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Laser method for dual-wavelength diagnosis and observation of spontaneous conversion of H_2O microparticles to H_2O_2

Mass spectrometry, fluorescence microscopy, and NMR methods are used to study the transformation of aerosol microparticles. A laser dual-wavelength method for microparticle diagnostics has been developed [1], which makes it possible to study in real time the spontaneous transformation of microparticles, for example, H_2O (in the size range from 1 to 20 μm and more) into H_2O_2 particles.

Recently, studies have been published [2, 3, 4], in which the effect of spontaneous conversion of H_2O microparticles into H_2O_2 microparticles by atomizing bulk water has been experimentally studied. Moreover, H_2O_2 production increases with decreasing diameter of H_2O, microdroplets generated in the range of 1 μm to 20 μm. In work [5], an experimental setup was created, including a mass spectrometer, with the help of which it was observed when spraying microdroplets of H_2O spontaneous formation of anion pyridine $C_5H_5N^-$ from a pre-prepared solution of pyridine: water. Moreover, this is the result of the experiment on spraying and formation $C_5H_5N^-$ was confirmed at both Nanjing University and Stanford University. The easy formation of $C_5H_5N^-$ in water microdroplets provides a direct route for green chemistry to synthesize chemicals. It can be noted that the chemistry of aqueous microdroplets is at the stage of active development. Let us give some examples that confirm this: the reduction of chlorogold acid ($H[AuCl_4]$) to gold nanoparticles [6], the reduction of a number of different carboxylic acids and the formation of hydrogen peroxide [2, 7]. No unambiguous theoretical explanation for such a phenomenon exists yet, but certainly points to the unique chemistry of aerosols occurring at the air-water interface.

In this paper discusses a new laser method for two-wave diagnostics of moving aerosol microparticles, which allows observing their spontaneous transformations in real time, for example, H_2O into H_2O_2.

A variant of construction of the sensing scheme of a laser dual-wavelength microparticle analyzer (LDAM) with symmetric reception of forward or backward scattered radiation with respect to two planes: the plane of two sensing beams *OXZ* and the plane *OYZ* located perpendicular to the plane *OXZ* and passing through the scheme axis *OZ* is considered. In this so-called axisymmetric two-frequency LDAM scheme, in which the frequency difference of the two probing beams is Ω_m, receiving optics axis OZ_3 coincides with the optical axis of the circuit *OZ*, and the scattered radiation is received in the spatial region of reception limited by the aperture of the diaphragm having two axes of symmetry OX_3 and OY_3 (see Fig. 1, where the OY_3Z_3 plane coincides with the *OXZ* plane and the OY_3Z_3 plane coincides with the *OYZ* plane) [8]. One of the variants of the design of the receiving diaphragm, providing axisymmetric reception, is, for example, a diaphragm with a cross-shaped opening, located in such a way that one of the slit-shaped openings of this diaphragm is oriented along the axis OX_3, and the other slit-shaped hole - along the axis OY_3. If the LDA sounding and reception scheme uses beams of equal intensity, having linearly matched polarizations with the direction of oscillation of the electric vectors in the *OYZ* plane, then, for example, when receiving forward-scattered radiation within a slit-shaped diaphragm oriented along the OY_3 axis, a high level of amplitude and phase matching is observed, and when receiving radiation within another slit-shaped opening of the diaphragm oriented along the OX_3 axis, a high level of polarization matching of the mixed scattered beams is observed. Depending on the conditions of microparticle flow diagnostics, it is always possible to select such cross-shaped diaphragm sizes that ensure a high level of photocurrent modulation depth and signal-to-noise ratio.

A theoretical model of an axisymmetric LDAM design is considered, which uses a diaphragm with a circular opening located at a distance r_0 from the center of measurement. When receiving forward scattered radiation, the position of the center of symmetry of the diaphragm O_p determined by angles $\theta = \gamma/2$, $\varphi_0 = 0$, and when receiving backscattered radiation – by angles $\theta_0 = 180°+\frac{\gamma}{2}$, $\varphi_0 = 180°$ (Fig. 1).

It should be noted that in the considered scheme of LDAM probing at symmetric reception of backscattered radiation the function of focusing and collecting lenses is performed by one lens, which allows to simplify considerably the layout of LDAM optical block and its alignment. Previously, in [8], the symmetry properties of the spatial structure of the Doppler signal relative to the *OXZ* and *OYZ* planes were considered for different polarization states of the probing beams. These symmetry properties should also be taken into account when analyzing the high-frequency signal parameters of the axisymmetric LDAM circuit. In addition, the following properties of the symmetry of the spatial structure of the high-frequency LDAM scheme should also be taken into account, when two probing beams of equal intensity have elliptical polarizations with the same azimuths and ellipticity, or the probing beams have right-handed (left-handed) polarizations, or two beams are linearly polarized and have equal azimuths. In this case, for two arbitrary directions of reception of axisymmetrical relative to the OZ axis of the scheme, the elementary high-frequency signals are phase-conjugate and have equal amplitudes, as well as equal values of the polarization and amplitude matching coefficients. This is the so-called second type of symmetrical reception of scattered radiation [9].

The noted properties of the symmetry of the spatial structure of the useful high-frequency signal allow, when calculating the parameters of this signal for the LDAM scheme with axisymmetric reception of scattered radiation, in a finite angular aperture, to neglect the interference terms of the low-frequency component of the signal, as well as the high-frequency components of the signal formed from mutually orthogonal components of the corresponding probing beams, since they are equal to zero [12]. As for the remaining high-frequency components of the signal, arising respectively from "*x*" and "*y*" – the components of two probing beams, then when determining them in this case it is sufficient to calculate the integrals within one quarter of the diaphragm, i.e. the integration boundaries for ε are taken within the range from $\varepsilon = 0$ to $\varepsilon = \frac{\pi}{2}$, followed by multiplying the resulting signal value by four.

The parameters of the high-frequency LDAM signal for the four-wave optical shift mode are analyzed [12]. If the LDAM scheme uses probing beams that have elliptical polarizations with equal azimuths and ellipticity, or circular polarizations - right-circular or left-circular, or linear polarizations whose azimuths lie within the limits $0 < \alpha_1 < \frac{\pi}{2}$, $0 < \alpha_2 < \frac{\pi}{2}$, or within $-\frac{\pi}{2} < \alpha_2 < 0$, $-\frac{\pi}{2} < \alpha_1 < 0$, at axisymmetric reception of scattered radiation (the second type of symmetric reception).

The questions of calculation of the amplitude of the high-frequency signal and the depth of modulation of the photocurrent of axisymmetric scheme of sounding and reception taking into account their symmetry for some special cases of polarization of sounding beams were also considered in the works of [10, 11].

We have developed a method for calculating the parameters of the high-frequency signal of LDAM with axisymmetric reception of forward or backward scattered radiation, in which the determination of the high-frequency component of the signal is carried out within one quarter of the circular aperture of the receiving aperture. In this case for any states of polarization of the probing beams mutual compensation of the high-frequency component of the useful signal from linear mutually orthogonal components of the beams is observed and the high-frequency signal is formed only from linearly polarized components of two beams oriented in the plane or perpendicular to the plane of the probing beams.

Conclusions

The developed laser dual-wave microparticle analyzer (LDAM) allows for unambiguous and highly accurate measurement of the concentration of two types of particles with different values of the complex refractive index: $\dot{m}_1$ and $\dot{m}_2$, as well as their speed of movement in the case where the second type of symmetric reception of scattered radiation is implemented, and the probing beams have circular polarizations. LDAM can also operate in the mode of axisymmetric reception of backscattered radiation and diagnose the process of conversion of H2O to H2O2, as well as other processes of spontaneous conversion of microparticles.

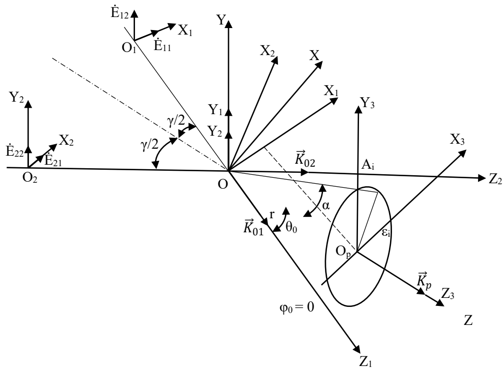

Figure 1 - Symmetrical reception of scattered radiation relative to the *OXZ* and *OYZ* planes

References

1. Laser two-wave method for diagnostics of a two-phase particle flow: patent a202403816 Ukraine. No. 479433; declared 25.07.2024. 9 p.
2. Jae Kyoo Lee, Hyun Soo Han, Settasit Chaikasetsin, Daniel P. Marron, Robert M. Waymouth, Fritz B. Prinz and Richard N. Zare. Condensing water vapor to droplets generates hydrogen peroxide. *Proceedings of the National Academy of Sciences of the United States of America.* 2020. Vol. 117, no. 49. P. 30934-30941.
3. Chongqin Zhu and Joseph S. Francisco. Production of hydrogen peroxide enabled by microdroplets. *Proceedings of the National Academy of Sciences of the United States of America.* 2019. Vol. 116, no. 39. P. 19222-19224.
4. Adair Gallo Jr., Nayara H. Musskopf, Xinlei Liu, Ziqiang Yang, Jeferson Petry, Peng Zhang, Sigurdur Thoroddsen, Hong Im and Himanshu Mishra. On the formation of hydrogen peroxide in water microdroplets. *Chemical Science*. 2022. Issue 9. P. 2574-2583.
5. Lingling Zhao, Xiaowei Song, Chu Gong, Dongmei Zhang, Ruijing Wang, Richard N. Zare. Sprayed water microdroplets containing dissolved pyridine spontaneously generate pyridyl anions. *Proceedings of the National Academy of Sciences of the United States of America.* 2022. Vol. 119, no. 12.
6. Jae Kyoo Lee, Devleena Samanta, Hong Gil Nam, Richard N. Zare. Spontaneous formation of gold nanostructures in aqueous microdroplets. *Nature Communications.* 2018. Vol. 9.
7. Jae Kyoo Lee, Katherine L. Walker, Hyun Soo Han, Jooyoun Kang, Fritz B. Prinz, Robert M. Waymouth, Hong Gil Nam and Richard N. Zare. Spontaneous generation of hydrogen peroxide from aqueous microdroplets. *Proceedings of the National Academy of Sciences of the United States of America.* 2019. Vol.116, no. 39. P. 19294-19298.
8. Zemlyansky V. M. Calculation of parameters of the Doppler signal of the LDA taking into account the polarization-phase effects of scattering. Kyiv: Vishcha school. Main publishing house, 1987. 177 p.
9. Zemlianskii V. M. A new phase method of measuring particle`s size with laser Doppler system. *Journal of Aerosol Science*. 1996. Vol. 27, suppl. 1. P. S325–S326.
10. C. R. Negus and L. E. Drain. Mie calculations of the scattered light from a spherical particle traversing a fringe pattern produced by two intersecting laser beams. *Journal of Physics D: Applied Physics*. 1982. Vol. 15. P. 375–402.
11. J. D. Pendleton. Mie and refraction theory comparison for particle sizing with the laser velocimeter. *Applied Optics*. 1982. Vol. 21, issue 4. P. 684–688.
12. Volkov O. E., Zemlianskyi V. M., Gusev M. O. Two-wave coherent-optical method for diagnostics of two-phase aerosol flow. *Materials, Methods & Technologies*. 2024. Vol. 18.