

## ELECTRO–OPTICAL CHARACTERISTICS OF AMMONIUM CHLORIDE AEROSOLS

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*A unique electro–optical device intended for the study of the optical characteristics of dispersed particles is described. The  $\text{NH}_4\text{Cl}$  aerosols with the organic matter (acetone and xylene with butanol) adsorbed on their surfaces are studied. The variations of electro–optical characteristics of particles are reported.*

A major portion of suspended particles in various aerodispersed media has a nonspherical form. They can acquire different orientations upon exposure to aerodynamic, electric, magnetic, and gravitational fields.<sup>1,2</sup> The optical characteristics of oriented nonspherical particles are of definite interest. For example, the occurrence of such an atmospheric phenomenon as halo is attributed to the absorption and refraction of light in oriented ice crystals. Light of far stars after passage of oriented dust clouds of an interstellar medium becomes polarized, and signals of space radio–communication systems undergo additional interference caused by rotation of polarization plane in the process of wave propagation.<sup>1,3</sup>

The electro–optical technique opens fresh opportunities for the study of light propagation through oriented systems of nonspherical particles. This enables one to extract information about electric, geometric, and optical characteristics of aerosols. In this case the particles are studied directly in air flow without their settling on a substrate.

The pioneering investigations of electro–optical characteristics of aerosols were carried out by Spartakov and Tolstoi<sup>4</sup> in 1955. They found a rigid dipole moment of aerosol particles and suggested its surface nature. Kapustin et al.<sup>5</sup> studied different aerosols and showed significant promise of electro–optics for the study of particle transformations and phase transitions.

The authors developed a setup for the study of the electro–optical characteristics of model aerodispersed media in which the particles under study were preliminary charged by a contact method or in a zone of corona discharge. A generator of orienting fields with capabilities being wider than those of the generators developed by other authors enabled us to carry out studies in continuous regime and to extract some new information about the electro–optical characteristics of dispersed particles. Diagram showing experimental configuration is illustrated in Fig. 1 *a*.

A light flux from a source, for which we use the incandescent lamp 1, passes through the polarizer 2. Then it is directed with a system of lenses to the electro–optical cell 3 filled with running liquid. Direct light from the source 1 is absorbed in the light trap 4. From the aerosol generator 10, the aerosol particles being studied enter the electro–optical cell 3 and fall in the interelectrode gap in which they are exposed to an electric field. The light scattered by an aerosol system is incident on the photomultiplier (PM) 5. An electric signal from the PM output is amplified with the amplifier 6, rectified with the synchronous detector 7, and recorded

with the recording system 8. The scattered light flux is measured against the background of a black body in the form of a cone–light trap (4 and 9). The setup also consists of the timing pulse generator 11 and the generator of high–voltage square pulses 12. The generator produces the pulses of positive polarity of the  $\Pi$ –shape (meander) with the widths of the edges  $\leq 1 \mu\text{s}$  at the smoothly varying pulse repetition frequency ( $10^{-2}$ – $10^{-4}$  Hz). The pulse amplitude can be increased up to 15 kV. In this case the voltage bias in a pulse plateau does not exceed 1%.

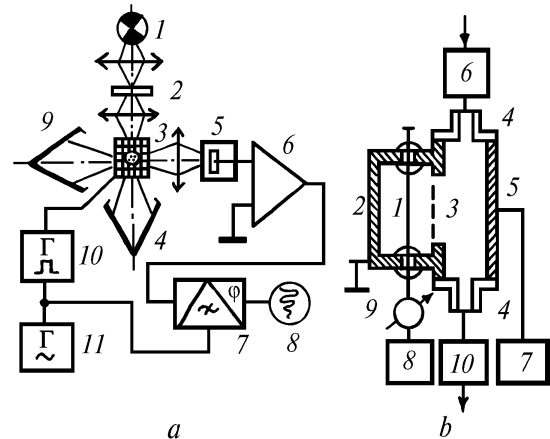


FIG. 1. Block diagram of the setup intended for the study of electro–optical characteristics of aerosol (*a*) and schematic drawing of the device for unipolar charging of aerosol particles (*b*): 8) source of high voltage in the range 0–15 kV and 9) microammeter with 0–100  $\mu\text{A}$  measuring range intended for checking of corona discharge current.

The aerosols under study are  $\text{NH}_4\text{Cl}$  crystals with a mean particle size of 0.6  $\mu\text{m}$ . They are formed in a gas–phase reaction of ammonia vapor with hydrochloric acid.

The aerosol passes through the electro–optical cell 3 in the form of a jet bounded by a clean air flow (perpendicularly to the figure plane). When pulses of an orienting field from the generator 10 are supplied to electrodes of the cell 3, the aerodispersed particles are periodically orientated in an electric field. This orientation is a function of both field strength and charge and state of the particle surface. In this case spatial distribution of light scattered by the particles (scattering phase function) periodically changes. We measured a light scattering intensity at an angle of 45° to the direction of an incident light beam.

For brevity, we use a term *electric light scattering* in the subsequent discussion. When the orienting field in the form of square pulses is applied to the system being investigated, it becomes possible to examine transient processes of electric light scattering. When the orienting field is switched on, a stationary particle orientation is reached after a while. Likewise, when the orienting field is switched off, the particle are disoriented due to Brownian movement also not instantaneously. The curves of electric light scattering increase or decrease attendant to changes in the orienting field strength are called the curves of light scattering relaxation. The shape of the relaxation curves is determined by geometric and electric characteristics of particles being studied as well as by the orienting field strength and environmental conditions (the presence of water vapor and air pollutants). Wippler<sup>6</sup> showed that for low degree of orientation of aerosol particles in the range of frequencies, where effect of the permanent dipole moment of particles is not manifested, an enhancement of light scattering is described by the formula  $\frac{a}{a_0} = 1 - \exp(-6Dt)$ , where  $D$  is the coefficient of particle rotational diffusion.

The degradation of the electro-optical effect is described by the expression  $a = a_0 \exp(-6Dt)$ . Thus the rotational diffusion coefficient  $D$  of aerosols can be reconstructed from experimental relaxation curves. The ratio of the permanent and induced dipole moments can be estimated from the light scattering intensification measured at different frequencies after switching on the orienting field.<sup>7</sup>

The electro-optical light scattering response  $\alpha$  as a function of the orienting field strength  $E$  at low degree of particle orientation was obtained at a scattering angle of  $45^\circ$ . A family of such curves taken at different repetition frequencies of orienting pulses is depicted in Fig. 2a. As can be seen from these curves, the electro-optical light scattering response decreases with frequency increase.

Shown in Fig. 2b are the plots of electric light scattering response as functions of the square of electric field strength taken at different repetition frequencies of orienting pulses. The dependence of the magnitude of electro-optical effect on the square of electric field strength is seen to be linear at low degree of particle orientation. Electric polarizabilities  $\gamma$  of aerosol particles can be found from a slope of experimental curves  $\alpha = \alpha(E^2)$ . However, polydispersity of real aerosol systems frequently results in significantly overestimated  $\gamma$ . A theoretical relation for the parameter  $\gamma$  was derived in the monodispersed approximation.<sup>7</sup>

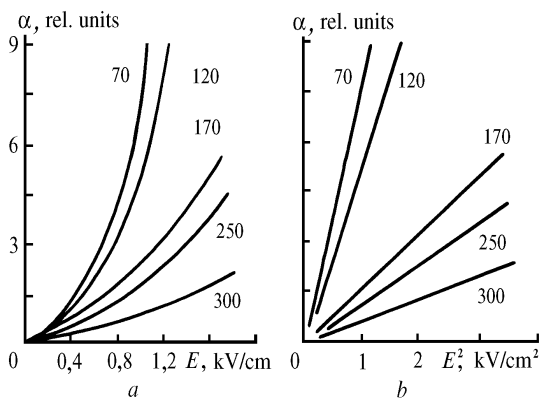


FIG. 2. Plots of electric light scattering response  $\alpha$  vs the orienting field strength (a) and the square of orienting field strength for low degree of particle orientation (b).

The study of electro-optical phenomena in charged aerodispersed media enables one to extract information about charges and electric dipole moments of particles. It is of particular interest for the study of electrization of aerosols and formation of binary electric layers. The state of a strongly developed aerosol surface markedly affects the behavior of aerosols in electric fields.

Figure 1b shows the diagram of a device we used for the electrization of the aerodispersed particles. It is similar to the device described by Hewitt.<sup>8</sup> The wire corona electrode 1 is placed on the axis of the cylindrical electrode 2. A part of the cylinder surface is formed by the metal cloth 3 with an adjacent charging volume. This volume is bounded by the insulating walls 4 and the electrode of drifting field 5 representing a part of the cylindrical surface of large radius arranged coaxially with the cylindrical electrode 2. The aerosol being charged from the aerosol generator 6 enters the charging volume bounded by the grounded metal cloth 3 and the electrode of drifting field 5. Gas ions formed in the corona discharge zone between the electrodes 1 and 2, when high voltage from the source 8 is applied to them, upon exposure to the electric field of the source 7 enter the charging volume through the grounded metal cloth 3. In this charging volume the aerosol particles are charged due to ordered ion movement.

When the electric field strength of the charging device does not exceed 100 V/cm, the particles are charged by a diffusion mechanism. For the electric field strengths higher than 1 kV/cm, they are charged primarily by a collisional mechanism. The particle charge time is experimentally determined as the quotient of the length of the charging device and aerosuspension flow rate. In collisional mode of particle charging, the drifting field must be produced by an alternating-voltage source. For the static drifting field of high strength, a large portion of aerosol particles is inevitably lost due to settling on the electrode 5. The particle concentration is measured with an AZ-5 aerosol counter. A particle charge is checked with the volume-charge density meter 10 developed at our laboratory.<sup>9</sup> In the diffusion mode the mean particle charge  $n$  can be found from the White formula

$$n = \frac{d \kappa T}{2 e} \ln \left( 1 + \frac{\pi d c N_0 e^2 t}{2 \kappa T} \right),$$

where  $d$  is the particle diameter,  $N_0$  is the mean ion concentration,  $c$  is the rms ion velocity,  $\kappa$  is the Boltzmann constant,  $T$  is the absolute temperature,  $e$  is the elementary charge, and  $t$  is the particle charge time.

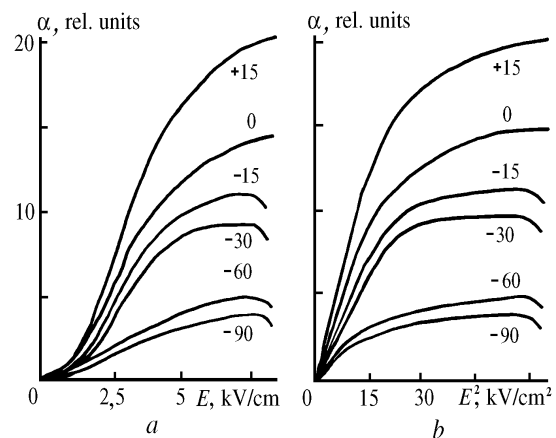


FIG. 3. Plots of electric light scattering response  $\alpha$  vs the orienting field strength for different magnitudes of unipolar charge of particles (a) and the square of orienting field strength (b).

Depicted in Fig. 3a is a family of plots of the electric light scattering responses as a function of the pulsed orienting field strengths at a pulse repetition frequency of 1 kHz which was taken for different particle charges.

It can be seen from the plots that the magnitude of photoresponse increases when particles are charged with positive ions and decreases when they are charged with negative ions. The larger is the charge which aerodispersed particles obtain, the more pronounced is this effect. For large negative charges (when a mean particle charge is equal to  $100 e$ ) the electric light scattering response almost vanishes. The observed effect of variation of electro-optical response attendant to changes in the particle charge can be accounted for by variation of permanent dipole moment of particles in the process of their charging. The permanent particle dipole moment is associated with effect of ordered orientation of adsorbed dipole molecules which form binary layer of particle.<sup>1</sup>

In the process of electrostatic adsorption, an interaction between adsorbed molecules is assumed to be between parallelly oriented dipoles. The moment of each dipole is determined by nature of a molecule and its interaction with the remaining dipoles. The magnitude of dipole moment of each adsorbed molecule and entire particle depends on the total number of adsorbed molecules, i.e., the degree of surface occupation. The degree of surface occupation in the process of adsorption of unipolar ions is different for different polarities of ions due to different positions of the Fermi level relative to the energy bands on different sections of the surface which depends, e.g., on degree of particle dispersion.<sup>10</sup> The charge magnitudes are shown near the curves for one particle.

Depicted in Fig. 3b is a family of plots of the electric light scattering responses vs the square of orienting field strength at a pulse repetition frequency of 1 kHz. The magnitude of mean charge per one particle is shown near the curves. In the plots three sections corresponding to different degrees of particle orientation are distinctly pronounced:

(1) linear dependence of light scattering response at the origin of the curve for low degree of orientation,

(2) point of inflection for intermediate degree of orientation, and

(3) gently sloping curve for completely orientated particles in the electric field.

This setup is capable of obtaining and studying dispersion of electric light scattering response as a function of switching frequency of orienting  $\Pi$ -shaped square pulses. A plot of frequency dependence of electric light scattering response for a polydispersed ensemble of solid anisodiametric particles has generally two dispersion sections separated by a section with constant light scattering response. Characteristic frequency determined from the experimental curve for the section of high-frequency dispersion (units of kilohertz) is of the order of the particle rotational diffusion coefficient  $D$ . The low-frequency dispersion section indicates the presence of slowly varying (surface) electric polarizability of aerosols with characteristic times of tens and hundreds of milliseconds.

Figure 4 depicts the plots of electric response for  $\text{NH}_4\text{Cl}$  crystals taken in the frequency range  $1\text{--}10^4$  Hz vs the square  $\Pi$ -shaped pulse repetition frequency for the fixed orienting electric field strength  $E = 4$  kV/cm. The particles under study are characterized by the fact that before they enter the electro-optical cell, a layer of

organic molecules has been adsorbed on them from a gas phase. Curve 1 corresponds to the particles affected by acetone vapor and curve 2 corresponds to the particles passed through vapor of xylene and butanol (solvent No. 646).

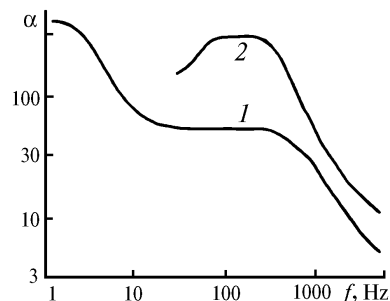


FIG. 4. Plots of electric light scattering response  $\alpha$  vs square  $\Pi$ -shaped pulse repetition frequency of orienting field for fixed electric field strength  $E = 4$  kV/cm: 1) adsorption of acetone molecules on aerosols and 2) adsorption of xylene and butanol on aerosols.

Adsorption from a gas phase of vapor of organic matter is seen to alter the shape of the electric response curve. The spectral behavior of curve 1 at low frequencies indicates the appearance of permanent particle dipole moment oriented along the major particle axis while curve 2 shows possible appearance of permanent dipole moment oriented along the minor particle axis<sup>7</sup> or at least variation of interphase electric polarizability.

Thus the electro-optical technique allows one to study adsorption of gaseous components on aerosol particles. We found characteristic frequencies for high-frequency and low-frequency dispersion from the experimental sections of curve 1 (Fig. 4). They are equal to 2 kHz and 5 kHz, respectively, i.e., characteristic time of fast varying volume polarizability of particles being studied is 400 times less than that of slowly varying surface polarizability. The given frequency dependences of electro-optical response allow one to observe change of state of particle surface connected with adsorption of organic matters on them.

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