SPECTROMETER FOR NONLINEAR SPECTROSCOPY OF MOLECULAR GASES IN THE NEAR IR

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A spectrometer for the near IR with resolution not worse than 0.05 cm^{-1} *is built based on an optical parametric oscillator (OPO). The spectrometer uses a* $LiIO_3$ *crystal with a transmission band up to 3.7* μm*; its frequency tuning is performed automatically (the tuning region is determined by the resonator mirrors); in the 1.7–2.3* μm *band it provides an output pulse energy of up to 30* mJ *at a repetition rate of 0.2–0.5* Hz. *The absorption of powerful IR radiation by molecular* NH_3 *is studied using this spectrometer.*

Nonlinear absorption and excitation processes, taking place in molecules of some atmospheric gases under the action of high-power resonance laser radiation in the IR, can substantially change the conditions of propagation of the laser radiation itself in the atmosphere. A detailed investigation of these processes is of considerable interest for spectroscopy[1] and laser chemistry.[2]

Theoretical and experimental investigations of the multiphoton excitation and dissociation of molecules in the IR range for vibrational- rotational transitions were carried out in a number of papers cited in Ref. 2. Here usually CO_2 lasers, emitting in the range from 9 to 10 μm were used. There are a number of molecules normally with hydrogen bonds (including some atmospheric components) which have strong absorption bands in the range $\lambda = 2$ to 5 μm (e.g., water vapor, hydrides, hydrocarbons, and some metalloorganic compounds). In addition, the frequencies of the overtones and the combination vibrations of some of these molecules also fall in this range. And though the dipole moments of the transitions in this case are usually considerably less than the main ones, nevertheless the investigation of processes starting with a transition of such a type is of definite interest.

The lack of investigations into the multiphoton excitation and dissociation processes in the middle IR is caused by the absence of effectively operating radiation sources of sufficient power. The specific features of the investigated object (molecular gases) imposes certain specific requirements on such sources. First, they must be frequency-tunable over a wide range and highly stable both in intensity and in frequency. Second, the linewidth $\Delta\nu$ of such sources must lie in the range 10^{-3}–10^{-2} cm^{-1} because the widths of the gaseous absorption lines in this range at a pressure of a few Torr are typically of this same order. And finally, since nonlinear processes in molecules subjected to the action of radiation are known to appear at high (tens to hundreds of MW/cm^2) intensity levels, the sources must produce high-power radiation with a high degree of spatial coherence.

At present, these requirements can be most suitable satisfied by sources of coherent radiation based on the use of frequency conversion of laser radiation by methods of nonlinear optics, in particular, optical parametric oscillators (OPO) and parametric frequency converters.

The spectrometer described here consists of a pumping generator, an OPO, a cell with the investigated gas, and a recording system. The single-frequency pumping generator emits at a repetition rate up to 0.5 Hz at the wavelength 1.053 μm and yields an output energy of ~ 1 J in a pulse of 50 ns duration. The OPO with a noncollinear interaction was assembled according to a scheme with nonresonant pumping reflection.[3] All of the operations of wavelength tuning and recording and output power control are automated. Coarse tuning of the generation wavelength (within the limits of several cm^{-1}) is carried out by turning the nonlinear crystal with a stepper motor while the fine tuning is performed by varying the voltage applied to the piezoceramic drive of one of the intracavity Fabry-Perot etalon mirrors. As a nonlinear element in the master oscillator we used a $LiIO_3$ crystal 7 cm long, the boundary of whose transparency range is at about 3.7 μm. The width of the emission line with no intracavity Fabry-Perot etalon was about 1 cm^{-1}, and about 0.05 cm^{-1} with such an etalon.

The output energy of the OPO was as high as 20–30 mJ in the range 1.7 to 2.3 μm (the tuning region is determined by the resonator mirrors), and the beam divergence was close to diffraction limited, i.e., about 10^{-4} rad in the horizontal plane and $5 \cdot 10^{-4}$ rad in the vertical plane.

The measurements of the wavelength of the output radiation and the spectral width of the radiation of the OPO as well as tuning control were performed using an automated grating spectrograph.[4] The spectral range of this device is determined by the sensitivity range of a commercial KTP-67 TV camera (from 0.4 to 1.2 μm). That is why for recording the OPO spectral characteristics its output radiation was frequency converted into the second harmonic in $LiIO_3$ crystal (to the spectral region at $\lambda \sim 1$ μm). The resolution of the spectrograph in the range 2–3 μm proved to be not worse than 0.05 cm^{-1}. In addition to the spectrograph, the data aquisition and recording system includes power meters and an optoacoustlc detector of the absorbed energy and a computer for experimental control and data processing.

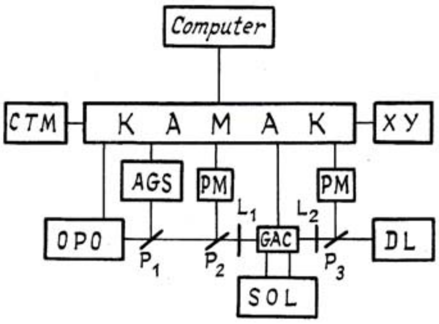

FIG. 1. Block diagram of the complex for investigation of the nonlinear absorption of NH_3 *molecules: color TV monitor (CTM); X-Y plotter (XY); automated grating spectrograph (AGS); optical parametric oscillator (OPO); power meter PPM); dye-laser (DL); gas absorption cell (GAO of the optoacoustic absorption detector; a system for observing the luminescence (SOL) in the visible range using a PMT (FEU-28) and an MDR-2 grating monochromator and a C8-12 oscilloscope;* $L_{1,2}$ *are quartz lines;* $P_{1,2,3}$ *are quartz plates.*

As our object of study we chose gaseous ammonia since the OPO emission range includes the NH_3 molecular absorption bands due to the combination vibrations $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$.[5] The strongest lines belong to the band $\nu_3 + \nu_4$. We have investigated absorption by the NH_3 molecule within this band for strong resonant pumping by OPO radiation. In Ref. 6, where a CO_2 laser was used, dissociation of the ammonia molecule was observed using single-frequency irradiation in the IR. In our case the energy of a photon of incident radiation is five times greater than in Ref. 6, that is why the occurrence of the multiphoton vibrational dissociation of NH_3 was not excluded even for single-frequency excitation. The most probable product of NH_3 dissociation is the NH_2 radical (the binding energy of the H–NH_2 bond is ~ 4.4 eV (Ref. 7)). These molecules can be detected by illuminating the region of accumulation of these radicals with dye-laser radiation at $\lambda = 5979$ Å and observing the visible luminescence of the excited NH_2 radicals (see, e.g., Refs. 8 and 9). For this reason we have also included in the experimental setup a dye-laser, a monochromator, and a PMT to provide for observations of the above-mentioned fluorescence. The data acquisition and processing system consisted of primary sensors which transformed the optical and acoustic signals into electric ones, which are then fed via ADC's into the computer memory, which are incorporated into a CAMAC block. An LST-11/23 minicomputer records and processes the data, sends them to the display, and controls the experiment. A block diagram of the entire complex is shown in Fig. 1.

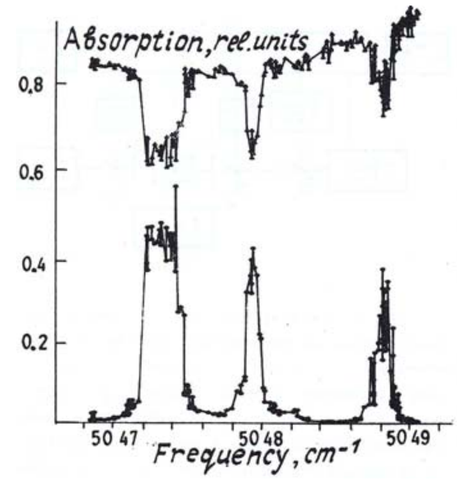

FIG. 2. A portion of the NH_3 *absorption spectrum.*

Figure 2 shows a portion of the NH_3 absorption spectrum in the region 5047–5048 cm^{-1}, corresponding to the $\nu_3 + \nu_4$ band obtained from optoacoustic measurements (lower curve) and from direct measurements of the absorbed energy (upper curve). The spectra were measured at a pressure of 18 Torr. As the investigations showed, the strongest line in the range 4985–5050 cm^{-1} was the line in the vicinity of 5047.3 cm^{-1}. For this line we measured the dependences of the optoacoustic signal A_{oac} on the energy density in the caustic region at high (Fig. 3) and low (Fig. 4) levels of energy density.

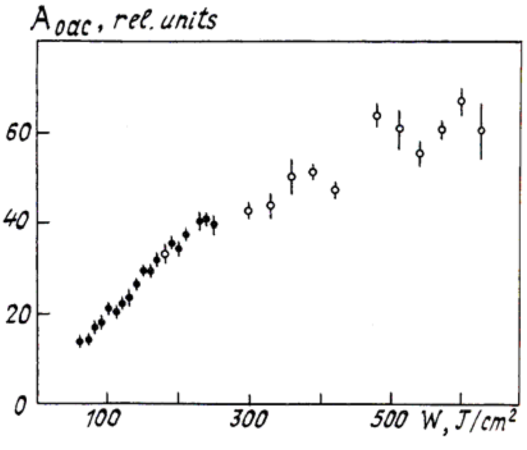

FIG. 3. Dependence of the absorption optoacoustic signal on energy density at the focus of the lens L_1 *at* $W \approx 12$ J/cm².

Note that the signal amplitude, which was recorded by a microphone, was proportional to the energy absorbed in the region of the focal caustic of the lens. This was achieved by means of two diaphragms, which made it possible to separate out the signal from the region of the caustic. Figure 4 shows that absorption saturation begins at a very low (0.1–0.2 J/cm^2) energy density. Estimates show that an average absorption level of about 10 photons per molecule is achieved, which corresponds approximately to the dissociation energy (7–8 photons/molecule). Nevertheless, visible luminescence from the illuminated volume was not observed, neither without illumination of the focal caustic region by the dye-laser radiation nor with it.

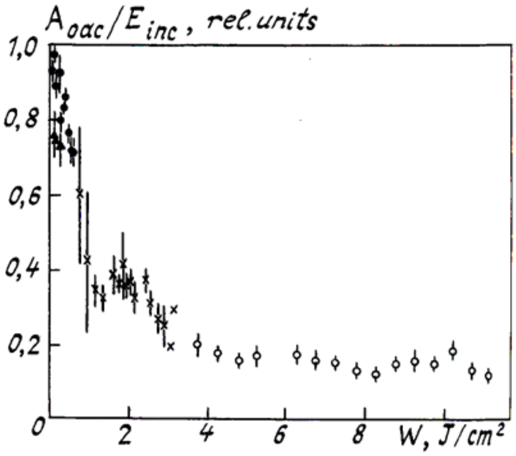

FIG. 4. Dependence of the absorption optoacoustic signal normalized by the incident energy at $\lambda = 5047.3$ cm^{-1} *on energy density at the focus of the lens* L_1 *at* $W \approx 12$ J/cm^2.

In our case the process of thermal relaxation (V–T relaxation) seems to be inessential since the characteristic time of V–T relaxation in NH_3 at a pressure of 18 Torr is, according to Ref. 7, about 150 ns, which significantly exceeds the duration of the exciting radiation pulse (τ_p = 30 ns).

Thus onthe basis of the obtained data one can conclude that nonlinear absorption of IR radiation by the ammonia molecule takes place; however, the achieved level of excitation seems to be insufficient for the dissociation of this molecule.

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