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Ions in the Terrestrial Atmosphere and Other Solar System Atmospheres

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Abstract Charged molecular clusters, traditionally called *small ions*, carry electric currents in atmospheres. Charged airborne particles, or *aerosol ions*, play an important role in generation and evolution of atmospheric aerosols. Growth of ions depends on the trace gas content, which is highly variable in the time and space. Even at sub-ppb concentrations, electrically active organic compounds (*e.g.* pyridine derivatives) can affect the ion composition and size. The size and mobility are closely related, although the form of the relationship varies depending on the critical diameter, which, at 273 K, is about 1.6 nm. For ions smaller than this the separation of quantum levels exceeds the average thermal energy, allowing use of a molecular aggregate model for the size-mobility relation. For larger ions the size-mobility relation approaches the Stokes-Cunningham-Millikan law. The lifetime of a cluster ion in the terrestrial lower atmosphere is about one minute, determined by the balance between ion production rate, ion-ion recombination, and ion-aerosol attachment.

Keywords Atmospheric electricity · Lightning · Atomic and molecular clusters · Electrical properties · Particles and aerosols in meteorology

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1 Sources of Ions and Ionization Rate

The ionization rate q quantifies how many ion pairs are created per unit volume of gas per unit time (Israël 1970). Ions and free electrons are generated in a gas when a molecule or atom is excited with an energy exceeding the ionization potential. Typical ionization potentials for some gases in the terrestrial atmosphere are: H_2 15.4 eV, N_2 15.6 eV, and O_2

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12.1 eV. Ions are also created when an ion or electron encounters a neutral molecule in a strong electric field, which leads to an ionization avalanche and electric breakdown, such as in a lightning discharge.

In the terrestrial upper atmosphere, the mean free path of ions is long and even a relatively low electric field can cause ionization by ion-molecule collisions. This is not, however, a dominant ionization process in planetary upper atmospheres, where the main ionizing agents are electromagnetic and corpuscular radiation emitted by the Sun.

Thermal ionization is generally negligible in atmospheres, which can be demonstrated from the Saha-Langmuir theory (Engel 1965). Using this theory, the concentration of ions (in cm^{-3}) generated by thermal collisions is roughly estimated as $1.3 \times 10^{17}\sqrt{p\sqrt{T}\exp(-11600\varphi/T)}$, where the gas pressure p is in mbar, the ionization potential ϕ is in eV, and temperature T in Kelvin. For an ionization potential of 10 eV, an ion concentration of $\sim$1 cm^{-3} requires a temperature of $\sim$1300 K at 1000 mbar pressure, and $\sim$1400 K at 1 mbar. As typical maximum temperatures in planetary atmospheres are about 850 K, the probability of thermal ionization is therefore small.

Electromagnetic ultra-violet radiation ionizes dayside planetary atmospheres for wavelengths λ less than the Lyman beta wavelength ($\lambda = 103$ nm). Only exceptional gases like NO (ionization potential 9.3 eV) can be ionized by the more intense Lyman alpha radiation ($\lambda = 122$ nm), although dayside photoionization also seems important in the Martian atmosphere (Tripathi et al. 2008). Another important factor in upper atmosphere ionization is the precipitation of solar electrons and protons, and meteoritic sources (Molina-Cuberos et al. 2008). The maximum ionization rate in the terrestrial upper atmosphere is of order $10^3\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$.

Solar corpuscular and shortwave electromagnetic radiation are efficiently absorbed in the terrestrial upper atmosphere and do not generally directly affect the lower atmosphere. In the terrestrial lower troposphere, some ions are generated by photoemission of electrons from aerosol particles, a process which requires less than half the energy necessary for ionization of gas molecules. Photoemission is usually neglected in the terrestrial atmosphere. In Titan's atmosphere, photoemission charging has been considered important (Borucki et al. 2006), from assuming that the photoemission threshold appropriate for Titan's haze is that for graphitic particles (Bakes et al. 2002). Predictions of the Titan conductivity profile derived from such assumptions differ from the Huygens probe's preliminary findings however, therefore photoemission may be considerably less important (Borucki and Whitten 2008).

The terrestrial lower atmosphere is ionized by galactic cosmic rays, from which the ionization rate reaches a maximum of about 50 $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ in the stratosphere, between 10 and 20 km (Bazilevskaya et al. 2008). Ion transport occurs in planetary atmospheres having global circuits, which leads to vertical ion transport in the earth's atmosphere (Aplin 2006; Aplin et al. 2008). Near to the terrestrial surface, an additional source of ionization is from natural radioactivity, and the decay of radon and airborne radon daughter nuclides. In summary, the ionizing factors in the terrestrial lower atmosphere are (Israël 1970):

- Galactic cosmic rays ($\sim$2 ion pairs $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ in the lowest kilometre, increasing with height up to 50 $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ in the stratosphere). Terrestrial magnetic field variations cause the cosmic ray ion production rate to vary with geomagnetic latitude.
- Gamma rays emitted from soil and rocks ($\sim$4 ion pairs $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ up to 200–300 m from surface).
- Alpha radiation from ^{222}Rn and its progeny ($\sim$3 ion pairs $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ up to 1–2 km from surface).

The typical ionization rate from all sources near to the terrestrial continental surface is 4 to 8 $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ (Hirsikko et al. 2007) but during calm nocturnal conditions accumulations of radon (^{222}Rn) and thoron (^{220}Rn) occasionally enhance the ionization rate up to at least 100 $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ in the lowest metre (Nagaraja et al. 2003, 2006). Additionally, deposited radon daughters can create ions immediately adjacent to the surface. Willett (1985) modelled the atmospheric electric field close to the surface in calm conditions (known as "the electrode effect") over a grass surface, and pointed out that despite the short path of alpha particles, radon daughter nuclide deposition is an important ionizing factor.

2 Evolution and Classification of Ions in the Terrestrial Troposphere

A free electron and a positive ion are the primary particles resulting from ionization. In a typical lower atmosphere, the electron encounters an electronegative molecule (*e.g.* O_2) during the first microsecond, forming a negative molecular ion. If the collision frequency is high, minor traces of electronegative gases will scavenge all the electrons. In general, electrons can remain free at low pressure in upper atmospheres, but can only remain free in lower atmospheres if electronegative gases are absent. For example, in Titan's atmosphere, no electrophilic species are present, and free electrons and positive ions remain.

The enhanced chemical activity of ions results in a chain of ion-molecule reactions from ion-neutral collisions, and a charged molecular cluster known as a "cluster ion" or "small ion" is formed. The cluster ion lifetime in earth's lower atmosphere is about one minute, during which it undergoes thousands of ion-molecular reactions (Luts and Salm 2004; Beig and Brasseur 2000). The corresponding evolution in ion size and electric mobility depends on the air's trace gas content, which is highly variable in the time and space. Theoretical calculations indicate that, in terrestrial air free of exotic trace gases, the following cluster ions would be typical (Luts and Salm 2004; Beig and Brasseur 2000):

$$\mathrm{NO_3^-(HNO_3)H_2O}, \qquad \mathrm{NO_3^-(HNO_3)}_n, \qquad \mathrm{HSO_4^-(H_2O)}_n,$$
$$\mathrm{NH_4^+(H_2O)}_n, \qquad \mathrm{H^+(NH_3)}_m\mathrm{(H_2O)}_n, \qquad \mathrm{H_3O^+(H_2O)}_n,$$

where n and m are small integers. If the air contains trace gases with high electron or proton affinity then longer-lived cluster ions will also include molecules of these gases (Beig and Brasseur 2000; Parts and Luts 2004). Some electrically-active compounds like pyridine derivatives can affect the ion composition and size, even at concentrations of less than one ppb. Thus the measured size and mobility distributions of the cluster ions depend on the minor contaminants present in the air, therefore the ion property measurements contain some indirect information about air pollution.

Most cluster ions will be lost through their attachment to an aerosol particle or through their recombination with another cluster ion having the opposite polarity. In some situations the cluster ions can continue their growth and become charged aerosol particles, called aerosol ions. This is known as ion-induced or ion-mediated nucleation (Curtius et al. 2006; Yu 2006; Kazil et al. 2008; Arnold 2008). This is one mechanism by which new aerosol particle formation occurs in the earth's atmosphere (Harrison and Carslaw 2003; Kulmala 2003; Kanawade and Tripathi 2006). The aerosol particles formed encounter further small ions, and will be neutralized or recharged on timescales of minutes. Many new neutral aerosol particles form through other mechanisms, becoming aerosol ions by the attachment of cluster ions.

Table 1 Classification of terrestrial atmospheric ions according to Hõrrak et al. (2000)

Class of air ions		Mobility μ (cm^2 V^{-1} s^{-1})	Diameter d (nm)	Typical concentrations n_{typ} (cm^{-3})
Cluster ions	Small cluster ions	1.3–3.2	0.36–0.85	250
	Big cluster ions	0.5–1.3	0.85–1.6	100
Aerosol ions	Intermediate ions	0.034–0.5	1.6–7.4	100
	Light large ions	0.0042–0.034	7.4–22	400
	Heavy large ions	0.00087–0.0042	22–80	1300

Cluster ions and aerosol ions may be discriminated by the ratio of the average separation of internal energy levels ΔE to the thermal energy kT, where k ($k = 1.38 \times 10^{-23}$ J K^{-1}) is Boltzmann's constant and T is temperature. If $\Delta E \gg kT$, the internal energy will be unaffected by thermal collisions and the scattering of gas molecules by ions will be elastic. If $\Delta E \ll kT$, then the colliding molecules will acquire the ion's internal temperature, causing the scattering to be inelastic. In the first case ($\Delta E \gg kT$) the ion can be considered as a charged molecular aggregate, *i.e.* a cluster ion. In the second case ($E \ll kT$) the ion can be considered to be a macroscopic particle, *i.e.* an aerosol ion. At standard temperature (273 K), the transition diameter between terrestrial cluster ions and aerosol ions is about 1.6 nm, from theoretical considerations and measurements of ion masses and mobilities (Tammet 1995). This concept can be extended to other atmospheres, as the transition diameter varies with temperature T as $T^{-1/3}$, but it does not depend on the pressure and gas composition.

A detailed classification is based on the measurements of distribution of ions according to their electric mobility. The mobility μ is a directly measurable parameter defined by $\mu = v/E$, where v is the drift speed of an ion in electric field E. Traditionally, terrestrial atmospheric ions have been classified according to their mobility as *small* (or fast) ions, *intermediate* ions and *large* (or slow or Langevin) ions. The mobility and size range of small ions is essentially the same as that of cluster ions, with the boundary between intermediate and large ions arising by convention. Hõrrak et al. (2000) analyzed the correlations between narrow mobility fractions of atmospheric ions and proposed a classification based on factor analysis, which is summarised in Table 1.

Concentrations of air ions vary in space and time, and, in general, are different for positive and negative ions. The typical concentrations n_{typ} presented in Table 1 are close to the long-term averages of measurements made at a rural site in Estonia (Hõrrak 2001).

3 Relations Between Ion Size, Mass, and Mobility

Mass and mobility are well-defined concepts for any particle. Measurements provide good information about the mobilities for all ion classes, but only limited information about masses for small ions and poor information about sizes for the largest ions. Time-of-flight methods (Eiceman and Karpas 1994; Eiceman et al. 2001) permit measurement of cluster ion mobilities, whereas aspiration methods (Tammet 2006; Mirme et al. 2007) allow measurement of both cluster ion and aerosol ion mobilities. Mass spectrometers can measure cluster ion masses (Viggiano 1993), but determining sizes of large aerosol ions requires an electron microscope. Radiative methods, permitting remote sensing of ions in planetary atmospheres, may also become possible (Aplin and McPheat 2005). There are no known methods for direct measurements of the geometric sizes of cluster ions and intermediate ions: sizes of these ions are usually calculated from their measured mobility or mass, using theoretical models.

The geometric size is an unambiguous and well-defined parameter only in the case of spherical macroscopic particles. In the nanometre size range, the traditional macroscopic model of a spherical particle with an exactly determined geometric surface is inadequate. Although the concept of "mobility diameter" is widely used, this requires that the appropriate mobility-size relationship is known. This presents a paradox, as the mobility-size relation cannot be established if size itself is not able to be defined. Calculating the cluster ion size by the Stokes-Cunningham-Millikan equations is unjustified, as these ideas do not apply to such small particles. Atomic ions are characterized by continuous coordinate functions, in which the concept of the size does not play any fundamental role. Instead, an acceptable geometric parameter for a cluster ion is the mass diameter d_p, defined as

$$d_p = \sqrt[3]{\frac{6m}{\pi\rho}}, \tag{1}$$

where m is the particle mass and the particle density ρ is considered independent of the particle size. The internal density of the particles will exceed the bulk macroscopic density. An array of packed spheres has a density of 0.52ρ for a simple cubic lattice and 0.74ρ for the closest packing. Uncertainty in the mass diameter arises from uncertainty in the density of the particulate matter, which depends on the bond length within a cluster. The variation in bond lengths is a few percent, which presents a lower boundary on the uncertainty of mass diameter.

In the kinetic theory of particle mobility (Chapman and Cowling 1970; Mason and McDaniel 1988) the concept of size is explicitly used in the $(\infty - 4)$ potential model. This model approximates an ion by a virtual rigid sphere, which attracts gas molecules by the electric polarization force. The mobility is expressed via the collision cross-section. Collision cross-section calculation is complicated by several factors: (1) the effect of inelastic scattering of the gas molecules, (2) the diameter dependence of the virtual rigid sphere on temperature and (3) the effect of van der Waals' forces. The physics of collisions is rather complicated and the existing knowledge is not sufficient for *ab initio* calculation of cluster ion collision cross-sections. Tammet (1995) proposed a semi-empirical model for cluster ion and nanometre particle mobility, where the transition from the elastic to inelastic scattering was described by the Einstein factor for melting a cluster's internal degrees of freedom. The model approaches the kinetic theory results in the zero size limit, and the Stokes-Cunningham-Millikan law in the large particle limit. Differences between carrier gases can be considered through the choice of gas viscosity, mass and polarizability. The three parameters of the model were validated by a fit to laboratory measurements (Kilpatrick 1971), as shown in Fig. 1.

A theory of cluster ions and nanometre particle mobility was developed by Li and Wang (2003a, 2003b), and Shandakov et al. (2005). The associated mass-mobility relation was tested by Loscertales (2000) and Fernandez de la Mora et al. (2003). Discrepancies between recent theoretical and experimental results, with values calculated from the semi-empirical model (Tammet 1995) are small. Thus the semi-empirical model is used for the calculations which follow.

In the zero-size limit studied by Langevin (Mason and McDaniel 1988) the ion mobility appears inversely proportional to the gas density. Thus ion mobilities are often reduced to

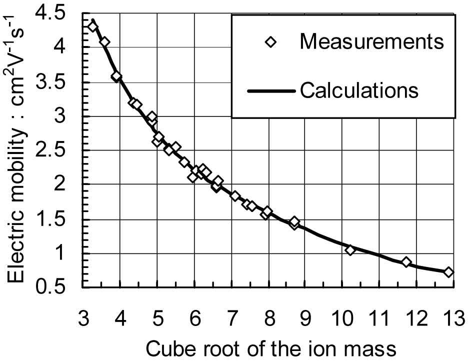


Fig. 1 Measured (Kilpatrick 1971) and calculated (Tammet 1995) mass-mobility correlation for ions in nitrogen. Calculations are made assuming $p = 1013$ mbar, $T = 473$ K, and ion density $= 2.07\ \mathrm{g\,cm^{-3}}$

standard conditions on this basis, according to the Langevin formula:

$$\mu_{reduced} = \mu_{measured} \frac{273.15\ \mathrm{K}}{T} \frac{p}{101325\ \mathrm{Pa}}. \tag{2}$$

The Langevin theory is only a rough approximation when considering real cluster ions. The mobility can be formally reduced according to (2) for an ion of any size, but the result can differ substantially from the actual mobility of the same ion when measured in standard conditions (Tammet 1998). However, (2) will flatten the dependence of mobility on the gas temperature, pressure and ion diameter. The size-mobility relationships can be trimmed further using the approximate inverse proportionality of mobility to the expression $(d+d_0)^2$, where $d_0 = 0.3$ nm is a good choice for ions in nitrogen or air. The "trim mobility", which is conventionally defined as

$$\mu_{trim} = \mu \frac{273\ \mathrm{K}}{T} \frac{p}{1013\ \mathrm{mb}} \left(\frac{d}{1\ \mathrm{nm}} + 0.3 \right)^2, \tag{3}$$

equals the actual mobility of typical 0.7 nm cluster ions in standard terrestrial conditions. Figure 2a shows the trim mobility dependence on the ion mass diameter, for three values of the ionic matter density. A typical density for ionic matter of terrestrial atmospheric ions is about 2 $\mathrm{g\,cm^{-3}}$. The example shows that the density of ionic matter affects the mobility only for cluster ions smaller than 1.6 nm. The mobility of intermediate and large ions depends only on the geometric size and is practically independent of the ionic matter density.

Figure 2b shows that the proportionality of the mobility to temperature, also described in the Langevin model, is only a very rough approximation. According to the Langevin theory, the curves in Fig. 2b should be horizontal lines. Intuitively this suggests that the mobilities of large particles, which can be described by the Stokes-Cunningham-Millikan model, may not follow the temperature proportionality. However, even in case of small cluster ions with diameter 0.5 nm in Fig. 2b, the deviation from horizontal lines is substantial. A final point is that, in accordance with the Langevin theory, mobility should be inversely proportional to gas pressure and therefore the curves in Fig. 2c should be horizontal. The 0.5 nm ions satisfy this condition well, with only small deviation from the inverse proportionality even for 1 nm cluster ions. In conclusion, the Langevin model is more effective in describing the pressure variation of mobility than the temperature variation.

Cluster ions in different carrier gases usually have different chemical compositions and sizes. If it were possible for ions of the same composition and size to exist in different carrier gases then the mobility will be, very roughly, inversely proportional to the square

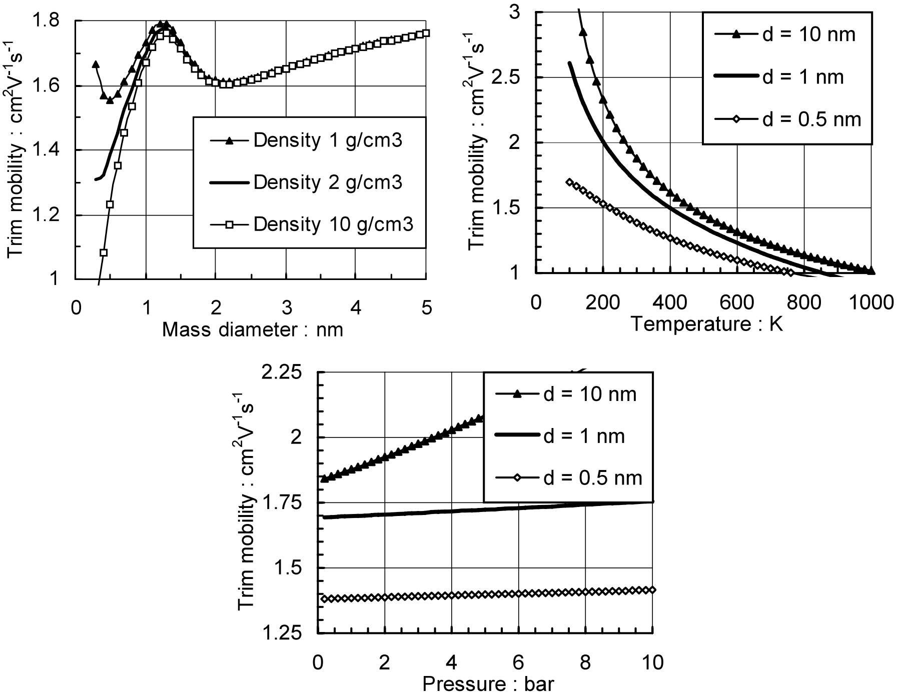
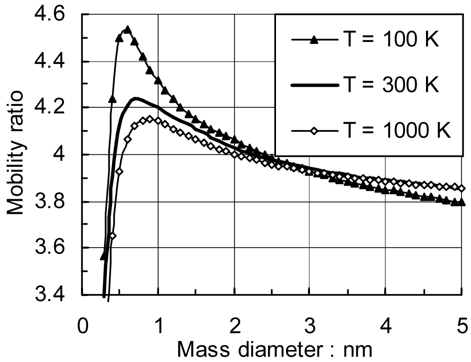


Fig. 2 (**a**) Trim mobility of ions of three different densities in nitrogen ($p = 1000$ mbar, $T = 300$ K). (**b**) Trim mobility of ions of three different sizes in nitrogen ($p = 1000$ mbar, density of ionic matter 2 g cm^{-3}). (**c**) Trim mobility of ions of three different sizes in nitrogen ($T = 300$ K, density of ionic matter 2 g cm^{-3})

Fig. 3 Ratio of ion mobility in H_2 to the mobility of the same ion in N_2 at three different temperatures ($p = 1000$ mbar density of ionic matter 2 g cm^{-3})



root of the molecular mass of the gas. For example, the ion mobility in hydrogen should be about $\sqrt{14} \approx 3.7$ times greater than in nitrogen. The actual mobility ratio is not far from this value, although it also varies with environmental parameters, see Fig. 3.

4 Ion Balance Equations

The concentration of cluster ions arises from the balance between ion production, and losses from ion-ion mutual recombination and ion-aerosol attachment to background aerosol particles, which occurs in many atmospheres (Tripathi et al. 2008). For positive and negative cluster ion concentrations n_+ and n_-, the bipolar ion balance equations are

$$\begin{aligned} \frac{dn_+}{dt} &= q - \alpha n_- n_+ + s_p^+ n_+, \\ \frac{dn_-}{dt} &= q - \alpha n_+ n_- + s_p^- n_-, \end{aligned} \tag{4}$$

where α is the cluster ion-ion recombination coefficient and s_p is the sink rate of cluster ions to aerosol particles. The cluster ion recombination coefficient α for the terrestrial lower atmosphere is generally in the range of $1.4{-}1.6 \times 10^{-12}$ $\mathrm{m^3\,s^{-1}}$ (Israël 1970; Hoppel and Frick 1986), close to values calculated from the three-body recombination theory of Thomson (1924). In the simplest case of a clean atmosphere, when ion-ion recombination is the only loss term ($s_p = 0$), $n_+ = n_-$. Measurement of the bipolar ion concentrations therefore provides a test on whether aerosol is present in an atmosphere and if the aerosol is charged.

To consider the ion loss rates in an atmosphere containing aerosol particles, the sink rates s_p need to be evaluated. These coefficients are predicted using an attachment theory, which considers the collection rate of ions by a particle. This can be illustrated by considering the effect on a spherical particle of radius a exposed to a bipolar concentration of ions, see Fig. 4. Ions pass to the particle by diffusion and electric migration, with a net local ion flux I_r given by

$$I_r = D\frac{dn}{dr} + \mu E(r)n(r), \tag{5}$$

where the first term represents diffusive transport (ion diffusivity D) and the second term electrical transport under an electric field E, if no account is taken of the relative polarities of ions and particle. The radial electric field $E(r)$ experienced by an ion at a distance r from

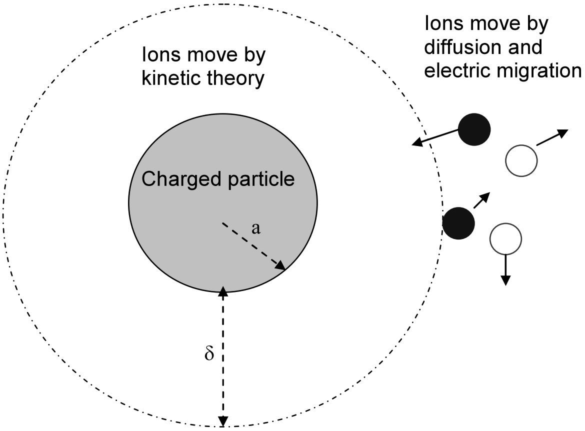


Fig. 4 Motion of ions close to a charged aerosol particle, and the limiting sphere concept

a sphere carrying a total charge je is

$$E(r) = \frac{e}{4\pi\varepsilon_0}\left(\frac{j}{r^2} + \frac{2(2r^2 - a^2)e}{r^3(r^2 - a^2)^2}\right), \tag{6}$$

in which the first term arises from the Coulomb potential, and the second term from image charge effects (Jackson 1975). (The elementary charge $e = 1.6 \times 10^{-19}$ C and the permittivity of free space, $\varepsilon_0 = 8.85 \times 10^{-12}\ \mathrm{F\,m^{-1}}$.) Gunn (1954) neglected image effects, using only the Coulomb force, leading to a particularly simple form for the local ion flux to the particle

$$D\frac{dn}{dr} - \frac{je}{4\pi\varepsilon_0 r^2}\mu n(r) = \frac{I}{4\pi r^2 e}, \tag{7}$$

to which an analytical solution can be found using an integrating factor. Up to a small distance δ (of order one ionic mean free path) from the particle, the ions are considered to move by kinetic theory.

Within this *limiting sphere* region, the ion current can be estimated from ion concentrations and thermal speeds as

$$I = 4\pi a^2 ecn(\delta), \tag{8}$$

where c is the mean ion speed. Equating the two ion fluxes at the limiting sphere, Gunn (1954) found analytic attachment coefficient expressions

$$\beta_{\pm 1j}(a) = \frac{je\mu_\pm}{\varepsilon_0[\pm\exp(\pm 2Lj) \mp 1]}, \tag{9}$$

where $\beta_{\pm 1j}$ is the attachment coefficient for ions (sign ± 1) to a particle carrying j elementary charges, $L = e^2/8\pi\varepsilon_0 akT$, and μ_+ and μ_- are the positive and negative ion mobilities respectively. (In terms of the sink rate s_p, $s_p = \beta Z$.) For the special case of neutral particles, the limiting value is

$$\beta(a) = \frac{4\pi kT\mu_\pm}{e}a. \tag{10}$$

Using this relationship for neutral particles, it can be shown that

$$\frac{n_+}{n_-} = \frac{\mu_-}{\mu_+}. \tag{11}$$

Thus if the bipolar ion concentrations have the inverse ratio to the ion mobilities, there is aerosol present which is uncharged. (This condition is equivalent to equal positive and negative air conductivities.) However, this leads to the presence of space charge and a corresponding electric field, which will complicate the problem.

Table 2 presents the ratios between ion concentrations and ion mobilities for the three cases of no aerosol, neutral aerosol and charged aerosol.

In general, charged aerosol consists of particles of different sizes carrying different charges. The charge distributions can be found by detailed balance equations for charge-exchange between ions and particles (*e.g.* Boisdron and Brock 1970; Yair and Levin 1989; Clement and Harrison 1992).

Figure 5 summarises measurements of ion mobility and ion concentration made in urban air at Reading during 2006. The instrument used (Aplin and Harrison 2001) determines both polarities of ion mobility and ion concentration (Harrison and Aplin 2007), which are plotted

Table 2 Ratio of bipolar ion concentrations with different aerosol properties

Aerosol concentration	Electrical state*	Ion concentration ratio
Aerosol-free air		$\frac{n_+}{n_-} = 1$
Aerosol-laden air	Neutral ($j = 0$)	$\frac{n_+}{n_-} = \frac{\mu_-}{\mu_+}$
	Charged ($j \neq 0$)	$\frac{n_+}{n_-} = \frac{\mu_-}{\mu_+} \exp(\frac{je^2}{4\pi\varepsilon_0 akT})$

* j is the mean number of elementary charges carried by each aerosol particle

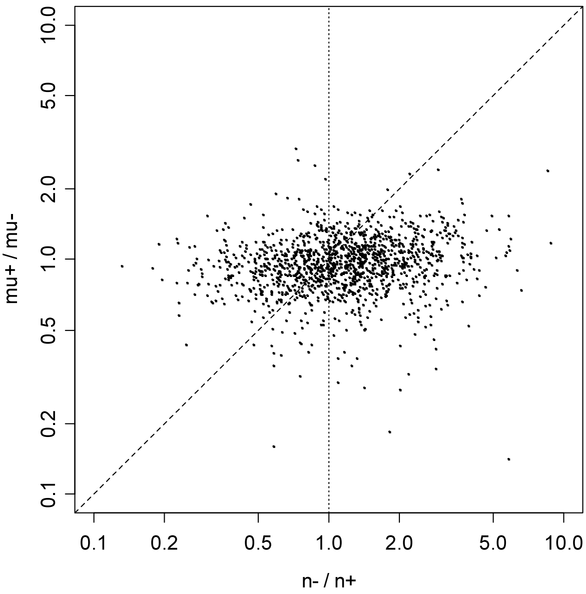


Fig. 5 Ion mobility ratio and ion concentration ratio determined using a Programmable Ion Mobility Spectrometer instrument (PIMS) at Reading during 2006, obtained on year days 44–61 and 143–180 with a 30 min measurement cycle. The *dotted line* marks the clean air (no aerosol) case, and the *dashed line* the uncharged aerosol case

as bipolar ratios. Referring to Table 2, it is clear that data points do not cluster around the zero aerosol case or the neutral aerosol case, but show a spread associated with the presence of charged aerosol. The greater relative variability in n_-/n_+ than μ_+/μ_- illustrates that, in relative terms, ion concentrations vary more than ion compositions.

For smaller aerosol particles the Gunn assumption of no image forces breaks down, and a more sophisticated theory is required (Fuchs 1963; Hoppel and Frick 1986; Jensen and Thomas 1991; Stommel and Riebel 2007). A simple mathematical approximation (Tammet et al. 2006) is

$$\begin{aligned} s_p^+ &= 2\pi \frac{kT}{e} \mu_+ \left((d_p - 1.5\ \text{nm}) - \frac{d_p + 9\ \text{nm}}{d_p + 23\ \text{nm}} q_p d_q \right) Z, \\ s_p^- &= 2\pi \frac{kT}{e} \mu_- \left((d_p - 1.5\ \text{nm}) + \frac{d_p + 9\ \text{nm}}{d_p + 23\ \text{nm}} q_p d_q \right) Z, \end{aligned} \tag{12}$$

where Z and d_p are the concentration and the mean diameter of particles, q_p is the dimensionless algebraic mean charge of aerosol particles expressed in elementary charges, and d_q

is the characteristic length of Coulomb attachment

$$d_q = \frac{e^2}{4\pi \varepsilon_\circ kT} \approx 1.671 \times 10^4/(T:\mathrm{K})\ \mathrm{nm}. \tag{13}$$

In the general case of steady-state charging, the derivatives of the ion concentrations become equal to zero and $s_p^+ n_+ = s_p^- n_-$. The solutions for n_+ and n_- are

$$\begin{aligned} n_+ &= \frac{\sqrt{\left(s_p^-\right)^2 + 4\frac{s_p^-}{s_p^+}\alpha} - s_p^-}{2\alpha}, \\ n_- &= \frac{\sqrt{\left(s_p^+\right)^2 + 4\frac{s_p^+}{s_p^-}\alpha} - s_p^+}{2\alpha}, \end{aligned} \tag{14}$$

although (14) is not an explicit solution of the ion balance problem because the ratio s_p^+/s_p^- weakly depends on the average charge of aerosol particles q_p. This, in turn, depends on the ion concentrations. If charge exchange by electric currents can be neglected, the space charge density $n_+ - n_- + q_p N = 0$ and $q_p = (n_- - n_+)/N$. In this case the ion concentrations can be easily calculated in a rapidly converging iterative process using (14) and starting from the first approximation $q_p = 0$.

5 Conclusion

The properties of cluster ions are influenced by the properties of the atmosphere in which they are formed, both in terms of their composition, which is related to the trace gases present, and their concentration, which primarily depends on the amount of aerosol. Because of the large variability in aerosol concentrations, the concentration of ions varies more than the mobility. In most cases charge exchange between the cluster ions and the aerosol present will cause the aerosol to become charged. The possible role of ions and charged aerosol in cloud formation in planetary atmospheres presents a new frontier in this science area.

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