\text{CO}_2$  absorption line profiles, our experimental data indicate an exponential drop in the absorption coefficients with increasing  $(\nu - \nu_i)$  in the high- and low-frequency wings of the  $\text{CO}_2$  absorption line profiles, both with self broadening and with nitrogen collisional broadening, while the absorption line profiles are close to symmetric. Table 1 lists the parameters  $a$ ,  $b$ ,  $c$ , and  $\alpha$  of  $\text{CO}_2$  absorption lines with self broadening and with nitrogen collisional broadening.

A high-temperature atlas of the parameters of  $\text{CO}_2$  absorption line profiles [7] has been developed with all the isotopes of  $\text{CO}_2$  and experimental data on the influence of the Fermi resonance on the intensity of the  $\text{CO}_2$  absorption lines taken into account. Figure 3 compares the fine structure of the measured  $\text{CO}_2$  spectra with spectra calculated by direct integration.

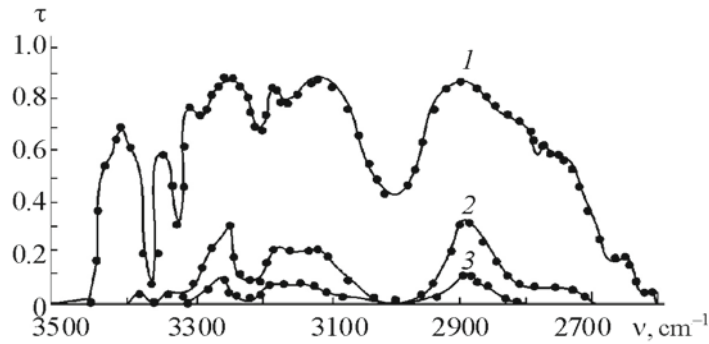


Fig. 3. Comparison of absorption spectra of carbon dioxide gas in the 2600–3500  $\text{cm}^{-1}$  range measured with a resolution of  $\Delta \approx 10 \text{ cm}^{-1}$  (curves) and calculated by direct integration (points); the abundances are  $\omega_{\text{CO}_2} = 4 \cdot 10^4$  (1),  $12 \cdot 10^4$  (2),  $23 \cdot 10^4 \text{ atm}\cdot\text{cm}$  (3) and the pressures are  $P_{\text{CO}_2} = 10$  (1), 30 (2), and 35 atm (3).

TABLE 1. The Parameters  $a$ ,  $c$ ,  $d$ , and  $\alpha$  of the Absorption Spectrum Line Profiles of  $\text{CO}_2$  for  $\text{CO}_2\text{--CO}_2$  and  $\text{CO}_2\text{--N}_2$  Molecular Collisions

Band, $\mu\text{m}$	Collisions	$a$	$c$	$d$	$\alpha$
1.4	$\text{CO}_2\text{--N}_2$	0.61	0.52	2	-0.02
1.4	$\text{CO}_2\text{--CO}_2$	0.08	0.58	46	-0.06
1.6	$\text{CO}_2\text{--N}_2$	0.64	0.42	3	+0.02
1.6	$\text{CO}_2\text{--CO}_2$	0.09	0.64	39	-0.05
2.0	$\text{CO}_2\text{--N}_2$	0.56	0.42	1	+0.03
2.0	$\text{CO}_2\text{--CO}_2$	0.06	0.75	32	0.03
2.7	$\text{CO}_2\text{--N}_2$	0.61	0.36	2	0
2.7	$\text{CO}_2\text{--CO}_2$	0.065	0.80	6	-0.01
4.3	$\text{CO}_2\text{--N}_2$	0.49	0.46	1	0
4.3	$\text{CO}_2\text{--CO}_2$	0.098	0.72	10	0
15.0	$\text{CO}_2\text{--N}_2$	0.044	0.61	3	0
15.0	$\text{CO}_2\text{--CO}_2$	0.090	0.85	4	0

The pressure induced absorption of  $\text{CO}_2$  is taken into account using experimental data obtained with the measurement system described in this paper. The satisfactory agreement between these spectra indicates that the parametrization developed for the absorption spectra of gases is applicable to radiative heat transfer problems. The continuum absorption coefficients of water vapor a given in [2] for self-broadening and nitrogen collisional broadening.

With regard to the effect of intermolecular collisions on molecular absorption spectra, we note that the  $P$ -,  $R$ -, and  $Q$ -branches have been resolved in the pressure-induced absorption spectra. Thus, for parallel vibrational-rotational bands without a  $Q$ -branch, this prohibition is partially removed for high pressures of broadening  $\text{CO}_2$  or  $\text{N}_2$  gas. A  $Q$ -branch may appear in the vibrational-rotational spectra and more strongly so with increasing pressure of  $\text{CO}_2$  or  $\text{N}_2$ .

**Conclusions.** A measurement system has been developed for studying the absorption spectra of gaseous media at high pressures. This system has been tested and used to investigate pressure-induced absorption and the profiles of absorption lines, measure the integrated intensities of vibrational-rotational absorption bands of various species in planetary atmospheres, and study the spectral transmission functions in structurally inhomogeneous media.

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