

Role of water vapour in the absorption of nanosecond 266-nm laser pulses by atmospheric air

A.N. Kuryak, B.A. Tikhomirov

Abstract. The absorption of the Nd:YAG fourth harmonic in air and binary mixtures of water vapour with nitrogen and oxygen at atmospheric pressure has been measured as a function of pulse energy (peak intensity). The mixtures obtained by adding equal amounts of water vapour to dry nitrogen and oxygen have been found to differ significantly in absorption. Preliminary quantitative data have been obtained for two- and three-photon absorption cross sections of water and oxygen molecules: $\sigma^{(2)}(\text{H}_2\text{O}) = (4 \pm 1) \times 10^{-49} \text{ cm}^4 \text{ s}$ and $\sigma^{(3)}(\text{O}_2) = (5.6 \pm 1.4) \times 10^{-78} \text{ cm}^6 \text{ s}^2$. The absorption of 266-nm pulses with peak intensities from 0.05 to 2 GW cm⁻² in the near-surface atmosphere has been shown to be determined by two-photon absorption in water vapour and three-photon absorption in oxygen. In moist air containing 1% water vapour, the absorption coefficient for 266-nm laser pulses exceeds that in dry air by four to five times. There is no absorption in nitrogen. We have developed a technique for photoacoustic measurements of multiphoton absorption cross sections in single-component gases and gas mixtures.

Keywords: atmospheric air, water vapour, UV radiation, multiphoton absorption, photoacoustic detector.

1. Introduction

Recent years have seen a considerable growth of interest in research on the role of water vapour in the absorption of high-intensity UV laser radiation in air [1, 2], in particular in the case of laser beam filamentation in the atmosphere [3]. The increased interest in this issue is primarily due to the fact that, despite the relatively low content of water vapour in air, its contribution to the absorption of high-intensity UV radiation significantly exceeds that of the major components of air (nitrogen and oxygen), but this issue has not yet been addressed in detail. For example, Ionin et al. [1] demonstrated for the first time using photoacoustic (PA) spectroscopy that the absorption of femtosecond pulses with a wavelength of 248 nm and intensity $I \approx 10 \text{ GW cm}^{-2}$ in atmospheric air was an order of magnitude stronger than that in dry air and increased in proportion to the square of the light intensity. Using photogalvanic (PG) spectroscopy, Shutov et al. [2] showed that the absorption coefficient of water vapour in air and binary mixtures with nitrogen and oxygen for nano-

second 248-nm laser pulses at intensities in the range 0.1–10 GW cm⁻² was also proportional to the square of their intensity. As a physical mechanism, Shutov et al. [2] considered (2 + 1) resonance-enhanced multiphoton ionisation (REMPI), a process in which H₂O molecules are first promoted to highly excited electronic states via two-photon excitation and then ionised through absorption of another photon. The absorption coefficient of water vapour for femtosecond laser pulses with an intensity from 0.01 to 10 TW cm⁻² is proportional to the cube of their intensity. In this case, light absorption is due to (3 + 1) REMPI of H₂O molecules. The absorption in oxygen, observed throughout the intensity range examined (0.1 to 10⁴ GW cm⁻²), is due to three-photon ionisation of O₂ molecules. In nitrogen, there is no absorption of nanosecond pulses in the range 0.1–10 GW cm⁻², whereas femtosecond pulses are absorbed in the range 0.01–10 TW cm⁻² owing to (3 + 1) REMPI of N₂ molecules. According to Shutov et al. [2], the contributions of oxygen and nitrogen to the ionisation of atmospheric air by femtosecond laser pulses are in the ratio 5 : 3. If air contains ~2.5 vol % H₂O molecules, their contribution to absorption exceeds the total contribution of N₂ and O₂ molecules by an order of magnitude or even more for both femtosecond and nanosecond laser pulses.

As distinct from PG spectroscopy [4], which measures free electron concentration in a laser pulse propagation channel, PA spectroscopy [5] measures the amplitude of the pressure signal resulting from light absorption and a subsequent increase in the translational energy of molecules. Whereas the PG signal results only from ionisation of molecules, the PA signal can be due to a variety of physical processes: absorption on rovibrational and electronic transitions of molecules, stimulated Raman scattering, ionisation and dissociation of molecules, light absorption by photochemical reaction products, and others. PA spectroscopy was successfully used in gas analysis and to study absorption spectra of molecular gases in the visible, IR, and microwave spectral regions. In the UV spectral region, where light absorption is typically associated with electron excitation and multiphoton ionisation of atoms and molecules, the performance of PA spectroscopy, in our opinion, has not yet been studied in sufficient detail.

Pulsed Nd:YAG lasers with nonlinear frequency converters, capable of generating intense nanosecond pulses at five wavelengths, including three wavelengths in the UV, have been used in a large number of laboratory and full-scale experiments, e.g. in studies of the atmosphere by optical methods. However, quantitative data on multiphoton absorption cross sections of the main gaseous components of air (nitrogen, oxygen, and water vapour) for UV Nd:YAG laser radiation are not available in the literature.

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In this paper, we present quantitative data on multiphoton absorption cross sections of oxygen and water vapour for the fourth harmonic of a nanosecond Nd:YAG laser (266-nm wavelength). The data were obtained by measuring the PA signal amplitude as a function of pulse energy (light intensity) for binary mixtures of nitrogen and oxygen with water vapour.

2. Measurement technique

Figure 1 shows a schematic of the experimental setup used, which includes a Nd:YAG laser and PA detector for time-resolved measurements.

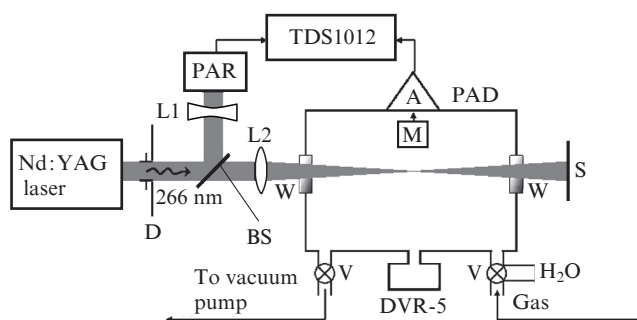


Figure 1. Schematic of the experimental setup: (BS) beam-splitting wedge; (L1) negative lens; (S) absorbing screen; (V) vacuum valve.

In combination with nonlinear converters of its fundamental frequency (1064 nm) to harmonics, the laser (model LS-2134U, Minsk, Belarus) allows one to obtain pulses of linearly polarised light at a wavelength of 266 nm (photon energy $h\nu \approx 4.7$ eV) with a duration $\tau_{0.5} = 6$ ns (FWHM) and a repetition rate of up to 15 Hz. The beam radius, with an intensity distribution in the form of concentric rings behind a diaphragm (D), is 4 mm. The pulse energy is varied in the range 0–20 mJ by discretely changing the discharge energy in a flash lamp and is measured by a calibrated PA receiver (PAR).

The PAD includes a cylindrical chamber 20 cm in diameter and 25 cm in length, with KU quartz glass optical windows (W) on its end faces for light propagation. The chamber contains an MK-301 condenser microphone (M) located in the focal plane of a lens (L2) with a focal length $F = 100$ cm. Absorption of a part of the laser pulse energy leads to the generation of a bipolar acoustic pulse in the PAD chamber. The amplitude of the acoustic pulse is proportional to the absorbed laser pulse energy and it is converted to an electrical signal by the microphone. The electrical signal from the microphone output is amplified by a broadband amplifier (A) and fed to a TDS1012 digital oscilloscope. In our experiments, the PAD signal amplitude U_0 was measured as a function of laser pulse energy E , with synchronous acquisition of 64 PAD and PAR signals for each laser pulse energy. It should be noted that, in the case of a PAD with time-resolved wanted and background acoustic signals, the amplitude U_0 is proportional to the absorbed laser pulse energy in a wide dynamic range (up to 120 dB) and is zero if there is no absorption in the gas under study.

Prior to measurements, the PAD chamber was pumped down several times to a residual pressure $P \approx 0.01$ mbar and

purged with nitrogen. Next, nitrogen or oxygen was admitted to the chamber. In our experiments, we used nitrogen (99.996%) and oxygen (99.999%) containing no more than 10 ppm of moisture (manufactured by OOO PGS-servis). In the experiments with mixtures of these gases with water vapour, first water vapour was introduced into the chamber by evaporating double-distilled water into vacuum and then nitrogen or oxygen was added. Ambient air was introduced by prolonged pumping of air through the chamber. Gas pressure in the PAD chamber was measured with DVR-5 and VIT-2 vacuum gauges.

3. Technique for evaluating absorption cross sections

In the case of n -photon absorption of laser pulses with a Gaussian intensity distribution by a single-component gas, the PAD signal amplitude is given by [6]

$$U_0 \approx \alpha n^{3/4} [\sigma^{(n)} N n^{-3/2} I_0^{n-1}] E$$

$$= \alpha \sigma^{(n)} N n^{-3/2} \left(\frac{2\sqrt{\ln 2}}{\pi^{3/2} r_0^2 \tau_{0.5}} \right) E^n, \quad (1)$$

where α is the sensitivity of the PAD in the case of a linear absorption and $\sigma^{(n)}$ is the n -photon absorption cross section. The number of molecules of the absorbing gas is $N = LP$, where $L = 2.68 \times 10^{19} \text{ cm}^{-3}$ is the Loschmidt number and P is gas pressure. If there are a linear absorption ($n = 1$) and components of a nonlinear multiphoton absorption ($n = 2, 3, \dots$), the contributions of all the components in (1) should be summed up over n . The term $\sigma^{(n)} N n^{-3/2} I_0^{n-1}$ has the meaning of an effective n -photon absorption coefficient expressed through the peak intensity of a Gaussian pulse:

$$I_0 = \frac{2E}{\pi^{3/2} r_0^2 \tau},$$

where $\tau = \tau_{0.5} \sqrt{\ln 2}$ and r_0 is the Gaussian beam radius at which $I(r_0) = I_0 e^{-2}$. At $E = 1$ J, $r_0 = \sqrt{\lambda F / 2\pi} = 2.06 \times 10^{-2}$ cm [7], and $\tau_{0.5} = 6$ ns, the peak intensity is $I_0 = 141$ GW cm $^{-2}$.

From relation (1) for the n -photon absorption cross section, we obtain

$$\sigma^{(n)} \approx b^{(n)} n^{3/4} \left[\alpha \left(\frac{2\sqrt{\ln 2}}{\pi^{3/2} r_0^2 \tau_{0.5}} \right)^{n-1} L P E^{n-1} \right]^{-1}, \quad (2)$$

where $b^{(n)}$ is the fitting coefficient for the corresponding component in the experimental $U_0(E)$ data represented by an n th-degree polynomial. The physical quantities involved are expressed in the following units: $\sigma^{(n)}$, cm $^{2n} \text{ s}^{n-1} \text{ J}^{1-n}$; α , V J $^{-1}$ cm; P , bar; and E , J. To switch in (2) to the classic dimensions of the multiphoton absorption cross section, $\sigma^{(n)}$ [cm $^{2n} \text{ s}^{n-1}$] [8], the values obtained using (2) should be divided $n - 1$ times by 1.33×10^{18} , i.e. by the number of 266-nm photons per joule. Relation (1) was first used by us to find two-photon absorption cross sections of water vapour and dry air for femtosecond laser pulses at a wavelength of 800 nm [9].

Relation (1) is applicable if sensitivity α remains unchanged for all of the gases under study, i.e. at gas pressures, laser pulse durations, and laser beam radii for which the following relation is met [10]:

$$\frac{\tau_0}{P_{\text{total}}} \ll 1.316 \left(\tau^2 + \frac{r_0^2}{2V_s^2} \right)^{1/2}, \quad (3)$$

where τ_0 is the lifetime of molecules in an excited/ionised state at a total gas pressure $P_{\text{total}} = 1$ mbar, and V_s is the speed of sound. According to measurements by different methods [2, 11, 12], the plasma lifetime in a channel of femtosecond laser pulse propagation in air at atmospheric pressure does not exceed 10 ns. This means that, under the experimental conditions of this study, relation (3) is met at pressures $P_{\text{total}} \geq 200$ mbar.

Thus, to find the n -photon absorption cross section of a single-component gas, it is necessary to fit experimental $U_0(E)$ data with an n th-degree polynomial and then calculate the absorption cross sections using the fitting coefficients $b^{(n)}$ thus found and Eqn (2).

To increase the contribution of the linear absorption to $U_0(E)$, it is necessary to perform measurements using collimated beams or long-focus lenses. To increase the contribution of multiphoton absorption, short-focus lenses should be used. In the case of a gas for which relation (3) is difficult to meet (water vapour in this study), measurements are made using binary mixtures of this gas with another gas in which there is no absorption or which has a known absorption coefficient. The PAD is calibrated using the known absorption of laser pulses by a span gas.

4. Results and discussion

Figure 2 shows the PA signal amplitude U_0 as a function of laser pulse energy E (peak intensity I_0) at a wavelength of 266 nm for absorption by air, dry nitrogen, dry oxygen, and mixtures of nitrogen and oxygen with water vapour at a total gas and mixture pressure in the chamber $P_{\text{total}} = 1$ bar. The water vapour partial pressure $P_{\text{H}_2\text{O}}$ is 9.6 mbar in the binary mixtures and 17.1 mbar in air. It is seen from these data that the data points for all the gases under study on the whole fall close to the fitting curves.

Table 1 gives the composition of the gases under study and the coefficients $b^{(n)}$ obtained by fitting experimental data with a cubic polynomial: $U_0 = b^{(1)}E + b^{(2)}E^2 + b^{(3)}E^3$. It follows from Table 1 and Fig. 2 that, at peak intensities of laser pulses from 5.5×10^{-2} to 2 GW cm⁻² in dry oxygen, there are linear and three-photon absorption processes. The coefficients $b^{(1)}(\text{O}_2)$ and $b^{(3)}(\text{O}_2)$ are reconstructed as a result of fitting with a relative uncertainty of 3.3% and 0.7%, respectively. The negligible coefficient $b^{(2)}(\text{O}_2) = 5.9 \times 10^{-13}$, which is reconstructed as a result of fitting with no standard deviation (SD), suggests that there is no two-photon process in oxygen.

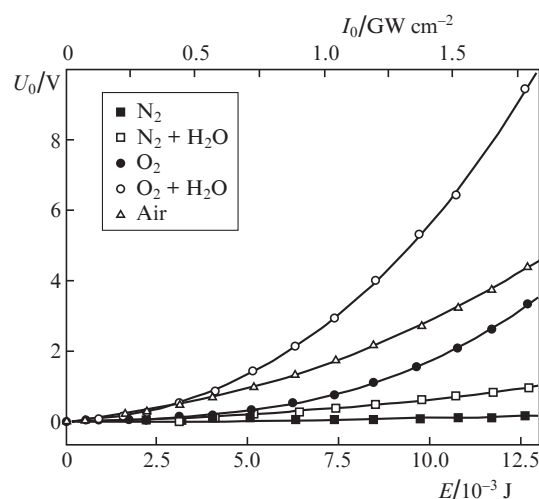


Figure 2. PA signal amplitude as a function of the energy and intensity of Gaussian laser pulses at a wavelength of 266 nm in nitrogen, oxygen, and their mixtures with water vapour and atmospheric air.

According to Bogumil et al. [13], the linear absorption cross section of oxygen at a wavelength of 266 nm in the Herzberg I band is $\sigma^{(1)}(\text{O}_2) = 9.4 \times 10^{-25}$ cm². We use $\sigma^{(1)}$ and the fitting coefficient $b^{(1)}(\text{O}_2) = 23.4$ from Table 1 for calibrating the PAD, i.e. using (2) we find the sensitivity of the PAD to be $\alpha = 9.3 \times 10^7$ V J⁻¹ cm, which agrees well with previous calibration results for this PAD ($\alpha = 10.5 \times 10^7$ V J⁻¹ cm) from the known absorption of nanosecond Gaussian pulses ($\lambda = 694$ nm) on rovibrational transitions of water vapour molecules in atmospheric air [14]. The term in round brackets in (2) is 1.2×10^{11} cm⁻² s⁻¹. Substituting the values thus found into (3), we obtain simple relations for the absorption components in a single-component gas:

$$\sigma^{(1)} \approx 4.0 \times 10^{-26} b^{(1)}/P, \quad (4a)$$

$$\sigma^{(2)} \approx 4.4 \times 10^{-55} b^{(2)}/P, \quad (4b)$$

$$\sigma^{(3)} \approx 3.8 \times 10^{-84} b^{(3)}/P. \quad (4c)$$

These relations and the fitting coefficients presented in Table 1 were used to find absorption cross sections. The estimated cross sections are listed in Table 2, which indicates uncertainties corresponding to the SDs in reconstructing the coefficients $b^{(n)}$ from Table 1. Next to the chemical formula of

Table 1. Coefficients obtained by fitting experimental data with a cubic polynomial.

Gas	$P_{\text{total}}/\text{mbar}$	$P_{\text{H}_2\text{O}}/\text{mbar}$	$b^{(1)}$	$b^{(2)}/10^2$	$b^{(3)}/10^5$
1. O ₂	1000	0	23.4 ± 0.8	5.9 × 10 ⁻¹⁵	14.7 ± 0.1
2. O ₂ + H ₂ O	1000	9.6	37.2 ± 14.5	388.7 ± 34.9	13.5 ± 2.0
3. N ₂	1000	0	0.9 ± 0.1	8.2 ± 0.1	5.1 × 10 ⁻¹⁶
4. N ₂ + H ₂ O	1000	9.6	14.3 ± 1.1	48.8 ± 0.1	6.8 × 10 ⁻¹⁵
5. Air + H ₂ O	977	17.1	102.1 ± 7.0	155.3 ± 16.8	2.8 ± 0.1
6. O ₂ + H ₂ O	1000	9.6	23.4 + (22.1 ± 6.0)	48.8 + (317.9 ± 5.6)	14.7
7. Air + H ₂ O	977	17.1	0.2 × 23.4 + (99 ± 2.9)	1.78 × 48.8 + (150.0 ± 2.8)	0.2 × 14.7

Note: The italicised numbers represent fixed coefficients used in experimental data processing.

Table 2. Absorption cross sections for laser pulses (266 nm).

Gas	H_2O , $U_i = 12.6$ eV, $D_0 = 5.1$ eV		N_2 , $U_i = 15.6$ eV, $D_0 = 9.8$ eV		O_2 , $U_i = 12.1$ eV, $D_0 = 5.1$ eV	
	$\sigma^{(1)}/10^{-23}$ cm ²	$\sigma^{(2)}/10^{-50}$ cm ⁴ s	$\sigma^{(1)}/10^{-26}$ cm ²	$\sigma^{(2)}/10^{-53}$ cm ⁴ s	$\sigma^{(1)}/10^{-25}$ cm ²	$\sigma^{(3)}/10^{-78}$ cm ⁶ s ²
1. O_2	–	–	–	–	9.4 ± 0.3	5.6 ± 0.1
2. $\text{O}_2 + \text{H}_2\text{O}$	15.6 ± 6.1	176.5 ± 15.9	–	–	0	5.2 ± 0.8
3. N_2	–	–	3.7 ± 0.5	3.6 ± 0.1	–	–
4. $\text{N}_2 + \text{H}_2\text{O}$	6.0 ± 0.5	2.2 ± 0.1	–	–	–	–
5. Air + H_2O	24.0 ± 1.6	39.6 ± 4.3	0	0	0	5.3 ± 0.2
6. $\text{O}_2 + \text{H}_2\text{O}$	9.3 ± 2.5	$2.2 + (144.7 \pm 2.7)$	0	0	9.4	5.6
7. Air + H_2O	23.4 ± 0.7	$2.2 + (38.2 \pm 0.7)$	0	0	9.4	5.6

Note: The italicised numbers represent fixed absorption cross sections used in experimental data processing.

each molecule, we give its first ionisation potential U_i and dissociation energy D_0 borrowed from Ref. [15]. In particular, for dry oxygen (the first row in the body of Table 2) we obtain $\sigma^{(1)}(\text{O}_2) = (9.4 \pm 0.3) \times 10^{-25}$ cm² and $\sigma^{(3)}(\text{O}_2) = (5.6 \pm 0.1) \times 10^{-78}$ cm⁶ s².

In the case of the mixture of nitrogen and water vapour, we observe a linear and two-photon absorption, without a three-photon process. At the present stage, we are at a loss as to the origin of the linear absorption in moist nitrogen, but it is reasonable to assume that the absorption is unrelated to ionisation of N_2 or H_2O molecules, because the ionisation of these molecules requires at least three or two photons, respectively. Recall that, using PG spectroscopy, Shutov et al. [2] demonstrated two-photon ionisation of H_2O molecules in the range $I_0 = 0.1$ – 10 GW cm⁻², without detecting nitrogen ionisation by nanosecond pulses at a wavelength of 248 nm ($h\nu \approx 5$ eV). Using femtosecond pulses, they detected three-photon ionisation of nitrogen molecules in the range $I_0 = 0.01$ – 10 TW cm⁻².

The likely mechanism behind the linear absorption of nanosecond laser pulses at a wavelength of 266 nm by water vapour is the dissociation of H_2O molecules and subsequent absorption of light by the resultant OH molecules. The dissociation of molecules in a single-photon process under the effect of UV radiation at a photon energy $h\nu < D_0$ is possible in the case of vibrationally excited molecules in their electronic ground state [16]. In our case, a suitable candidate is the $2\nu_2$ vibrational state of H_2O molecules, with an excitation energy $E_{\text{osc}} = 0.4$ eV sufficient for bringing a H_2O molecule to a state near the dissociation threshold. The feasibility of such UV absorption by H_2O molecules was analysed in detail by Buldakov et al. [17]. According to Merola et al. [18] and Sulakshina and Borkov [19], the range 250–320 nm contains strong absorption bands of OH radicals, corresponding to the Π – Σ electronic transition.

The absorption (amplitude U_0) in dry nitrogen is about one order of magnitude weaker than that in the binary mixture of nitrogen and water vapour (Fig. 2). The absorption cross sections obtained for water vapour molecules (Table 2, fourth row) are about three orders of magnitude larger than those of a nitrogen molecule (third row). Therefore, it is reasonable to attribute the observed linear and two-photon absorption at 266 nm in dry nitrogen to the small amount of residual H_2O molecules in the PAD chamber. Using repeated pumping, with prolonged holding under vacuum, and purging of the PAD chamber with nitrogen, we were able to reduce the PA signal by a factor of two relative to the first filling with nitrogen, but not to zero.

The addition of water vapour to dry gases (nitrogen and oxygen) considerably increases the absorption in them, leading however to different increases (Fig. 2). For example, at a peak intensity $I_0 = 1.5$ GW cm⁻² the addition of water vapour (9.6 mbar) to nitrogen increases the amplitude U_0 from 0.1 V in dry nitrogen to 0.7 V in the mixture of nitrogen with water vapour. The addition of the same amount of water vapour to oxygen leads to an increase in U_0 from 2 to 6.4 V, i.e. the contribution of water vapour to the absorption in oxygen is seven times that to the absorption in nitrogen. Analysis of the $U_0(I_0)$ experimental data obtained for the mixtures of oxygen and nitrogen with water vapour throughout the range studied demonstrates an even larger difference (by 80 times) between the two-photon absorption cross sections of water vapour and a smaller difference (by a factor of 2.6) between the linear absorption cross sections. The only possible reason for this is that, in the case of the mixture of oxygen with water vapour, raising the light intensity leads to effective generation of not only OH but also other strongly absorbing species, e.g. ozone molecules and oxygen ions, as a result of photochemical reactions in the laser pulse propagation channel. Therefore, the $\sigma^{(2)}(\text{H}_2\text{O})$ values extracted from the data for moist oxygen and air (Table 2, second and fifth rows) can be only formally assigned to two-photon absorption by water vapour: actually, this is not so.

It should be noted that the $\sigma^{(3)}(\text{H}_2\text{O})$ cross sections evaluated from the experimental data for dry and moist oxygen differ little (to within fitting accuracy). Besides, a similar $\sigma^{(3)}(\text{H}_2\text{O})$ value follows from measurement results for air (Table 2, fifth row). The $\sigma^{(1)}(\text{H}_2\text{O})$ evaluated from the $U_0(E)$ experimental data for air (fifth row) considerably exceeds the values extracted from the analogous data for the mixtures of oxygen and nitrogen with water vapour (second and fourth rows). This is attributable to contamination of atmospheric air.

In the mixture of oxygen and water vapour (Table 2, second row), the contribution of linear absorption is attributable to the water vapour (we neglect the linear absorption component in oxygen). In the sixth row of Table 1, we take into account the contribution of the linear absorption by oxygen, i.e. in fitting the relevant experimental data the coefficient $b^{(1)}$ is represented in the form $b^{(1)}(\text{O}_2 + \text{H}_2\text{O}) = b^{(1)}(\text{O}_2) + b^{(1)}(\text{H}_2\text{O})$, where $b^{(1)}(\text{O}_2) = 23.4$ (Table 1, first row); the coefficient $b^{(3)}(\text{O}_2)$ is taken to be 14.7×10^5 (Table 1, first row); and the coefficient $b^{(2)}(\text{O}_2 + \text{H}_2\text{O})$ is divided into two terms: $b^{(2)}(\text{N}_2 + \text{H}_2\text{O}) + b^{(2)}(\text{H}_2\text{O})$, where $b^{(2)}(\text{N}_2 + \text{H}_2\text{O}) = 48.8 \times 10^2$ (ibid.). As a result, we obtain $\sigma^{(1)}(\text{H}_2\text{O})$ (Table 2, sixth row), which is only a factor of 1.5 larger than that of the mixture of

water vapour and nitrogen. Similar changes in analysis of the $U_0(E)$ experimental data for air have little effect on $\sigma^{(3)}(\text{H}_2\text{O})$ (Table 2, seventh row) relative to $\sigma^{(3)}(\text{H}_2\text{O})$ (Table 2, fifth row), which attests to air contamination. The factor 0.2 in the seventh row in Table 1 takes into account the oxygen content of air (20%), and the factor 1.78 is the ratio of the water vapour partial pressure in air to that in the $\text{N}_2 + \text{H}_2\text{O}$ mixture.

The largest contribution to the error of determination of the absorption cross sections of molecules is made by PAD calibration. Usually, the total $\sigma^{(n)}$ measurement error is taken to be at a level of 25% [5]. Therefore, the following absorption cross sections can be recommended for evaluating the absorption of laser pulses at a wavelength of 266 nm in the atmosphere: $\sigma^{(1)}(\text{O}_2) = 9.4 \times 10^{-25} \text{ cm}^2$ [13], $\sigma^{(1)}(\text{H}_2\text{O}) = (7 \pm 1.8) \times 10^{-23} \text{ cm}^2$, $\sigma^{(2)}(\text{H}_2\text{O}) = (4 \pm 1) \times 10^{-49} \text{ cm}^4 \text{ s}$, and $\sigma^{(3)}(\text{O}_2) = (5.6 \pm 1.4) \times 10^{-78} \text{ cm}^6 \text{ s}^2$.

Figure 3 illustrates the effect of light intensity on the absorption coefficients of dry air (20% oxygen) at $P_{\text{total}} = 1 \text{ bar}$ and moist air (1% water vapour) for 266-nm laser pulses. The data were obtained using the recommended absorption cross sections. Also shown in Fig. 3 are the contributions of oxygen (dashed lines) and water vapour (dotted lines) to the coefficient k . It is seen that, in the range $I_0 = 0.05\text{--}2 \text{ GW cm}^{-2}$ in dry air, k increases from 5×10^{-6} to $4.5 \times 10^{-5} \text{ cm}^{-1}$. At the lower boundary of this intensity range, the absorption in dry air is determined by the linear absorption in oxygen, whereas at the upper boundary the three-photon absorption process in oxygen prevails. The addition of water vapour (10 mbar) to dry air increases the absorption by four to five times, with a predominant contribution from the two-photon absorption by water molecules at the upper boundary of the range under consideration. At its lower boundary, absorption in moist air is determined by the linear absorption in both water vapour and oxygen. The reduced absorption coefficient k of water vapour in air ($1.8 \times 10^{-6} \text{ cm}^{-1} \text{ mbar}^{-1}$)

for a focused Nd:YAG fourth harmonic is essentially identical to the k obtained by cuvette measurements of the absorption of unfocused laser pulses ($\lambda = 266 \text{ nm}$) in water vapour without buffer gases [20].

5. Conclusions

We have developed a technique for PA measurements of multiphoton absorption cross sections of gases and gas mixtures and studied the effect of pulse energy (peak intensity) on the absorption of the Nd:YAG fourth harmonic in air and binary mixtures of water vapour with nitrogen and oxygen at atmospheric pressure. The mixtures obtained by adding a particular amount of water vapour to dry nitrogen or oxygen have been found to differ significantly in absorption. Possible causes of this effect have been discussed. Preliminary quantitative data have been obtained for absorption cross sections: $\sigma^{(2)}(\text{H}_2\text{O}) = (4 \pm 1) \times 10^{-49} \text{ cm}^4 \text{ s}$ for water vapour in air, $\sigma^{(2)}(\text{H}_2\text{O}) = (2.2 \pm 0.5) \times 10^{-50} \text{ cm}^4 \text{ s}$ for water vapour in nitrogen, and $\sigma^{(3)}(\text{O}_2) = (5.6 \pm 1.4) \times 10^{-78} \text{ cm}^6 \text{ s}^2$. In moist air containing 1% water vapour, the absorption coefficient for 266-nm laser pulses at intensities in the range $I_0 = 0.05\text{--}2 \text{ GW cm}^{-2}$ exceeds that in dry air by four to five times. At the lower boundary of this range, the absorption coefficient in air is determined by the linear absorption in water vapour and oxygen, whereas at the upper boundary the major contributions are made by a two-photon absorption in water vapour and three-photon absorption in oxygen. Absorption in nitrogen is negligible.

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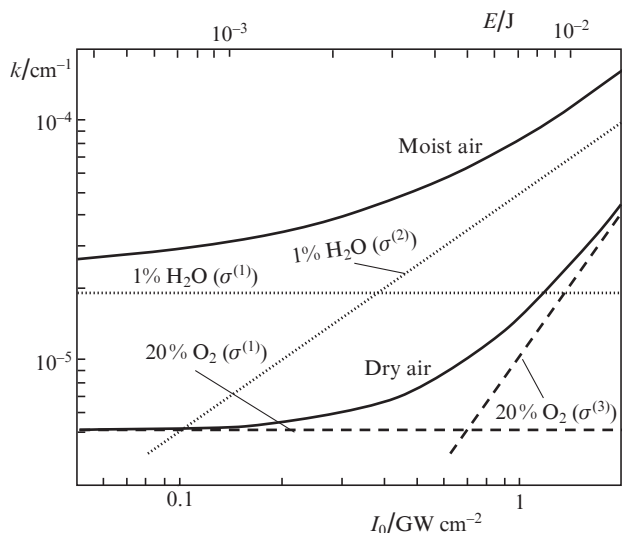


Figure 3. Absorption coefficient as a function of the intensity and energy of Gaussian laser pulses at a wavelength of 266 nm in dry and moist air and oxygen at a pressure $P_{\text{total}} = 1 \text{ bar}$. The dashed lines represent the linear and nonlinear absorption in oxygen, and the dotted lines represent that in water vapour.

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